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(54) **MULTILAYERED SPUN YARN, HEAT-RESISTANT FABRIC OBTAINED USING SAME, AND HEAT-RESISTANT PROTECTIVE GARMENT**

(57) A multilayer-structured spun yarn (20) of the present invention includes a core component (21) and a sheath component (22). The core component (21) includes a stretch-broken spun yarn of a para-aramid fiber. The sheath component (22) includes a polybenzimidazole fiber and a meta-aramid fiber, which are blended together. The polybenzimidazole fiber and the meta-aramid fiber have at least two different colors. The multilayer-structured spun yarn (20) appears to be different in color from the polybenzimidazole fiber and the meta-aramid fiber. A heat-resistant textile of the present invention uses the multilayer-structured spun yarn. A heat-resistant protective suit of the present invention uses the heat-resistant textile. Thus, the present invention can provide the multilayer-structured spun yarn that can facilitate color matching, improve the washing resistance, and can achieve high heat resistance and high flame retardance, and the heat-resistant textile and the heat-resistant protective suit that use the multilayer-structured spun yarn.

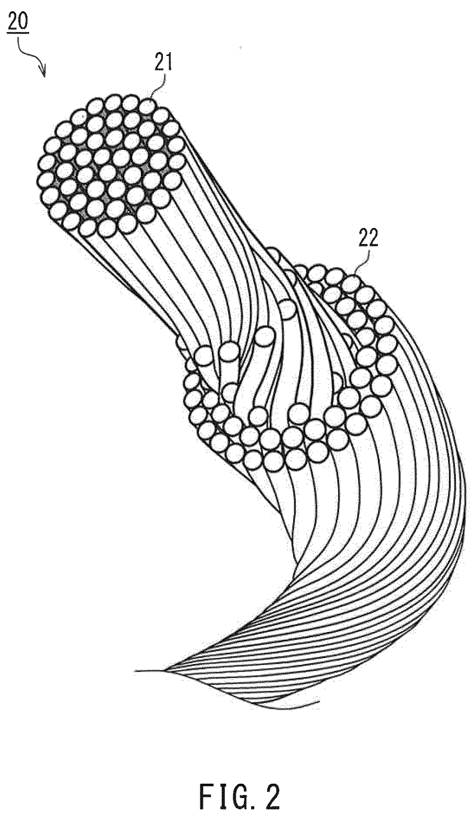


FIG. 2

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## Description

Technical Field

**[0001]** The present invention relates to a multilayer-structured spun yarn including a polybenzimidazole fiber and a para-aramid fiber, and a heat-resistant textile and a heat-resistant protective suit that use the multilayer-structured spun yarn.

Background Art

**[0002]** Protective suits have been used widely, for example as work clothing worn by fire fighters, ambulance crews, rescue workers, maritime lifeguards, military, workers at oil-related facilities, and workers at chemical facilities. In recent years, a polybenzimidazole fiber, which has excellent heat resistance and flame retardance, has been used for a firefighter suit in the U.S., Canada, Australia and some countries in Europe. However, since the polybenzimidazole fiber has a strength of about 2.4 cN/decitex (hereinafter decitex is abbreviated as dtex) that is weak, a woven fabric woven with the polybenzimidazole fiber and a para-aramid fiber is usually used. In this woven fabric, either one of warp or weft is a spun yarn composed of the polybenzimidazole fiber, and the other is a filament yarn composed of the para-aramid fiber. As another woven fabric excellent in heat resistance and flame retardance, the present inventors have proposed a sheath-core spun yarn including a core of a stretch-broken spun yarn of a para-aramid fiber and a sheath of a meta-aramid fiber, a flame-retardant acrylic fiber, a polyetherimide fiber or the like (Patent Documents 1-2).

Prior Art Documents

Patent Documents

**[0003]**

Patent Document 1: WO 2009/014007 A
Patent Document 2: WO 2012/137556 A

Disclosure of Invention

Problems to be Solved by the Invention

**[0004]** However, there are problems with the polybenzimidazole fiber. Since the polybenzimidazole fiber is not dyeable and only fibers spun-dyed with limited range of colors are available, it is difficult to obtain fibers and textiles with a variety of colors. In the conventional woven fabric that is woven with a spun yarn composed of the polybenzimidazole fiber and a filament yarn composed of the para-aramid fiber, the para-aramid fiber will be fibrillated easily due to abrasion or the like at the time of washing and wearing. This causes a whitening phenomenon on the textile surface, resulting in significantly poor appearance. Furthermore, the para-aramid fiber undergoes color change by light, and tends to lose strength. The heat resistance and flame retardance are still insufficient in the fiber compositions proposed in Patent Documents 1 and 2.

**[0005]** In order to solve the above-mentioned problems, the present invention provides a multilayer-structured spun yarn that can facilitate color matching, prevent damage to the appearance due to fibrillation and prevent embrittlement by light, and can also achieve high heat resistance and flame retardance, and a heat-resistant textile and a heat-resistant protective suit that use the multilayer-structured spun yarn.

Means for Solving Problem

**[0006]** A multilayer-structured spun yarn of the present invention includes a core component including a stretch-broken spun yarn of a para-aramid fiber and a sheath component including a polybenzimidazole fiber. The sheath component includes the polybenzimidazole fiber and a flame-retardant fiber (however, excluding the para-aramid fiber and the polybenzimidazole fiber), which are blended together, the polybenzimidazole fiber and the flame-retardant fiber have at least two different colors, and the multilayer-structured spun yarn appears to be different in color tone from the polybenzimidazole fiber and the flame-retardant fiber.

**[0007]** A heat-resistant textile of the present invention is characterized by the use of the multilayer-structured spun yarn. A heat-resistant protective suit of the present invention is characterized by the use of the heat-resistant textile.

Effects of the Invention

**[0008]** A multilayer-structured spun yarn of the present invention includes a core component including a stretch-broken spun yarn of a para-aramid fiber and a sheath component including a polybenzimidazole fiber. The sheath component includes the polybenzimidazole fiber and a flame-retardant fiber (however, excluding the para-aramid fiber and the polybenzimidazole fiber), which are blended together, the polybenzimidazole fiber and the flame-retardant fiber have at least two different colors, and the multilayer-structured spun yarn appears to be different in color tone from the polybenzimidazole fiber and the flame-retardant fiber. With this configuration, the present invention can provide the multilayer-structured spun yarn that can facilitate color matching, can improve the washing resistance in terms of preventing damage to the appearance due to fibrillation, and can also achieve high heat resistance and high flame retardance, and the heat-resistant textile and the heat-resistant protective suit that use the multilayer-structured spun yarn. That is, by blending fibers of different colors and at the same time by mixing colors, color matching is facilitated, and by arranging the sheath component including the polybenzimidazole fiber having higher heat resistance and higher flame retardance in portions directly exposed to flames, and arranging the stretch-broken spun yarn of a para-aramid fiber in the core component, a textile that can maintain high overall strength, high heat resistance and high flame retardance, and also hardly causes a whitening phenomenon on the textile surface due to fibrillation of the para-amid fiber even after repeated washing is achieved. In addition, the polybenzimidazole fiber has high moisture content and a large total heat loss, which enables heat generated by the body of a user to move largely, thereby providing a comfortable heat-resistant protective suit.

Brief Description of Drawings

**[0009]**

[FIG. 1] FIG. 1 is a perspective view showing main elements of a ring frame for producing a sheath-core structured spun yarn according to an example of the present invention.
[FIG. 2] FIG. 2 is a schematic perspective view showing a sheath-core structured spun yarn according to an example of the present invention.
[FIG. 3] FIG. 3 is a weave construction chart of a woven fabric according to an example of the present invention.

Description of the Invention

**[0010]** A multilayer-structured spun yarn of the present invention includes a core component and a sheath component. The core component includes a stretch-broken para-aramid fiber. The sheath component includes a polybenzimidazole fiber and a flame-retardant fiber (however, excluding the para-aramid fiber and the polybenzimidazole fiber), which are blended together. The polybenzimidazole fiber (hereinafter, referred also to as "PBI fiber") is a fiber made of, e.g., a polymer of 2,2'-(m-phenylen)-5,5'-bibenzimidazole and has a thermal decomposition temperature of more than 600°C, a deflection temperature under load of 410°C, a glass transition temperature of 427°C, and an oxygen index (OI) of 41 or more. The PBI fiber can maintain a strength retention of 95% even when exposed to the air at 230°C for two weeks, and can maintain fiber properties to a temperature of 1000°C in nitrogen, and inherently has both incombustibility and high heat resistance (above is cited from "Encyclopedia of fiber" page 848, Maruzen, March 25, 2002). PBI fiber products manufactured by PBI Performance Products, Inc. in the US are known. The PBI fiber has a high equilibrium moisture regain of about 14.6 mass%, which allows a textile including the PBI fiber to have a total heat loss of 300 W/m$^2$ or more measured in accordance with ASTM F 1868 Part C, and enables heat generated by the body of a user to move largely, thereby providing a comfortable heat-resistant protective suit.
**[0011]** Examples of the para-aramid fiber include, as homopolymer-based para-aramid fibers, "Kevlar" (trade name) manufactured by DuPont in the U.S. (the same trade name is used for the product of Du Pont-Toray Co., Ltd. in Japan) and "Twaron" (trade name) manufactured by Teijin, Ltd., and as copolymer-based para-aramid fibers, "Technora" (trade name) manufactured by Teijin, Ltd. These fibers have a tensile strength of 20.3 to 24.7 cN/dtex, a thermal decomposition starting temperature of about 500°C, and an oxygen index (OI) of in a range of 25 to 29. The heat resistance and flame retardance of the para-aramid fiber are inferior to those of the PBI fiber, but are higher than those of the ordinary fibers.
**[0012]** In the multilayer-structured spun yarn of the present invention, the sheath component includes the PBI fiber and a flame-retardant fiber (however, excluding the para-aramid fiber and the PBI fiber), which are blended together. The PBI fiber and the flame-retardant fiber have at least two different colors, and the multilayer-structured spun yarn appears to be different in color tone from the PBI fiber and the flame-retardant fiber. Color mixing can be achieved by blending the respective fibers to produce a predetermined color tone, so that color matching is facilitated.
**[0013]** The PBI fiber is preferably an unbleached fiber or spun-dyed fiber. In this context, the term unbleached indicates a fiber state of being neither spun-dyed nor dyed. The PBI fiber is yellow in the unbleached state. This yellow color is used as it is for color mixing. Spin-dyeing indicates coloring a polymer by adding a coloring agent and forming the polymer

