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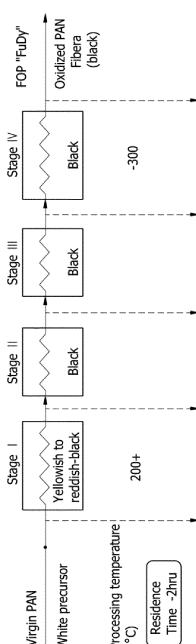
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(54) **POLYACRYLONITRILE-BASED PRECURSOR FIBER FOR CARBON FIBRE, AND PRODUCTION METHOD THEREFOR**

(57) Disclosed are a polyacrylonitrile-based precursor fiber for a carbon fiber and a method of producing the same, wherein the polyacrylonitrile-based precursor fiber includes a conductive carbon material.

Figure 1



**Description****Technical Field**

5     **[0001]** The present invention relates to a polyacrylonitrile-based precursor fiber for a carbon fiber and a method of producing the same.

**Background Art**

10    **[0002]** Generally, carbon fibers are manufactured in a manner in which a polyacrylonitrile-based precursor fiber is subjected to a flameproofing process through thermal treatment at about 200 to 300°C so that the molecular structure thereof is cyclized, yielding a thermally stable oxidized acrylonitrile fiber (Oxi-PAN fiber), which is then carbonized through thermal treatment at a high temperature of 800°C or more, finally obtaining a hexagonal structure composed exclusively of carbons.

15    **[0003]** In the typical flameproofing process of carbon fibers, as shown in FIG. 1, a polyacrylonitrile (PAN)-based precursor for carbon fibers is subjected to a flameproofing process through three or four thermal treatment steps. As such, individual polyacrylonitrile-based precursor fibers are thermally stabilized inward from the surface thereof due to the thermal treatment effect.

20    **[0004]** Depending on the heat transfer rate and time, the surface layer of the precursor fiber is thermally stabilized and flameproofed through contact with, and diffusion of, oxygen. Accordingly, the precursor fiber is configured to include the outer region, which has undergone thermal stabilization and flameproofing through the contact with oxygen, and the inner region, which has undergone thermal stabilization only, because oxygen does not penetrate into the precursor fibers in the flameproofing process.

25    **[0005]** In the case where excessive thermal stabilization occurs in the flameproofing process, holes may be formed in the precursor, or the precursor may be broken. In this case, the mechanical properties of carbon fibers may deteriorate. On the other hand, in the case where insufficient thermal stabilization occurs, yarn breakage may occur, attributable to ignition. As the flameproofing temperature is decreased, thermal stabilization may become easier, but the processing time is increased. In contrast, as the thermal stabilization temperature is increased, the difference in thermal stability may increase between the surface layer and the inner layer of the fiber, thus facilitating the generation of pores. Thus, even when the same precursor fiber, which is typically prepared, is used, the mechanical strength may vary widely from 1.0 to 3.0 GPa depending on the degree of flameproofness.

30    **[0006]** In lieu of the flameproofing process using hot air, a flameproofing process that takes only 10 minutes using microwaves such as plasma has been devised, but may suffer from many problems in terms of flameproofing uniformity, making it difficult to realize commercialization. Accordingly, there is an urgent demand for techniques for generating economic benefits by reducing the flameproofing treatment time upon the preparation of the precursor for carbon fibers.

**Disclosure****Technical Problem**

40    **[0007]** Therefore, the present invention is intended to provide a polyacrylonitrile-based precursor fiber for a carbon fiber and a method of producing the same, in which the thermal treatment time for a flameproofing process may be reduced upon the production of a carbon fiber.

**Technical Solution**

**[0008]** A first embodiment of the present invention provides a polyacrylonitrile-based precursor fiber for a carbon fiber, comprising a conductive carbon material.

50    **[0009]** In this embodiment, the conductive carbon material may comprise at least one selected from the group consisting of carbon black, carbon nanotubes (CNT), graphene, and graphene oxide.