into a fiber. Accordingly, the color tone of the spun-dyed fiber is limited. The three stages for imparting color phases to a dyeable fiber are described as follows. (1) Cotton stage: this stage includes loose stock-dyeing to directly dye fiber masses in a separate state; sliver-dyeing to dye a staple bundle, i.e., a fiber bundle in a sliver state; and top-dyeing to wind up a staple bundle to make a top and dye the top. (2) Yarn stage: yarn-dyeing means to dye a fiber in a yarn state, and this stage includes, depending on the form of dyeing; hank (skein)-dyeing and cone-dyeing to wind up a fiber bundle softly on a specific dye cone tube for allowing a dyeing liquid to permeate easily, and dye the fibers. (3) Knitted or woven fabric stage: this stage includes fabric-dyeing to dye a textile in a cloth state. This stage (3) is called after-dyeing because dyeing is performed after knitting or weaving of yarns into a fabric. On the other hand, the stage (1) and stage (2), in which fibers or yarns are dyed before knitting or weaving, are colored yarns and dyed yarns respectively. The stages (1) and (2) are also called fiber-dyeing.

**[0014]** The flame-retardant fiber of the multilayer-structured spun yarn is preferably at least one selected from a spun-dyed fiber, a loose stock-dyed fiber, a sliver dyed fiber, a top dyed fiber, and yarn-dyed fiber. The flame-retardant fiber after made into a textile may be piece-dyed. By doing so, it is possible to develop a desired color tone by using the flame-retardant fibers with a variety of color tones and by blending or dyeing them, despite that the PBI fiber is unbleached or spun-dyed and is limited in color tone.

**[0015]** It is preferable that the content of the PBI fiber is 10 mass% or more and 90 mass% or less, and the content of the flame-retardant fiber is 10 mass% or more and 90 mass% or less when the amount of the sheath component is 100 mass%. More preferably, the content of the PBI fiber is 20 mass% or more and 80 mass% or less, and the content of the flame-retardant fiber is 20 mass% or more and 80 mass% or less, and further preferably the content of the PBI fiber is 30 mass% or more and 70 mass% or less, and the content of the flame-retardant fiber is 30 mass% or more and 70 mass% or less when the amount of the sheath component is 100 mass%. When the contents are in the above ranges, color matching is facilitated and high heat resistance is achieved.

**[0016]** It is preferable that the content of the core component is 20 to 40 mass% and the content of the sheath component is 60 to 80 mass%, and more preferably, the content of the core component is 22 to 35 mass% and the content of the sheath component is 65 to 78 mass% when the amount of the multilayer-structured spun yarn is 100 mass%. When the content of the core component is less than 20 mass%, a stretch-broken yarn of the core component should have a very small diameter, and makes it difficult to produce the stretch-broken yarn. When the content of the core component is more than 40 mass%, coatability of the sheath fiber deteriorates. When the content of the sheath component is less than 60 mass%, coatability is not favorable and when the content of the sheath component is more than 80 mass%, the fineness of the multilayer-structured spun yarn as a whole increases, and it is not preferred.

**[0017]** The PBI fiber is preferably a stretch-broken fiber obtained by breaking a tow, a bias-cut fiber, or a square-cut fiber. The stretch-broken fiber is a fiber closely similar to the stretch-broken spun yarn of a para-aramid fiber of the core component (as both fibers are tear-off fibers), and provides excellent affinity between the core component and the sheath component, thereby achieving a multilayer structured spun yarn having excellent conformity. The sheath component may be bias-cut or square-cut. To bias-cut means to cut a filament bundle (tow) perpendicularly and diagonally to the yarn advancing direction alternately and repeatedly. For example, in a bias-cut fiber with a fiber length of 76/102 mm, the fiber lengths are distributed uniformly from a minimal length of 76 mm to a maximum length of 102 mm. In contrast, to square-cut means to cut a filament bundle (tow) perpendicularly with a fixed fiber length. For example, in a square-cut fiber with a fiber length of 51 mm, all fiber lengths are distributed uniformly in 51mm.

**[0018]** In addition, in recent years, some products called mix-cut fibers, in which square-cut fibers with different fiber lengths are mixed to create a step-like distribution of the fibers represented by, e.g., 76 mm (33%) + 89 mm (34%) + 102 mm (33%), have been distributed in the market. The fiber length of the cut-fiber is preferably in a range of 30 to 180 mm, more preferably in a range of 45 to 150 mm, and particularly preferably in a range of 50 to 125 mm. With these ranges, the strength can be maintained even higher. The single yarn fineness of the cut-fiber is preferably in a range of 1 to 5 dtex, and more preferably in a range of 1.5 to 4 dtex.

**[0019]** It is preferable that the flame-retardant fiber has an oxygen index (OI) of 26 or more measured in accordance with JIS K 7201-2. When the oxygen index is in the above-range, both of the stretch-broken para-aramid fiber of the core component and the PBI fiber of the sheath component can provide a multilayer-structured spun yarn having high heat resistance and high flame retardance. The flame-retardant fiber is preferably at least one fiber selected from a meta-aramid fiber, a polyalylate fiber, a polybenzoxazole fiber, a polyetherimide fiber, a flame-retardant wool, a flame-retardant rayon, a flame-retardant cotton, and a flame-retardant acrylic fiber.

**[0020]** With a spinning method corresponding to the fineness and length of the sheath component fiber, the sheath component fiber is processed into a staple bundle for a sheath fiber having an optimal shape and configuration. French system worsted spinning is a suitable method for wool having a large fineness and a long fiber length. In this case, when mixing color phases and mixing different kinds of fibers, for example, several kinds of fiber bundles (slivers), each having a fiber content of 100%, are allowed to pass through a wool mixing intersecting gill box, and then are parallelized and balanced by doubling and drafting effects in the subsequent comber process and fore-spinning process. Hereinafter, this method is referred to as "sliver blending". This method provides a high yield and is suitable for manufacturing a wide range of products in small quantities. In contrast, cotton spinning is a suitable method for cotton having a small yarn fineness and a short fiber length. In this case, when mixing color phases and mixing different kinds of fibers, the fibers are mixed mainly by a carding machine in a mixing and blowing process and a carding process. Hereinafter, this method is referred to as "carding blending". This method provides a poor yield but is suitable for manufacturing a small kind of products in large quantities.

**[0021]** It is preferable that an antistatic fiber further is blended with the sheath fiber. When the antistatic fiber is blended, firing due to a static electricity can be prevented. The antistatic fiber is blended preferably in a range of 0.1 to 1 mass%.

**[0022]** The multilayer-structured spun yarn has a metric count preferably in a range of 28 to 52 (fineness: 357 to 192 dtex). When the metric count is in this range, a protective suit having an excellent workability can be obtained.

**[0023]** In the present invention, the multilayer-structured spun yarn is used to make a heat-resistant textile. The heat-resistant textile is preferably a woven fabric. As a result of a proofness test in accordance with EN532, it is preferable that the heat-resistant textile shows that a flame does not reach side edges, no hole is formed, no molten debris is produced, an average afterflame time is 2 seconds or less, and an average afterglow time is 2 second or less. The heat-resistant textile is preferably free from melting, dripping, separation and firing, and has a shrinkage rate of 5% or less in a heat resistance test in accordance with ISO 11613-1999 at 180°C for 5 minutes. The above physical properties can provide a textile having heat resistance and flame retardance at an excellent level. It is preferable that the heat-resistant textile has an oxygen index (OI) of 26 or more, more preferably 26 to 50, still more preferably 32 to 50, and particularly preferably 37 to 48 measured in accordance with JIS K 7201-2. With these ranges, the flame retardance can be improved further.

**[0024]** It is preferable that when the heat-resistant textile is washed 5 times in a washing test in accordance with ISO 6330-1984, 2A-E specified in ISO 11613-1999 as the international performance standards, which is intended to measure washing resistance in terms of preventing damage to the appearance of the fabric due to fibrillation, the heat-resistant textile is free from a whitening phenomenon. With this characteristic, the product value can be maintained higher. It is preferable that the light resistance of the heat-resistant textile is grade 2 to 3 in both a carbon arc light irradiation test according to JIS L 0842.7.2 (a) and a xenon arc light irradiation test according to JIS L 0843. With this characteristic, color change by light can be reduced and the product value can be maintained higher.

**[0025]** The heat-resistant protective suit that uses the heat-resistant textile of the present invention is suitable for a fire fighter suit, and work clothing worn by ambulance crews, rescue workers, maritime lifeguards, military, workers at oil-related facilities, and workers at chemical facilities. In the case of the fire fighter suit, the outer layer of the suit is preferably provided with the heat-resistant textile of the present invention, because it has high heat resistance.

**[0026]** Hereinafter, the flame-retardant fibers to be blended in the sheath component are described below.

(1) Meta-aramid fiber

**[0027]** Examples of the meta-aramid fiber include "Nomex" (trade name) manufactured by DuPont in the US (the same trade name for meta-aramid fiber manufactured by DuPont-Toray Co., Ltd in Japan) and "Conex" (trade name) manufactured by Teijin, Ltd. The meta-aramid fibers has an oxygen index (OI) of 29 to 30.

(2) Flame-retardant wool

**[0028]** As the flame-retardant wool, commonly-used merino wool or the like treated with a Zirpro process, which is a process with titanium and zirconium salt is available. The wool may be either unmodified wool or wool that has been modified by removing the surface scales for shrink proofing. Such unmodified or modified wool is used to improve hygroscopicity and to shield a radiant heat so that the comfort in wearing is kept preferable despite wetting from sweat during exertion under a high-temperature and severe environment, thereby exhibiting heat resistance for protecting the human body. The flame-retardant wool has an oxygen index (OI) of 27 to 33.

(3) Flame-retardant rayon

**[0029]** Examples of the flame-retardant rayon include a rayon treated with a Proban process (an ammonium curing process using tetrakis (hydroxymethyl) phosphonium chloride developed by Albright & Wilson Ltd.), a rayon treated with a Pyrovatex CP process (process with N-methylol dimethylphosphonopropionamide) developed by Ciba-Geigy, and "Viscose FR" (trade name) manufactured by Lenzing AG in Austria. The flame-retardant rayon has an oxygen index (OI) of 26.

(4) Flame-retardant cotton

**[0030]** For the flame-retardant cotton, a cotton treated with a Proban process (in which tetrakis (hydroxyethyl) phosphonium chloride was applied to the cotton by ammonia curing), a cotton treated with a Pyrovatex CP process (process with N-methylol dimethylphosphonopropionamide), or the like can be used. The flame-retardant cotton has an oxygen index (OI) of 26.

(5) Flame-retardant acrylic fiber

**[0031]** For the flame-retardant acrylic fiber, an acrylic fiber obtained by copolymerizing an acrylonitrile with a vinyl chloride-based monomer as a flame retarder, and "PROTEX" (trade name) manufactured by Kaneka Corporation, or the like can be used. The flame-retardant acrylic fiber has an oxygen index (OI) of 29 to 37.

(6) Polyetherimide Fiber

**[0032]** An example of the polyetherimide (PEI) fiber is "Ultem" (trade name) manufactured by Sabic Innovative Plastics (oxygen index (OI): 32). This fiber has a tensile strength of about 3 cN/dtex. It is preferable that the polyetherimide single fiber has a fineness of 3.9 dtex (3.5 deniers) or less and more preferably 2.8 dtex (2.5 deniers) or less. When the fineness is 3.9 dtex (3.5 deniers) or less, the fiber has flexibility and preferable feeling, and it can be applied suitably to work clothing. A preferable average fiber length of the polyetherimide fiber is in a range of 30 to 180 mm, and more preferably in a range of 45 to 150 mm, and particularly preferably in a range of 50 to 125 mm. The polyetherimide fiber having the fiber length in this range can be spun easily.

(7) Polyalylate fiber

**[0033]** An example of the polyalylate fiber is "VECTRAN" (trade name) manufactured by KURARAY CO., LTD. This fiber has a strength of 18 to 22 cN/dtex, an elastic modulus of 600 to 741 cN/dtex, a melting point or decomposition temperature of 300°C, and an oxygen index (OI) of 27 to 28.

(8) Polybenzoxazole fiber

**[0034]** An example of the polybenzoxazole (PBO) fiber is "ZYLON" (trade name) manufactured by TOYOBO CO., LTD. This fiber has a tensile strength of 37 cN/dtex, an elastic modulus of 270 MPa, a melting point or decomposition temperature of 670°C, and an oxygen index (OI) of 64.

**[0035]** Next, the sheath-core spun yarn will be described. A stretch-broken spun yarn is used for the core component. The core component is a stretch-broken spun yarn of a para-aramid fiber. Here, the stretch-broken spun yarn indicates a yarn prepared by drafting and cutting (tearing off) a filament bundle (tow), and twisting. The spinning may be a direct spinning to perform drafting and twisting at a single frame. Alternatively, the spinning may be a Perlok spinning or a converter spinning, in which the fiber is once made as a sliver and twisted to make a spun yarn in two or more steps. The direct spinning is preferred. By using the stretch-broken yarn, the strength can be maintained high, and thus a sheath-core structured spun yarn having excellent conformity with the sheath fiber is obtained.

**[0036]** For a single fiber, the preferred fineness of the stretch-broken spun yarn is in a range of 5.56 to 20.0 tex (metric count: 50 to 180), and more preferably, in a range of 6.67 to 16.7 tex (metric count: 60 to 150). The stretch-broken spun yarn having a fineness in the above- ranges has a high strength and can be applied suitably to heat-resistant protective suit and the like in light of its feeling and the like. It is preferable that the twist number is 350 to 550 time/m or more preferably 400 to 500 time/m for a single yarn having a metric count of 125. When the twist number is in this range, conformity with the sheath fiber is improved further. Further, the preferred fiber lengths are distributed in the range of 30 to 180 mm, the average fiber length is in a range of 45 to 150 mm and preferably in a range of 50 to 125 mm. With these ranges, the strength can be maintained even higher.

**[0037]** In the present invention, when the fineness and twist number of a single yarn of a stretch-broken spun yarn are indicated respectively as So (tex) and $T_0$ (time/m), the twist factor $Ks_0$ of the single yarn is calculated by an equation below.

$$Ks_0 = T_0 \cdot \sqrt{S_0}$$

**[0038]** In a case of representing the spun yarn with a count, when a count of a single yarn and the twist number are indicated respectively as $C_0$ (m/g) and To (time/m), the twist factor $Kc_0$ of the single yarn is calculated by an equation below.

$$Kc_0 = T_0 \cdot \sqrt{C_0}$$

**[0039]** Next, an apparatus and a method for producing a sheath-core structured yarn of the present invention will be explained. FIG. 1 is a perspective view showing main elements of a ring frame in an example of the present invention. For each draft part, a pair of columns 2, 3 different from each other in diameter are provided on a front-bottom roller 1 that is driven to rotate positively. The columns 2, 3 are linked directly and coaxially in the axial direction. On the columns 2, 3, a pair of cylindrical front-top rollers 4, 5 different from each other in diameter are placed. The difference in diameter between the front-top rollers 4, 5 is substantially the same as the difference in diameter between the columns 2, 3 below, but the dimensional relationship is reverse to that of the columns 2, 3 below. The front-top rollers 4, 5 are covered with rubber cots, and fit respectively on a loaded common arbor 6 so as to roll independently. A staple bundle 16 drawn out from a rove bobbin is fed from a guide bar to a back roller 8 through a trumpet feeder 7.

**[0040]** The staple bundle 15 is prepared as a para-aramid stretch-broken fiber bundle for making a core fiber, while the staple bundle 16 is prepared as a sheath fiber bungle. Though not shown, the trumpet feeder 7 can be swung in the axial direction of the front-bottom roller 1, and the swing width can be adjusted. A staple bundle B that has been delivered from the back roller 8 and passed through the draft apron 9 is spun out in a state being held by the large-diameter column 3 and the small-diameter cylindrical front-top roller 5. A staple bundle A is fed through the yarn guide 14 to the small-diameter column 2 and the large-diameter cylindrical front-top roller 4, and then spun out.

**[0041]** The delivery speed of the staple bundle 16 spun out from the large-diameter column 3 is greater than the spinning speed of the staple bundle 15 spun out from the small-diameter column 2. Therefore, when the two spun staple bundles 15, 16 are twisted through a snail wire 10, the staple bundle 16 is entangled around the staple bundle 15, thereby a sheath-core type multilayer-structured spun yarn 17 is formed, with the staple bundle 15 as the core and the staple bundle 16 as the sheath.

**[0042]** It is preferable that the overfeeding rate of the staple bundle 16 to the staple bundle 15 is 5 to 9%, and more preferably 6 to 8%. When the overfeeding rate is within the above-mentioned range, the staple bundle 16 can wrap up the staple bundle 15 at a substantially 100% cover rate.

**[0043]** The produced multilayer-structured spun yarn 17 is wound up by a yarn pipe 13 on the draft part through an anti-node ring 11 and a traveler 12. Even when there is a variation in the positions to hold the staple bundles 15, 16 on the columns 2, 3 depending on the draft parts, since the delivery speed ratio between them is always constant, there is no possibility that the property of the produced sheath-core type multilayer-structured spun yarn 17 varies depending on the draft parts. Further, when the trumpet feeder 7 is swung in a possible range in the axial direction of the front-bottom roller 1, the frictional region of the rubber cot cover of the front-top roller 5 to be rubbed against the staple bundle 16 is dispersed to prevent early abrasion of the rubber cot cover. Though not shown, it is preferable that the yarn guide 14 is swung in the axial direction of the front-bottom roller 1 so as to decrease the abrasion of the rubber cot cover on the cylindrical front-top roller 4.

**[0044]** A preferred twist direction for a single yarn of a sheath-core type multilayer-structured spun yarn is the same as that of a single yarn of a stretch-broken yarn, and, the most preferred twist number $T_{max}$ (time/m) is decided by the fineness So (tex) and the twist number To (time/m) of the stretch-broken spun yarn irrespective of the single yarn fineness after covering with the sheath fiber, and thus the following equation is established.

$$T_{max} = R_s \cdot T_0 \cdot \sqrt{S_0}$$

**[0045]** In the equation, when the proportional constant $R_s$=0.495, the core fiber and the sheath fiber exhibit the optimal conformity such as a bolt-and-nut relationship, and the strength of the single yarn of the sheath-core type multilayer-structured spun yarn is maximized.

**[0046]** In a case of presenting the single yarn with a count, the most preferred twist number $T_{max}$ (time/m) is decided by the count $C_0$ (m/g) and the twist number To (time/m) of the single yarn of the stretch-broken spun yarn, and thus the following equation is established.

$$T_{max} = R_c \cdot T_0 / \sqrt{C_0}$$

**[0047]** In the equation, when the proportional constant $R_c$=15.7, the optimal conformity is exhibited, and the strength of the single yarn of the multilayer-structured spun yarn is maximized.

**[0048]** The obtained multilayer-structured spun yarn 20 is shown in FIG. 2. In FIG. 2, a core component fiber 21 is a stretch-broken spun yarn of a para-aramid fiber, and a sheath component fiber 22 includes the PBI fiber and the meta-aramid fiber, which covers around the core component 21 and has an excellent conformity. Therefore, damage caused by abrasion or the like in the para-aramid fiber at the time of washing can be reduced and/or the percentage of the para-aramid fiber exposed on the spun yarn surface is lowered, and thus the appearance will not deteriorate even when damage caused by abrasion or the like occurs due to wearing and washing. Similarly, color change and decrease in the strength are less likely to occur. In any way degradation in the quality can be prevented.