**[0010]** In this embodiment, the conductive carbon material may be used in an amount of 0.03 to 3.0 wt% based on the total amount of the polyacrylonitrile-based precursor fiber.

**[0011]** In this embodiment, the conductive carbon material may have an electrical resistivity ranging from  $3.5 \times 10^{-5}$  to  $10^3 \Omega\text{-cm}$ , a purity of 95% or more, and a particle diameter of 0.1 to 200 nm.

55    **[0012]** In this embodiment, the polyacrylonitrile-based precursor fiber may have a single-yarn fineness of 0.8 to 2.0 denier.

**[0013]** A second embodiment of the present invention provides a method of producing a polyacrylonitrile-based precursor fiber for a carbon fiber, comprising: preparing a polyacrylonitrile-based polymer solution; spinning a spinning

solution including a polyacrylonitrile-based polymer, thus obtaining a spun fiber; extracting a solvent from the spun fiber in a coagulation solution, thus manufacturing a coagulated fiber; washing the coagulated fiber with water; drawing the coagulated fiber; oiling the coagulated fiber; and drying the coagulated fiber, wherein in the preparing the polyacrylonitrile-based polymer solution, a conductive carbon material is added.

[0014] In this embodiment, in the preparing the polyacrylonitrile-based polymer solution, a solution containing monomers for a polyacrylonitrile copolymer may be added with the conductive carbon material and then polymerized.

[0015] In this embodiment, the conductive carbon material may be added in an amount of 0.03 to 3.0 wt% based on the total amount of the polyacrylonitrile-based precursor fiber.

[0016] In this embodiment, the conductive carbon material may comprise at least one selected from the group consisting of carbon black, CNT, graphene, and graphene oxide.

[0017] In this embodiment, the conductive carbon material may have an electrical resistivity ranging from  $3.5 \times 10^{-5}$  to  $10^3 \Omega\text{-cm}$ , a purity of 95% or more, and a particle diameter of 0.1 to 200 nm.

[0018] In this embodiment, the drawing may be performed at a drawing ratio of 4 to 20.

## Advantageous Effects

[0019] According to the present invention, a polyacrylonitrile-based precursor fiber for a carbon fiber includes a conductive carbon material, which has low thermal conductivity and resistivity and is not volatilized in the carbonization process, thereby increasing the rate of transfer of heat into the polyacrylonitrile-based precursor fiber to thus rapidly realize thermal stabilization. During the production of the polyacrylonitrile-based precursor fiber, the flameproofing treatment time can be reduced, and carbon fibers can thus be economically manufactured.

## Description of Drawing

[0020] FIG. 1 illustrates a flameproofing process in the conventional production of a polyacrylonitrile-based precursor fiber for a carbon fiber.

## Best Mode

[0021] Hereinafter, a detailed description will be given of the present invention.

[0022] The present invention addresses a polyacrylonitrile-based precursor fiber for a carbon fiber, which includes a conductive carbon material.

[0023] As used herein, the term "conductive carbon material" refers to a carbon material having an electrical resistivity of  $3.5 \times 10^{-5}$  to  $10^3 \Omega\text{-cm}$ .

[0024] According to the present invention, the polyacrylonitrile-based precursor fiber for a carbon fiber is composed of a polymer comprising a polyacrylonitrile-based polymer (which may be abbreviated as "PAN-based polymer"), the term "polyacrylonitrile-based polymer" indicating a polymer including acrylonitrile as a main component. Specifically, acrylonitrile is preferably used in an amount of 95 mol% or more based on the total amount of a monomer composition.

[0025] In the present invention, the conductive carbon material has low thermal conductivity and resistivity and is not volatilized in the carbonization process, in contrast with an organic precursor for a carbon fiber, such as polyacrylonitrile (PAN). Hence, when the conductive carbon material is used, the rate of transfer of heat into the precursor may increase, thus quickly realizing thermal stabilization and reducing the flameproofing time, whereby carbon fibers may be economically produced.