**[0049]** A protective suit textile of the present invention is preferably a woven fabric formed of a two-fold yarn prepared by twisting two yarns of the sheath-core spun yarn (single yarn). A two-fold yarn is used since the two-fold yarn has at least a doubled strength when compared to a single yarn and thereby can provide a conjugative power to prevent yarn breakage during weaving, and irregularity in thickness of the single yarn is compensated to provide a delicate mesh texture to the woven fabric. For example, the two-fold yarn is produced by use of a twister such as a double-twister. As the name itself suggests, the double-twister has a remarkable productivity because it can produce two twists at a single rotation of a spindle. However, the double-twister has 6 abrasion points on its extremely long yarn path and thus, a covered portion of the fiber can be peeled and scratched, and the core portion of the fiber tends to be exposed. A ring twister having two abrasion points is preferable, and an up-twister having two abrasion points and an extremely short twisting eyelet is more preferable.

**[0050]** In a woven fabric of a hydrophilic fiber represented by cotton, a sized single yarn is used for the warps. In weaving, the adjacent warps rub each other repeatedly at every shedding motion of the loom, and rotate in a direction to reversely twist every time tensile force is applied. As a result, the surface fuzzes of the warps get entangled. Thus, further fuzzes are drawn out from the yarns so as to degrade the conjunctive power. Finally, the yarn will be broken to stop the loom. If the fiber is hydrophilic, starches or the like easily adhere to the yarn. Since the surface fuzzes are hardened with the sizing agent, the conjugative power will not deteriorate during the weaving, and no breakage of the warps occurs. Furthermore, the thus woven fabric later can be desized easily by washing with water during a refining step.

**[0051]** In contrast, as wool and many kinds of synthetic fibers are hydrophobic, starches or the like do not work efficiently. Even if a special sizing agent could be applied to the yarn surface, at present there has been found no method to desize in an easy and inexpensive manner such as washing in water during the refining step after the weaving.

**[0052]** Warp breakage in a loom depends considerably on the conjugative power regarding the rubbing, entanglement and peeling of the surface fuzzes rather than the strength (cN/dtex) of the single fiber that forms the yarn. Therefore, it is preferable that warps of these fibers are prepared as two-fold yarns.

**[0053]** The twist direction (S-twist or Z-twist) and the twist factor $K_2$ of a two-fold yarn with respect to the twist direction and the twist factor $K_1$ of a single yarn are set depending on the type of the fabric to be woven. Here, a wool woven fabric will be explained as an example. For obtaining crimpy touch or crispy touch for georgette or voile, with respect to Z-twisted single yarn, the two-fold yarn is also Z-twisted and $K_2$ is set to be larger so as to make a so-called high twisted yarn. In contrast, in a case of saxony or flannel, it is preferable that the surface of the woven fabric is napped sufficiently to provide softness, bulkiness and shiny smoothness. In such a case, the single yarn is Z-twisted, while the two-fold yarn is S-twisted and its $K_2$ is set smaller in order to make a so-called loose twisted yarn, thereby promoting felting and raising.

**[0054]** In a case of presenting the spun yarn with a count, it is preferable that the count is in a range of 1/28 to 1/52, the twist factor $Kc_1$ of a single yarn is in a range of 81 to 87, the two-fold yarn is twisted in a direction opposite to the direction for twisting the single yarn, and the twist factor $Kc_2$ of the two-fold yarn is in a range of 78 to 84. Here, the twist factor $Kc_1$ of the single yarn and the twist factor $Kc_2$ of the two-fold yarn are calculated by equations below.

$$Kc_1 = T_1/\sqrt{C_1}$$

$$Kc_2 = T_2/\sqrt{C_1}$$

**[0055]** In the equations, $T_1$ indicates a twist number (time/m) of the single yarn, $T_2$ indicates a twist number (time/m) of the two-fold yarn, and $C_1$ indicates a single yarn count (m/g).

**[0056]** When the values of these items are in the above-deescribed ranges, the twist structure is stable, the yarn conjugative property is high, and thus a woven fabric with a delicate mesh texture and soft feeling can be obtained.

**[0057]** The obtained two-fold yarn is subjected to twist-fixing and used as warps and wefts to make a woven fabric. Examples of the woven fabric construction include plain weave, twill weave, satin weave and the like. In a case of knitted fabric, any of flat knitting, circular knitting, and warp knitting can be applied. There is no particular limitation on the weave construction. When air is to be included in the knitted fabric, a double linkage pile textile is formed. Among these woven fabric constructions, mat weave shown in FIG. 3 is particularly preferable, and this mat weave construction is referred to as plain weave and 3/3 mat weave. The plain woven portion is formed of a warp composed of 8 yarns and a weft composed of 8 yarns, and has a plain weave construction. The 3/3 mat woven portion is formed of a warp composed of 3 paralleled yarns and a weft composed of 3 paralleled yarns, and projects from the fabric surface. Accordingly, this weave construction has an anti-slip effect and is hardly broken because further fabric breakage can be prevented in the mat woven portion even when the plain woven construction is broken. This woven construction is also referred to as a rip stop weave because the ripping of the fabric can be stopped.

**[0058]** It is preferable that the weight per unit (metsuke) of the protective suit fabric of the present invention is in a range of 100 to 340 g/m$^2$, so that lighter and more comfortable work clothing can be provided. It is more preferable that the range is 140 to 300 g/m$^2$, and particularly preferably 180 to 260 g/m$^2$.

**[0059]** It is preferable that an antistatic fiber further is added to the fabric. This is to inhibit the charging of the fabric when the final product is in use. Examples of the antistatic fiber include a metal fiber, a carbon fiber, a fiber in which metallic particles and carbon particles are mixed, and the like. The antistatic fiber preferably is added in a range of 0.1 to 1 mass % relative to the spun yarn, and more preferably in a range of 0.3 to 0.7 mass %. The antistatic fiber may be added at the time of weaving. For example, it is preferred to add 0.1 to 1 mass % of "Beltron" (trade name) manufactured by KB Seiren Ltd., "Clacabo" (trade name) manufactured by KURARAY CO., LTD., a carbon fiber, a metal fiber or the like.

[Examples]

**[0060]** Hereinafter, the present invention will be described in more detail by way of examples. However, the present invention is not limited to the following examples.

**[0061]** The measurement methods used in the examples and comparative examples of the present invention are as follows.

< Oxygen index (OI) test >

**[0062]** The measurement was performed in accordance with JIS K 7201-2.

< Heat resistance test >

**[0063]** The measurement was performed in accordance with ISO 11613-1999 at 180°C for 5 minutes.

< Flame proofness test >

**[0064]** The measurement was performed in accordance with EN532.

< Flame resistance test >

**[0065]** The char length created when a flame of a Bunsen burner was brought into contact for 12 seconds with the lower end of a woven fabric sample placed vertically, the afterflame time after the flame was removed, and the afterglow time were measured by the method specified in JIS L1091A-4.

< Washing resistance test >

**[0066]** The washing is performed 5 times in accordance with ISO 6330-1984, 2A-E specified in ISO 11613-1999.

< Electrification voltage test >

**[0067]** The voltage immediately after electrification was measured by the frictional electrification attenuation measurement method specified in JIS L1094 5.4.

< Total heat loss >

**[0068]** The total heat loss was measured in accordance with ASTM F 1868 Part C.

< Other physical properties >

**[0069]** The other physical properties were measured in accordance with JIS or the industry standards.

(Examples 1 to 4)

1. Fibers used

(1) Core component

**[0070]** As a core component, a stretch-broken spun yarn (twist number: 45 times per 10 cm in the Z direction) of a para-aramid fiber "Technora" (trade name) manufactured by Teijin, Ltd. was used. The stretch-broken spun yarn was a black spun-dyed product and had a fineness of 8.0 tex (metric count: 1/125), a single-fiber fineness of 1.7 dtex, and an average fiber length of 100 mm.

(2) Sheath component

**[0071]** The following three types of fibers were blended.

(i) PBI fiber

**[0072]** A tow (790000 dtex (711000 denier), 444000 fibers) of PBI fibers (single-fiber fineness: 1.8 dtex) manufactured by PBI Performance Products, Inc. in the U.S. was obtained. The tow was cut into squares with a fiber length of 51 mm, and then a fiber bundle (sliver) was produced by carding blending. The PBI fiber was an unbleached product (yellow).

(ii) Meta-aramid fiber

**[0073]** "Conex" (trade name) (fiber length: 76/102 mm, bias cut, fineness: 2.2 dtex) manufactured by Teijin, Ltd. was used.

(iii) Antistatic fiber

**[0074]** "Belltron" (trade name) (single-fiber fineness: 5.6 dtex, fiber length: 89 mm, square cut) manufactured by KB Seiren, Ltd. was used.

2. Preparation of spun two-fold yarn

(1) Sheath-core spun yarn

**[0075]** With the method shown in FIG. 1, 25.6 mass% of the para-aramid fiber (black spun-dyed product) was used as a core, and a fiber bundle (sliver) obtained by carding blending 73.9 mass% of the blended fiber of PBI fiber and para-aramid fiber, and 0.5 mass% of the antistatic fiber was used as a sheath, so that a sheath-core spun yarn was prepared. The sheath-core spun yarn was twisted in the Z direction with a twist number of 63 times per 10 cm, and had a fineness of 312.5 dtex. The color tone of the yarns is shown in Table 1.

(2) Two-fold yarn

**[0076]** The sheath-core spun yarns were twisted by an up-twister to form a two-fold yarn. The two-fold yarn was twisted in the S direction with a twist number of 60 times per 10 cm, and had a fineness of 625 dtex.