[0026] The carbon material may include at least one selected from the group consisting of carbon black, CNT, graphene, and graphene oxide. In particular, when CNT is fed in a mixture with graphene, the dispersibility of particles in the polymer dope may increase, and the mixing ratio of CNT and graphene may range from 30 wt%:70 wt% to 70 wt%:30 wt%, in order to achieve the optimal dispersion of the particles.

[0027] Also, the conductive carbon material may be used in an amount of 0.03 to 3.0 wt% based on the total amount of the polyacrylonitrile-based precursor fiber. If the amount of the conductive carbon material is less than 0.03 wt%, resultant thermal conductivity may be poor. In contrast, if the amount thereof exceeds 3.0 wt%, dispersibility may deteriorate. As such, the amount of the conductive carbon material to be added may vary depending on the kind thereof.

[0028] The conductive carbon material functions to rapidly transfer external heat into the precursor to minimize the difference in flameproofness between the inner and outer layers of the precursor when viewed from the cross-section. Here, if the amount of the conductive carbon material is less than 0.03%, there is no real-world improvement in heat transfer rate due to the use of the conductive carbon material. In contrast, if the amount thereof exceeds 3.0 wt%, the dispersibility of the particles of the conductive carbon material may become low, whereby the strength of the precursor may decrease and processability may deteriorate due to the non-uniform dispersion, ultimately drastically reducing productivity and thus negating economic benefits.

**[0029]** The conductive carbon material has an electrical resistivity of  $3.5 \times 10^{-5}$  to  $10^3 \Omega\text{-cm}$ . As the electrical resistivity of the conductive carbon material is decreased, thermal conductivity may increase. However, the electrical resistivity of the conductive carbon material must not be less than  $3.5 \times 10^{-5} \Omega\text{-cm}$ . In contrast, if the electrical resistivity exceeds  $10^3 \Omega\text{-cm}$ , the conductive carbon material has to be substantially added in a large amount, and thus the effect due to the reduction of the flameproofing treatment time may be offset by the increase in the precursor preparation cost.

**[0030]** As a typical conductor, silver (Ag) has an electrical resistivity of  $1.47 \times 10^3 \Omega\text{-cm}$ , copper (Cu) has an electrical resistivity of  $1.72 \times 10^{-3} \Omega\text{-cm}$ , and iron (Fe) has an electrical resistivity of  $1.0 \times 10^{-7} \Omega\text{-cm}$ . As the resistivity value is decreased, superior thermal conductivity and electrical conductivity may result.

**[0031]** The conductive carbon material used in the present invention has a resistivity of  $3.5 \times 10^{-5} \Omega\text{-cm}$  and thus has excellent heat transfer performance. Also, conductive metals are regarded as having high thermal conductivity due to the very low resistivity thereof, but the metal may be easily ionized and may thus negatively affect the flameproofing process through a catalytic reaction, undesirably resulting in poor processing stability.

**[0032]** Hence, in the present invention, preferably useful is a conductive carbon material that exhibits stable properties, even in the flameproofing process, and has an electrical resistivity of  $3.5 \times 10^{-5}$  to  $10^3 \Omega\text{-cm}$ .

**[0033]** Furthermore, the conductive carbon material may have a purity of 95 to 99.9%. If the purity of the conductive carbon material is less than 95%, covalent bonding of carbon may be negatively affected in the flameproofing and carbonization processes due to impurities, undesirably deteriorating mechanical properties and decreasing the final yield. In particular, when metal, rather than conductive carbon material, is left behind, ignition potential may increase, and thus avoiding the use of metal is favorable.

**[0034]** The conductive carbon material has a particle diameter of 200 nm or less, and preferably from 0.1 to 200 nm. If the particle diameter of the conductive carbon material is less than 0.1 nm, dispersion stability may become weak, and the price of the conductive carbon material may be drastically increased. In contrast, if the particle diameter thereof exceeds 200 nm, it cannot penetrate into the polymer for the precursor, making it impossible to produce fibers.

**[0035]** According to the present invention, the polyacrylonitrile-based precursor fiber for a carbon fiber may have a single-yarn fineness of 0.8 to 2.0 denier. If the single-yarn fineness of the polyacrylonitrile-based precursor fiber is less than 0.8 denier, yarn breakage may occur during the carbonization. In contrast, if the single-yarn fineness thereof exceeds 2.0 denier, the quality of the precursor may become non-uniform and thermal stability may deteriorate in the flameproofing process.

**[0036]** In addition, the present invention addresses a method of producing a polyacrylonitrile-based precursor fiber for a carbon fiber, comprising: preparing a polyacrylonitrile-based polymer solution; spinning a spinning solution including the polyacrylonitrile-based polymer, thus obtaining a spun fiber; extracting the solvent from the spun fiber in a coagulation solution, thus manufacturing a coagulated fiber; washing the coagulated fiber with water; drawing the coagulated fiber; oiling the coagulated fiber; and drying the coagulated fiber, wherein a conductive carbon material is added when preparing the polyacrylonitrile-based polymer solution.

**[0037]** In the present invention, the precursor fiber for a carbon fiber comprises a polymer that includes a polyacrylonitrile-based polymer (which may be abbreviated as "PAN-based polymer"), the term "polyacrylonitrile-based polymer" indicating a polymer that includes acrylonitrile as a main component. Specifically, acrylonitrile may be contained in an amount of 95 mol% or more based on the total amount of a monomer composition.

**[0038]** The polyacrylonitrile-based polymer may be obtained by subjecting a solution including an acrylonitrile (AN) monomer as a main component and a conductive carbon material to solution polymerization using a polymerization initiator. In addition to the solution polymerization process, suspension polymerization or emulsion polymerization may be applied.

**[0039]** The conductive carbon material is preferably used in a manner such that it is dispersed in a solvent before polymerization. The reason why the conductive carbon material is added before polymerization is that the conductive carbon material may be efficiently added while being uniformly dispersed in the solvent having very low viscosity. In the case where the conductive carbon material is added after polymerization, the viscosity of the spinning dope is maintained at a high level of 400 poise or more, and thus, even when reactors are additionally provided to disperse the conductive carbon material, it is difficult to obtain a uniform spinning dope. Furthermore, a large number of coagulation spots are observed due to the non-uniform dispersion when viewed from the cross-section of the precursor, and it is difficult to perform drawing at the high drawing ratio necessary to ensure that the strength of the precursor corresponds to at least 6 g/denier.

**[0040]** The monomer may include an additional monomer that may be copolymerized with acrylonitrile, in addition to the acrylonitrile. Such an additional monomer functions to accelerate flameproofing treatment, and may include, for example, acrylic acid, methacrylic acid, or itaconic acid. Such a copolymerizable monomer is preferably used in an amount of 5 wt% or less based on the total amount of the polymer.

**[0041]** After the polymerization, neutralization is carried out using a polymerization terminator, which functions to prevent rapid coagulation in the coagulation bath upon spinning of the spinning dope including the polyacrylonitrile-based polymer. The polymerization terminator may be exemplified by ammonia, but the present invention is not limited

thereto.

**[0042]** The polymer, obtained from the monomer composition composed mainly of acrylonitrile, is neutralized using the above polymerization terminator, yielding a solution that includes the polyacrylonitrile-based polymer in salt form with an ammonium ion.

**[0043]** Used in the polymerization, the polymerization initiator is not particularly limited, and preferably includes an oil-soluble azo compound, a water-soluble azo compound, and a peroxide. Particularly useful is an azo compound, which enables safe handling and industrially efficient polymerization and additionally does not generate oxygen, which impedes polymerization when decomposed. When solution polymerization is carried out, an oil-soluble azo compound is preferably used from the aspect of solubility. Specific examples of the polymerization initiator may include 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile), 2,2'-azobis(2,4'-dimethylvaleronitrile), and 2,2'-azobisisobutyronitrile.

**[0044]** The polymerization temperature may vary depending on the kind and amount of the polymerization initiator, and preferably falls in the range from 30 to 90°C.