3. Preparation of woven fabric

**[0077]** The two-fold yarns of Example 1 were used for warp and weft. Using a rapier loom, a woven fabric having a weave construction of plain weave and 3/3 mat weave, as shown in FIG. 3, was produced. The condition and result of the woven fabrics are summarized in Table 2.

(Comparative Example 1)

**[0078]** A sheath-core spun yarn and a woven fabric were prepared in the same manner as Example 1 except that 73.9 mass% of the meta-aramid fiber "Conex" (trade name) (fiber length: 76/102 mm, bias cut, fineness: 2.2 dtex, beige) manufactured by Teijin, Ltd. was used for the sheath component. The color of the blended yarn is shown in Table 1, and the condition and result of the woven fabric are summarized in Table 2.

[TABLE 1]

| | Spun yarn structure | Composition (mass%) | | | | Overall color tone |
|---|---|---|---|---|---|---|
| | | Core component Para-aramid fiber | Sheath component | | | |
| | | | PBI fiber | Meta-aramid fiber | Antistatic fiber | |
| Ex. 1 | Sheath-corespun yarn | 25.6 | 37.0 (Yellow) | 36.9 (Red) | 0.5 (White) | Orange |
| Ex. 2 | Sheath-corespun yarn | 25.6 | 37.0 (Black) | 18.5 (Blue) 18.4 (Navy blue) | 0.5 (Black) | Dark blue |
| Ex. 3 | Sheath-corespun yarn | 25.6 | 18.5 (Yellow) 18.5 (Black) | 36.9 (Bright green) | 0.5 (Black) | Olive green |
| Ex. 4 | Sheath-corespun yarn | 25.6 | 37.0 (Yellow) | 36.9 (Green) | 0.5 (White) | Yellow green |
| Comparative Ex. 1 | Sheath-corespun yarn | 25.6 | - | 73.9 (Red) | 0.5 (White) | Red |

**[0079]** As shown in Table 1, yarns with a variety of color tones were obtained by uniformly blending the meta-aramid fibers with different colors, despite that the PBI fiber was limited in color tone.

[TABLE 2]

| Test item | Ex. 1 | Comparative Ex. 1 | Testing method |
|---|---|---|---|
| Mass (g/m$^2$) | 229.4 | 222.7 | JIS L1096-8.3.2 (Method A) |
| Pick density Warp (number/10cm)<br>Weft (number/10cm) | 194<br>166 | 194<br>158 | JIS L1096-8.6.1 |
| Tensile strength Warp (N)<br>Weft (N) | 1940<br>1620 | 1980<br>1710 | JIS L1096-8.14.1 (Method A) |
| Tensile elongation Warp (%)<br>Weft (%) | 13.6<br>10.7 | 13.9<br>10.5 | JIS L1096-8.14.1 (Method A) |
| Tear strength Warp (N)<br>Weft (N) | 233<br>220 | 225<br>219 | JIS L1096-8.17.1 (Method A-2) |
| Abrasion resistance (plane) (time) | 483 | 592 | JIS L1096.8.19.1 (Method A-1) |
| Dimensional change (method C) Warp (%)<br>Weft (%) | -0.1<br>-0.1 | -0.1<br>0.0 | JIS L1096.8.39.1 (Method C) |
| Washing dimensional change<br>5 times Warp (%)<br>5 times Weft (%)<br>5 times Appearance (grade) | <br>-2.8<br>-1.8<br>2 | <br>-1.9<br>-1.4<br>3-4 | ISO 6330 2A-E |
| Heat resistance Shrinkage rate<br>Warp (%)<br>Weft (%) | <br>0.0<br>0.0 | <br>0.0<br>0.0 | ISO 11613 |

(continued)

| Test item | | Ex. 1 | Comparative Ex. 1 | Testing method |
|---|---|---|---|---|
| Washing | Color change (grade) | 4-5 | 5 | JIS L0844.6.1 (Method A-1) |
| | Pollution (grade) | 5 | 5 | |
| Acidic sweat | Color change (grade) | 5 | 5 | JIS L0848 (Acid) |
| | Pollution (grade) | 4-5 | 5 | |
| Alkaline sweat | Color change (grade) | 5 | 5 | JIS L0848 (Alkali) |
| | Pollution (grade) | 4-5 | 5 | |
| Friction | Dry (grade) | 5 | 5 | JIS L0849.7.1 (b) |
| | Wet (grade) | 4-5 | 5 | |
| Carbon arc light | 40 h (grade) | 4 | 5 | JIS L0842.7.2 (a) |
| | 80 h (grade) | 3-4 | 5 | |
| Xenon arc light | 40 h (grade) | 3 | 5 | JIA L0843 |
| | 80 h (grade) | 4-5 | 5 | |
| Pilling | 10 h (grade) | 4-5 | 4-5 | JIS L1076.8.11 (Method A) |
| (MethodA, set) | 20 h (grade) | 4-5 | 3-4 | |
| | 30 h (grade) | 4-5 | 3-4 | |
| Frictional electrification attenuation | | | | JIS L1094.5.4 |
| Immediately after | Warp (V) | 150 or less | 1400 | |
| Immediately after | Weft (V) | 150 or less | 1400 | |
| Half-life period | Warp (second) | -*1 | 22 | |
| Half-life period | Weft (second) | -*1 | 23 | |
| Flammability | | | | ISO 1161-3-1999→in a case of afterflame afterglow time of 0 second, JIS L 1091A-4 alternate method (Annex 8), year of 1992 flame contact: 12 seconds (vertical method) |
| Char length | Warp (cm) | 2.6 | 3.4 | |
| Char length | Weft (cm) | 2.2 | 3.1 | |
| Afterflame | Warp (second) | 0.0 | 0.0 | |
| Afterflame | Weft (second) | 0.0 | 0.0 | |
| Afterglow | Warp (second) | 0.8 | 0.9 | |
| Afterglow | Weft (second) | 1.0 | 0.8 | |
| Oxygen index | (OI) | 43.5 | 35.5 | JIS K 7201-2 |
| (Remark) The electrification voltage of 150 V or less was unmeasurable in *1 of half-life period due to the characteristics of a device that required 150 V or more of the electrification voltage. | | | | |

**[0080]** Table 2 confirms the following.

(1) In particular, the char length of the woven fabric of example 1 was short, showing a great advantage of the PBI fiber in terms of the flammability. It is considered that the result indicates an extremely excellent surface maintability.
(2) The woven fabric including the PBI fiber had high oxygen index, and extremely high flame retardance.
(3) When the PBI fiber was included in the woven fabric, the frictional electrification voltage turned into an unmeas-

urable state of 150 V or less. This is assumed to be due to the moisture content of the PBI fiber of 14.6%. The textile having a low frictional electrification voltage hardly generates a static electricity, and thus has high safety.

(4) Similarly to the sheath-core spun yarn, in the woven fabric, woven fabrics with a variety of color tones were obtained by uniformly blending the meta-aramid fibers with different color tones, despite that the PBI fiber was limited in color tone.

(Example 5, Comparative Example 2)

**[0081]** These examples were performed using a woven fabric obtained by laminating three layers of an outer layer, an intermediate layer and an inner layer, assuming an actual use for a fireproof clothing.

(1) Outer layer

**[0082]** The woven fabrics obtained in example 1 and comparative example 1 were used.

(2) Intermediate layer (moisture-permeable waterproof layer, moisture barrier)

**[0083]** A base fabric, which is composed of a plain-woven fabric (mass: 77g/ m$^2$) made of a blended spun yarn including 85 mass% of the meta-aramid fiber (fineness: 2.2 dtex, fiber length: 76/102 mm, bias cut) and 15 mass% of wool, was laminated with a polytetrafluoroethylene film as a moisture-permeable waterproof layer to prepare an intermediate layer with a mass of 105 g/m$^2$, and used.

(3) Inner layer (Heat protection layer, inner liner)

**[0084]** A 16-shaft honeycomb fabric (mass: 213 g/ m$^2$) made of a blended spun yarn including 85 mass% of a meta-aramid fiber (fineness: 2.2 dtex, fiber length: 76/102 mm, bias cut) and 15 mass% of wool was used.

**[0085]** The measurement result of the above-described laminated woven fabric product is summarized in Table 3. In Table 3, the measurement was performed in European Approach in accordance with ISO 11613 European approach.

[TABLE 3]

| | | Ex. 5 Vertical Horizontal | Comparative Ex.2 Vertical Horizontal |
|---|---|---|---|
| Outer layer | | Woven fabric of Ex. 1 | Woven fabric of Comparative Ex. 1 |
| Outer layer Flame resistance in contact with flame | All layers are to be free from hole formation, dripping and melting, and Left afterflame time ≦2 (sec) Right afterglow time ≦ 2 (sec) | Pass<br>0 0 | Pass<br>0 0 |
| Inner layer Flame resistance in contact with flame | | Pass<br>0 0 | Pass<br>0 0 |
| Flame exposure Heat transmission | All layers<br>Left $I_{Q24}$ ≧13 Right $I_{Q24}$-$I_{Q12}$ ≧ 4 | Pass<br>17 5 | Pass<br>16 5 |
| Radiation exposure Heat transmission | Outer layer only<br>Left $t_2$ ≧22 Right $t_2$-$t_1$ ≧6 | Pass<br>29 12 | Pass<br>30 12 |
| Residual intensity | Outer layer only<br>≧450(N) | Pass<br>1760 | Pass<br>1750 |
| Heat resistance | Free from firing, separation, dripping and melting, and have a shrinkage rate ≧5(%) left vertical, right horizontal | Pass<br>1.0 0.7 | Pass<br>0.7 0.5 |
| Tensile strength | Outer layer only<br>≧ 450 (N) | Pass<br>2030 | Pass<br>2210 |

(continued)

| | | Ex. 5 Vertical Horizontal | Comparative Ex.2 Vertical Horizontal |
|---|---|---|---|
| Outer layer | | Woven fabric of Ex. 1 | Woven fabric of Comparative Ex. 1 |
| Tear strength | Outer layer only<br>≧ 25 (N) | Pass<br>322 | Pass<br>307 |
| Water resistance | Outer layer only<br>≧4 (grade) | Pass<br>5 | Pass<br>5 |
| Washing resistance | Outer layer only<br>shrinkage ≦3(%) left horizontal, right vertical | Pass<br>2.6 1.2 | Pass<br>1.7 1.2 |
| Liquid /chemical penetration pressure resistance | All layers are to be free from penetration of sodium hydroxide (NaOH), hydrochloric acid ($H_2SO_4$), sulfuric acid(HCl),and white spirit into inner side of layer, and surface downward flow rate ≧80(%) | Pass<br>NaOH 98.7<br>$H_2SO_4$ 96.5<br>HCl 97.8<br>W.S 89.0 | Pass<br>NaOH 99.1<br>$H_2SO_4$ 95.3<br>HCl 98.3<br>W.S 87.5 |

**[0086]** From Table 3, the result confirms that the woven fabrics of examples satisfied the conditions required for all of the test items. The total heat loss of the three-layered laminated products in accordance with ASTM F 1868 Part C are shown in Table 4.