**[0045]** The solution including the polyacrylonitrile-based polymer includes a solid content of 7.5 to 25 wt%. When this solution is utilized as a spinning solution for producing the precursor fiber for a carbon fiber, it is easy to remove the solvent during the spinning, and tar or impurities may be prevented from being generated in the flameproofing process upon the production of the carbon fiber. Furthermore, the uniform density of filaments may be maintained.

**[0046]** The solution including the polyacrylonitrile-based polymer may be used as a spinning solution for producing the precursor fiber for a carbon fiber, and the precursor fiber for a carbon fiber may be obtained by spinning the spinning solution. The spinning solution may include an organic or inorganic solvent, as well as the polyacrylonitrile-based copolymer. Examples of the organic solvent may include dimethylsulfoxide, dimethylformamide, and dimethylacetamide.

**[0047]** The spinning process may include a wet spinning process or a dry-wet spinning process. In particular, a wet spinning process is performed by discharging the spinning solution from the holes in a spinneret into a coagulation solution in a coagulation bath. Specifically, the spinning solution is coagulated while swelling at least three times just after being discharged from the holes of the spinneret, and thus, the spinning draft does not significantly rise even when the winding speed is increased, but the substantial draft ratio is drastically increased, undesirably causing yarn breakage on the surface of the spinneret, with the result that there is an upper limit to the winding speed.

**[0048]** The dry-wet spinning process is performed in a manner in which the spinning solution is discharged in the air (air gap), surface-crystallized, and then guided into the coagulation bath, whereby the spinning draft ratio is substantially controlled by the dope in the air gap to thus enable high-speed spinning.

**[0049]** The coagulation rate or the drawing process may be appropriately adopted depending on the end use of the flameproof fiber or carbon fiber.

**[0050]** The coagulation solution of the coagulation bath may contain a coagulation accelerator, in addition to a solvent such as dimethylsulfoxide, dimethylformamide, dimethylacetamide, a zinc chloride ( $\text{ZnCl}_2$ ) aqueous solution, and a sodium rhodanide ( $\text{NaSCN}$ ) aqueous solution. The coagulation accelerator is acceptable so long as it does not dissolve the polyacrylonitrile-based polymer and is compatible with the solvent for the spinning solution, and the coagulation accelerator is exemplified by water. As such, the concentration of the solvent contained in the coagulation solution is preferably 15 to 75% of the concentration of the solvent contained in the spinning solution. When the concentration of the solvent thereof is 15% or more, the rate of extraction of the solvent from the spun fiber may be prevented from excessively increasing, and when the concentration of the solvent thereof is 75% or less, the solvent may be extracted in at least a minimum amount from the spun fiber.

**[0051]** The temperature of the coagulation solution is set to the range from -35 to +15°C based on the temperature of the spinning solution, whereby the rate of extraction of the solvent from the spun fiber is appropriately controlled, thus improving the degree of surface crystallization, resulting in increased yarn density and strength. When the temperature of the coagulation solution is low, the solvent of the coagulation solution may also have a low concentration, and when the temperature of the coagulation solution is high, the solvent of the coagulation solution may also have a high concentration. This is intended to appropriately adjust the rate of extraction of the solvent.

**[0052]** The spun polymer is discharged into the coagulation bath, after which the fiber is coagulated, followed by water washing, drawing, oiling and drying, yielding a precursor fiber for a carbon fiber.

**[0053]** As such, the coagulated fiber may be directly drawn in the drawing bath, without water washing, or may be additionally drawn in the drawing bath after the removal of the solvent through water washing. Also, to obtain a strong precursor fiber for a carbon fiber after oiling, multiple drawing steps may be performed at a low drawing ratio, or alternatively, drawing may be carried out at a high drawing ratio with steam at high temperature. The drawing ratio may be set to the range from 4 to 20, thus enhancing the strength of the precursor fiber. In particular, the monofilament strength of the precursor fiber is preferably 6 g/denier or more, and more preferably 8.0 g/denier or more in order to ensure high strength of the carbon fiber. Also, the monofilament strength of the precursor fiber may range from 6 to 15 g/denier.