[TABLE 4]

| | Ex. 5 | Comparative Ex. 2 |
|---|---|---|
| Outer layer | Woven fabric of Ex. 1 | Woven fabric of Comparative Ex. 1 |
| Total heat loss Qt ($W/m^2$) | 317 | 299 |

**[0087]** From Table 4, the result confirms that the woven fabric provided with the woven fabric of the present invention in the outer layer had high total heat loss. In general, it is considered that the clothing having high total heat loss increases a heat flux generated from the body of a user during actual fire fighting, and a risk of heat illness caused by protection-oriented clothing is reduced, thereby increasing the comfort in wearing. This high total heat loss is assumed to be due to the moisture content of the PBI fiber of 14.6%.

(Comparative Examples 6 to 8)

**[0088]** These examples were performed in the same manner as Example 1 except that a blended product of the PBI fiber, the antistatic fiber and the meta-aramid fiber "Conex" (trade name) (fiber length: 76/102 mm, bias cut, fineness: 2.2 dtex, beige) manufactured by Teijin, Ltd. was used in place of the blended product of the PBI fiber and the antistatic fiber for the sheath component. The oxygen index of the yarns is shown in Table 5, and the condition and result of the woven fabrics are summarized in Table 6.

[TABLE 5]

| | Spun-yarn structure | Composition (mass%) | Oxygen index (OI) | Color tone |
|---|---|---|---|---|
| Ex. 6 | Sheath-core spun yarn | Core: Para-aramid fiber 25.6 Sheath: PBI fiber (Yellow) 55.4 Meta-aramid fiber (Red) 18.5 Antistatic fiber 0.5 | 45.5 | Orange with strong yellow |

(continued)

| | Spun-yarn structure | Composition (mass%) | Oxygen index (OI) | Color tone |
|---|---|---|---|---|
| Ex. 7 | Sheath-core spun yarn | Core: Para-aramid fiber 25.6 Sheath: PBI fiber (Yellow) 37.0, Meta-aramid fiber (Red) 36.9 Antistatic fiber 0.5 | 43.5 | Orange |
| Ex. 8 | Sheath-core spun yarn | Core: Para-aramid fiber 25.6 Sheath: PBI fiber (Yellow) 18.5 Meta-aramid fiber (Red) 55.4 Antistatic fiber 0.5 | 39.5 | Orange with strong red |

**[0089]** As shown in Table 5, the result confirms that the sheath-core spun yarns of examples of the present invention exhibited high oxygen index and high flame retardance. In addition, spun yarns of three different types of orange were obtained.

[TABLE 6]

| Test item | | Ex. 6 | Ex. 7 | Ex. 8 | Testing method |
|---|---|---|---|---|---|
| Mass | (g/m$^2$) | 230.3 | 229.4 | 231.7 | JIS L1096-8.3.2 (Method A) |
| Pick density | Warp (number/10cm) | 196 | 194 | 196 | JIS L1096-8.6.1 |
| | Weft (number/10cm) | 166 | 166 | 164 | |
| Tensile strength | Warp (N) | 1910 | 1940 | 1990 | JIS L1096-8.14.1 (Method A) |
| | Weft (N) | 1570 | 1620 | 1760 | |
| Tensile elongation | Warp (%) | 13.6 | 13.6 | 15.5 | JIS L1096-8.14.1 (Method A) |
| | Weft (%) | 10.0 | 10.7 | 10.8 | |
| Tear strength | Warp (N) | 227 | 233 | 230 | JIS L1096-8.17.1 (MethodA-2) |
| | Weft (N) | 210 | 220 | 222 | |
| Abrasion resistance (plane) (time) | | 454 | 483 | 556 | JIS L1096.8.19.1 (Method A-1) |
| Dimensional change (method C) | Warp (%) | -0.3 | -0.1 | -0.2 | JIS L1096.8.39.1 (Method C) |
| | Weft (%) | 0.1 | -0.1 | -0.1 | |
| Washing dimensional change | | | | | ISO 6330 2A-E |
| 5 times Warp (%) | | -3.2 | -2.8 | -2.2 | |
| 5 times Weft (%) | | -1.5 | -1.8 | -1.8 | |
| 5 times Appearance(grade) | | 2 | 2 | 2-3 | |
| Heat resistance Shrinkage rate | Warp (%) | 0.0 | 0.0 | 0.0 | ISO 11613 |
| | Weft (%) | 0.0 | 0.0 | 0.0 | |
| Washing | Color change (grade) | 4-5 | 4-5 | 5 | JIS L0844.6.1 (Method A-1) |
| | Pollution (grade) | 5 | 5 | 5 | |
| Acidic sweat | Color change (grade) | 5 | 5 | 5 | JIS L0848 (Acid) |
| | Pollution (grade) | 5 | 4-5 | 5 | |

(continued)

| Test item | | Ex. 6 | Ex. 7 | Ex. 8 | Testing method |
|---|---|---|---|---|---|
| Alkaline sweat | Color change (grade) | 5 | 5 | 5 | JIS L0848 (Alkali) |
| | Pollution (grade) | 5 | 4-5 | 5 | |
| Friction | Dry (grade) | 5 | 5 | 5 | JIS L0849.7.1 (b) |
| | Wet (grade) | 4-5 | 4-5 | 4-5 | |
| Carbon arc light | 40 h (grade) | 3 | 4 | 4-5 | JIS L0842.7.2 (a) |
| | 80 h (grade) | 3 | 4 | 4-5 | |
| Xenon arc light | 40 h (grade) | 2-3 | 3-4 | 4-5 | JIA L0843 |
| | 80 h (grade) | 2 | 3 | 4 | |
| Pilling | 10 h (grade) | 4-5 | 4-5 | 4-5 | JIS L1076.8.11 (Method A) |
| (Method A, set) | 20 h (grade) | 4-5 | 4-5 | 4-5 | |
| | 30 h (grade) | 4-5 | 4-5 | 4 | |
| Frictional electrification attenuation | | | | | JIS L1094.5.4 |
| Immediately after | Warp (V) | 150 or less | 150 or less | 150 or less | |
| Immediately after | Weft (V) | 150 or less | 150 or less | 150 or less | |
| Half-life period | Warp (second) | -*1 | -*1 | -*1 | |
| Half-life period | Weft (second) | -*1 | -*1 | -*1 | |
| Flammability | | | | | ISO 11613-1999→in a case of afterflame afterglow time of 0 second, JIS L 1091A-4 alternate method (Annex 8), year of 1992 flame contact:12 seconds (vertical method) |
| Char length | Warp (cm) | 2.0 | 2.6 | 2.9 | |
| Char length | Weft (cm) | 2.1 | 2.2 | 2.6 | |
| Afterflame | Warp (second) | 0.0 | 0.0 | 0.0 | |
| Afterflame | Weft (second) | 0.0 | 0.0 | 0.0 | |
| Afterglow | Warp (second) | 0.7 | 0.8 | 1.0 | |
| Afterglow | Weft (second) | 0.8 | 1.0 | 0.8 | |
| Oxygen index | (OI) | 45.5 | 43.5 | 39.5 | JIS K 7201-2 |
| (Remark) The electrification voltage of 150 V or less was unmeasurable in *1 of half-life period due to the characteristics of a device that required 150 V or more of the electrification voltage. | | | | | |

**[0090]** Table 6 confirms the following.

(1) In particular, the char length of the woven fabric considerably decreased as the blending ratio of the PBI fiber increased, showing a great advantage of the PBI fiber in terms of the flammability. It is considered that the result indicates an extremely excellent surface maintability.
(2) The woven fabric including the PBI fiber had high oxygen index, and extremely high flame retardance.
(3) When the PBI fiber was included in the woven fabric, the frictional electrification voltage turned into an unmeasurable state of 150 V or less. This is assumed to be due to the moisture content of the PBI fiber of 14.6%. The textile having a low frictional electrification voltage hardly generates a static electricity, and thus has high safety.
(4) The washing dimensional change increased as the blending ratio of the PBI fiber increased. This is assumed to be due to the moisture content of the PBI fiber of 14.6% that is higher when compared with the moisture content of the meta-aramid fiber of 2 to 3%. The textile having a high moisture content increase a difference between a degree of swelling and shrinkage of the fiber at the time of washing, and easily causes the dimensional change.
(5) The degree of color change of the woven fabric deteriorated as the blending ratio of the PBI fiber increased in the carbon arc light irradiation test and the xenon arc light irradiation test, which were intended to measure the light resistance.

(Examples 9 to 15)

**[0091]** These examples were performed in the same manner as Example 1 except that the blending ratio of each sheath component in the multilayer-structured spun yarn was set as shown in Table 7. In Table 7, the washing test was intended to measure the damage to the fabric. Moreover, the PBI was a stretch-broken fiber obtained by cutting the tow of the PBI fibers, and was an unbleached (yellow) product or a black spun-dyed product. The blending of the sheath components was sliver blending. The respective fibers used are specifically described below.

(1) Flame-retardant wool

**[0092]** Unmodified merino wool (average fiber length: 75 mm) made in Australia was used. The wool was dyed in olive green by an ordinary method with an acid dye. The wool had flame retardance due to the Zirpro process.

(2) Flame-retardant rayon

**[0093]** "Viscose FR" (trade name) (average fineness: 3.3 dtex, fiber length: 89 mm, mix cut) manufactured by Lenzing AG in Austria was used. The fiber was dyed in sky blue by an ordinary method with a reactive dye.

(3) Flame-retardant cotton

**[0094]** Cotton treated with the Proban process (in which tetrakis(hydroxymethyl)phosphonium chloride was applied to the cotton by ammonia curing) was used. In this case, the cotton was not dyed and remained unbleached (white).

(4) Flame-retardant acrylic fiber

**[0095]** "PROTEX M" (trade name) (average fineness: 3.3 dtex, fiber length 82/120 mm, bias cut) manufactured by Kaneka Corporation was used. The fiber was dyed in oriental blue by an ordinary method with a cationic dye.

(5) Polyetherimide (PEI) fiber

**[0096]** "ULTEM" (trade name) (single-fiber fineness: 3.3 dtex (3 denier), fiber length: 76/102 mm, bias cut) manufactured by SABIC Innovative Plastics was used. The fiber had an oxygen index (OI) of 32. The fiber was dyed in red by an ordinary method with a disperse dye.

(6) Polyalylate fiber

**[0097]** "VECTRAN" (trade name) (single-fiber fineness: 3.3 dtex (3 denier), fiber length 76/102 mm, bias cut) manufactured by KURARAY CO., LTD. was used. The fiber had an oxygen index (OI) of 27 to 28. In this case, the polyalylate fiber was a brown spun-dyed product.

(7) Polybenzoxazole (PBO) fiber

**[0098]** "ZYLON" (trade name) (single-fiber fineness: 3.3 dtex (3 denier), fiber length: 76/102 mm, bias cut) manufactured by TOYOBO CO., LTD. was used. The fiber had an oxygen index (OI) of 64. The PBO fiber was unbleached (light yellow) and used without dyeing.

[TABLE 7]

| Experiment No. | | Ex. 9 | Ex. 10 | Ex. 11 | Ex. 12 | Ex. 13 | Ex. 14 | Ex. 15 |
|---|---|---|---|---|---|---|---|---|
| Corefiber (mass%) | Para-aramid | 25.6 | 25.6 | 25.6 | 25.6 | 25.6 | 25.6 | 25.6 |
| Sheath fiber (mass%) | PBI | 37.0 (unbleached) | 37.0 (black) | 37.0 (black) | 37.0 (unbleached) | 37.0 (unbleached) | 37.0 (unbleached 17/black 20%) | 37.0 (unbleached) |
| | Flame-retardant wool | 36.9 (olive green) | | | | | | |
| | Flame-retardant rayon | | 36.9 (sky blue) | | | | | - |
| | Flame-retardant cotton | | - | 36.9 (unbleached) | | | | |
| | Flame-retardant acryl | | | | 36.9 (oriental blue) | | | |
| | PEI | | | | | 36.9 (red) | | |
| | Polyalylate fiber | | - | | | | 36.9 (brown) | |
| | PBO | | | | - | | | 36.9 (light yellow) |
| | Antistatic fiber | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |

(continued)

| | Experiment No. | Ex. 9 | Ex. 10 | Ex. 11 | Ex. 12 | Ex. 13 | Ex. 14 | Ex. 15 |
|---|---|---|---|---|---|---|---|---|
| Results | Color tone of spun yarn | yellow green | marble blue | marble gray | green | orange | khaki | beige |
| | Heat shrinkage (%) | 0.0 | 0.0 | 0.0 | 2.3 | 3.7 | 0.0 | 0.0 |
| | Char length (cm) | | | | | | | |
| | Warp | 5.2 | 4.3 | 5.9 | 3.8 | 3.9 | 2.2 | 0.5 |
| | Weft | 5.0 | 4.1 | 6.2 | 3.8 | 3.5 | 2.0 | 0.4 |
| | Appearance after 5 times of washing test (grade) | 4 | 3-4 | 3 | 4-5 | 5 | 5 | 54 |
| | Carbon arc light test with 80-hour irradiation (grade) | 4 | 4 | 5 | 5 | 4-5 | 2 | 2 |
| | Oxygen index (OI) | 42 | 40 | 38 | 45 | 46 | 48 | 59 |

**[0099]** Table 7 confirms that, since the multilayer-structured spun yarn includes (i) the core component including the para-aramid fiber and (ii) the sheath component including the blended fiber of the PBI fiber and any of the other flame-retardant fibers (e.g., the flame-retardant wool, the flame-retardant rayon, the flame-retardant cotton, the flame-retardant acrylic fiber, the PEI fiber, the polyalylate fiber, or the PBO fiber), the multilayer-structured spun yarn can facilitate color matching by mixing colors, can improve the washing resistance in terms of preventing damage to the appearance of the fabric due to fibrillation, and can also achieve high heat resistance and high flame retardancy.

Industrial applicability

**[0100]** The heat-resistant protective suit that use the heat-resistant textile of the present invention is suitable for a fire fighter suit, and work clothing worn by ambulance crews, rescue workers, maritime lifeguards, military, workers at oil-related facilities, and workers at chemical facilities. In particular, since the core component includes the stretch-broken spun yarn of a para-aramid fiber and the sheath component includes the PBI fiber and a meta-aramid fiber, which are blended together, it is possible to achieve high heat resistance and high flame retardance, and to achieve textiles with a variety of color tones.

Description of Reference Numerals

**[0101]**

| | |
|---|---|
| 1 | Front bottom roller |
| 2 | Large-diameter cylindrical member |
| 3 | Small-diameter cylindrical member |
| 4, 5 | Front top rollers |
| 6 | Arbor |
| 7 | Trumpet feeder |
| 8 | Back roller |
| 9 | Drafting apron |
| 10 | Snail wire |
| 11 | Anti-node ring |
| 12 | Traveler |
| 13 | Spindle |
| 14 | Yarn guide |
| 15 | Staple bundle (stretch-broken para-aramid fiber bundle for the core fiber) |
| 16 | Staple bundle (fiber bundle for the sheath fiber) |
| 17, 20 | Multilayer-structured spun yarn |
| 21 | Core component fiber |
| 22 | Sheath component fiber |

## Claims

**1.** A multilayer-structured spun yarn comprising:

a core component including a stretch-broken spun yarn of a para-aramid fiber; and
a sheath component including a polybenzimidazole fiber,

wherein the sheath component includes the polybenzimidazole fiber and a flame-retardant fiber (however, excluding the para-aramid fiber and the polybenzimidazole fiber), which are blended together,
the polybenzimidazole fiber and the flame-retardant fiber have at least two different colors, and
the multilayer-structured spun yarn appears to be different in color tone from the polybenzimidazole fiber and the flame-retardant fiber.

**2.** The multilayer-structured spun yarn according to claim 1, wherein the polybenzimidazole fiber is an unbleached fiber or a spun-dyed fiber.

**3.** The multilayer-structured spun yarn according to claim 1 or 2, wherein the flame-retardant fiber is at least one selected from a spun-dyed fiber, a cotton-dyed fiber and a yarn-dyed fiber.

**4.** The multilayer-structured spun yarn according to any one of claims 1 to 3, wherein a content of the polybenzimidazole fiber is 10 mass% or more and 90 mass% or less, and a content of the flame-retardant fiber is 10 mass% or more and 90 mass% or less when an amount of the sheath component is 100 mass%.

**5.** The multilayer-structured spun yarn according to any one of claims 1 to 4, wherein the flame-retardant fiber has an oxygen index (OI) of 26 or more measured in accordance with JIS K 7201-2.

**6.** The multilayer-structured spun yarn according to any one of claims 1 to 5 , wherein the flame-retardant fiber is at least one fiber selected from a meta-aramid fiber, a polyalylate fiber, a polybenzoxazole fiber, a polyetherimide fiber, a flame-retardant wool, a flame-retardant rayon, a flame-retardant cotton, and a flame-retardant acrylic fiber.

**7.** The multilayer-structured spun yarn according to any one of claims 1 to 6, wherein an antistatic fiber further is blended in a sheath fiber.

**8.** The multilayer-structured spun yarn according to any one of claims 1 to 7, wherein the multilayer-structured spun yarn has a metric count in a range of 28 to 52 (fineness: 357 to 192 decitex).

**9.** A heat-resistant textile using the multilayer-structured spun yarn according to any one of claims 1 to 8.

**10.** The heat-resistant textile according to claim 9, wherein in a proofness test in accordance with EN532, the heat-resistant textile shows that a flame does not reach side edges, no hole is formed, no molten debris is produced, an average afterflame time is 2 seconds or less, and an average afterglow time is 2 second or less.

**11.** The heat-resistant textile according to claim 9 or 10, wherein the heat-resistant textile is free from melting, dripping, separation and firing, and has a shrinkage rate of 5% or less in a heat resistance test in accordance with ISO 11613-1999 at 180°C for 5 minutes.

**12.** The heat-resistant textile according to any one of claims 9 to 11, wherein the heat-resistant textile has an oxygen index (OI) of 26 or more measured in accordance with JIS K 7201-2.

**13.** The heat-resistant textile according to any one of claims 9 to 12, wherein the flame-retardant fiber of the heat-resistant textile is fabric-dyed.

**14.** A heat-resistant protective suit using the heat-resistant textile according to any one of claims 9 to 13.

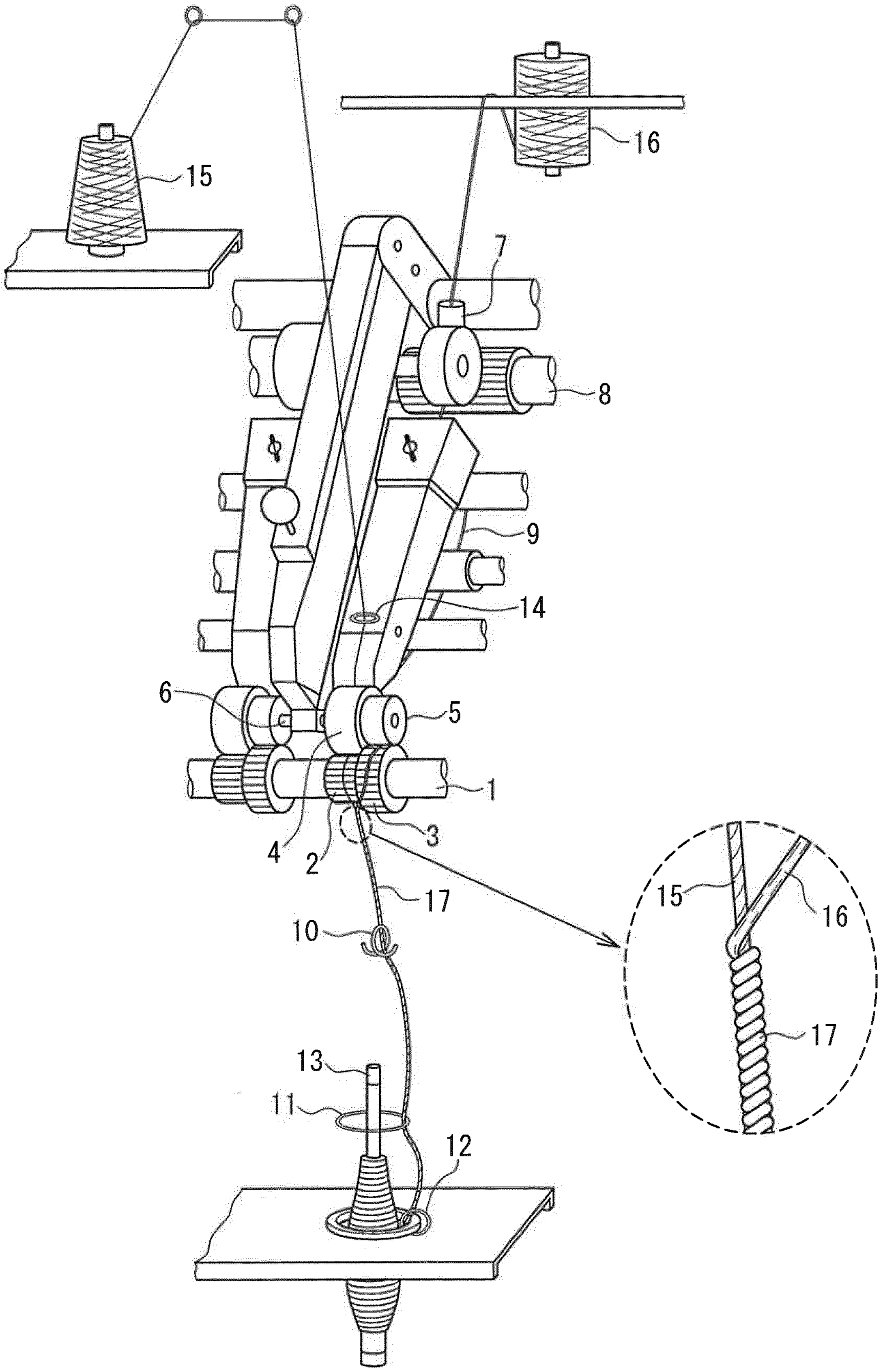


FIG. 1

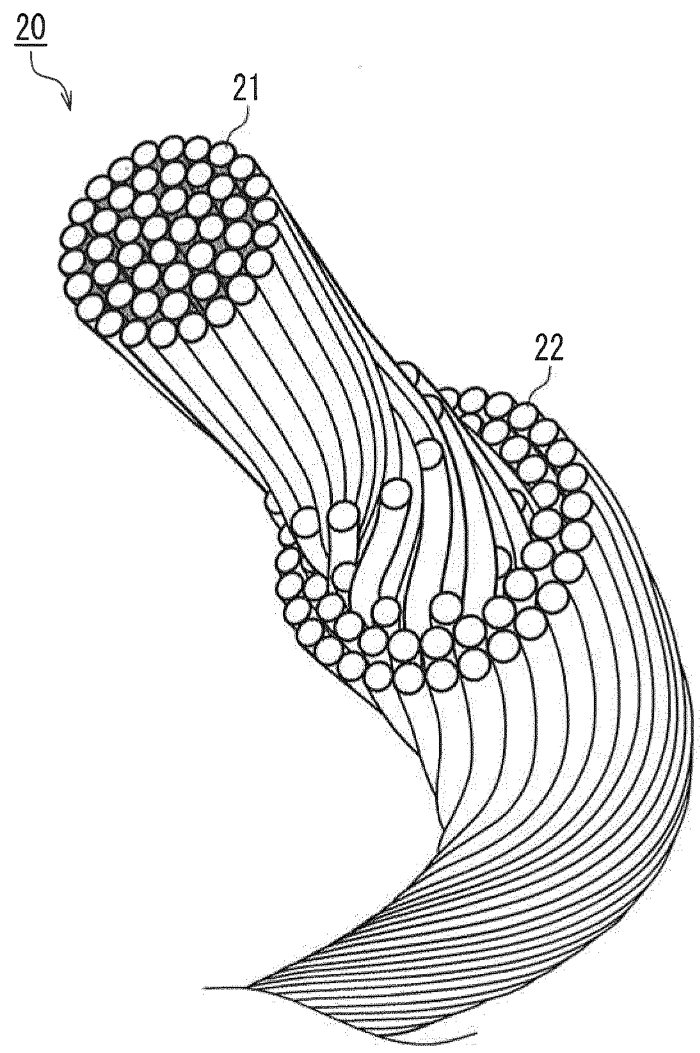


FIG. 2

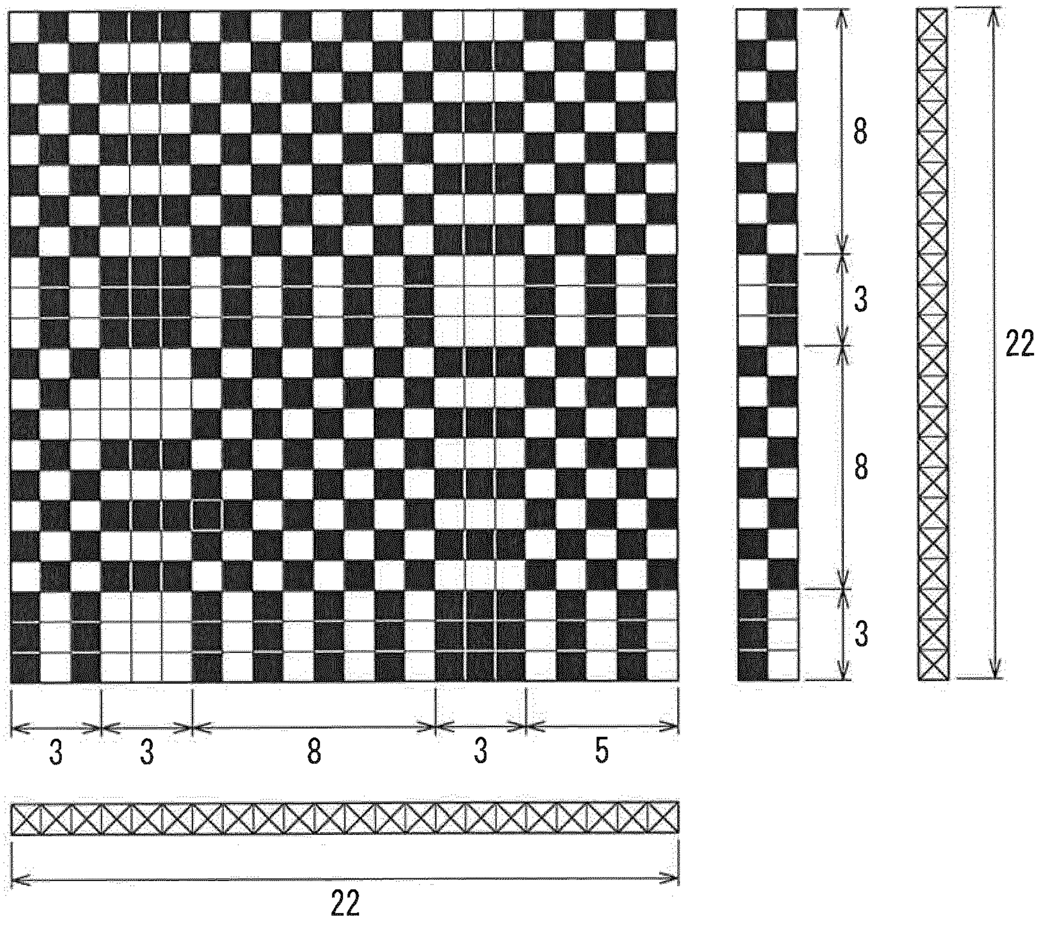


FIG. 3

## INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2016/054388

A. CLASSIFICATION OF SUBJECT MATTER
*D02G3/36*(2006.01)i, *D02G3/04*(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
D02G3/36-3/38, D02G3/04, D03D15/00

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

| | | | |
|---|---|---|---|
| Jitsuyo Shinan Koho | 1922-1996 | Jitsuyo Shinan Toroku Koho | 1996-2016 |
| Kokai Jitsuyo Shinan Koho | 1971-2016 | Toroku Jitsuyo Shinan Koho | 1994-2016 |

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 04 April 2016 (04.04.16) | 12 April 2016 (12.04.16) |

| Name and mailing address of the ISA/ | Authorized officer |
|---|---|
| Japan Patent Office<br>3-4-3,Kasumigaseki,Chiyoda-ku,<br>Tokyo 100-8915,Japan | Telephone No. |

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**INTERNATIONAL SEARCH REPORT**

International application No. PCT/JP2016/054388

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**INTERNATIONAL SEARCH REPORT**

International application No.
PCT/JP2016/054388

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| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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## REFERENCES CITED IN THE DESCRIPTION

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