**[0054]** Oiling the fiber is performed to prevent the monofilaments from adhering, and an oiling agent including silicone may be used. Such a silicone oiling agent may be exemplified by modified silicone, and modified silicone having high heat resistance and a mesh structure is preferably used.

[0055] The monofilament fineness of the precursor fiber thus obtained preferably falls in the range of 0.7 to 2.0 denier/filament. If the monofilament fineness is too low, yarn breakage may occur due to contact with a roller or a guide, undesirably deteriorating processing stability in the processes of spinning and firing the carbon fiber. On the other hand, if the monofilament fineness is too high, the structural difference between the inner and outer layers of each monofilament when viewed from the cross-section may increase after the flameproofing process, undesirably resulting in low processability in the subsequent carbonization process or poor tensile strength and tension modulus of the obtained carbon fiber. Briefly, if the monofilament fineness falls out of the above range, firing efficiency may be remarkably decreased. In the present invention, the monofilament fineness is set to the range of 0.7 to 2.0 denier/filament, whereby the difference in thermal stability and flameproofness between the inner and outer layers may be minimized, thereby ensuring uniform properties, including strength.

[0056] A better understanding of the present invention may be obtained through the following examples and comparative examples which are set forth to illustrate, but are not to be construed to limit the present invention, as is apparent to those skilled in the art.

## Mode for Invention

### Example 1-1

#### Production of polyacrylonitrile-based precursor fiber

[0057] A composition for a copolymer, comprising 95 mol% of acrylonitrile, 3 mol% of methacrylic acid, and 2 mol% of itaconic acid, was added with 0.2 wt% of a carbon material, CNT, based on the amount of acrylonitrile, after which solution polymerization was performed using a dimethylsulfoxide solvent, followed by neutralization with ammonia in an amount equal to the amount of itaconic acid, thus preparing a polyacrylonitrile-based copolymer in ammonium salt form, yielding a spinning dope having a copolymer content of 20 wt%.

[0058] The spinning dope was discharged through a spinneret (temperature: 45°C, diameter: 0.10 mm, 3,000 holes), and then placed in a coagulation bath containing a 40% dimethylsulfoxide aqueous solution at 45°C, thus manufacturing a coagulated fiber. The calorific value H of the coagulated fiber was measured using a DSC (Differential Scanning Calorimeter). The results are shown in Table 1 below. As flameproofing treatment was carried out, polyacrylonitrile molecules were formed into a condensed pyridine ring, which is thermally stable, and thus the calorific value H, obtained using the DSC, was reduced.

[0059] The coagulated fiber was washed with water and drawn five times, thus affording an intermediate drawn fiber.

[0060] The intermediate drawn fiber was dried using a heating roller, and drawn under compressed steam, yielding a polyacrylonitrile-based fiber bundle having a total drawing ratio of 8, a single-yarn fineness of 1.5 denier, and 3,000 filaments, which is referred to as a polyacrylonitrile-based precursor fiber for a carbon fiber.

#### Production of carbon fiber

[0061] The polyacrylonitrile-based fiber bundle was subjected to flameproofing treatment (including drawing) at regular time intervals in a four-stage hot-air oven having a temperature distribution of 220 to 270°C in an ambient atmosphere without twisting.

[0062] Thereafter, the fiber bundle was preliminarily carbonized at 400 to 700°C in an inert atmosphere to remove off-gas, followed by final carbonization (including drawing) at 1,350°C to enhance strength, thereby obtaining a carbon fiber.

### Other Examples and Comparative Examples (Comparative Examples 1-1, 1-2, 2-1, 3-1, 4-1, 5-1 and Comparative Examples 6 and 7)

[0063] Polyacrylonitrile-based precursor fibers and carbon fibers were manufactured in the same manner as in Example 1-1, with the exception that the kinds and amounts of conductive carbon material that were added were changed, as shown in Table 1 below.

#### Comparative Examples 1-3, 2-2 and 3-2

[0064] In Comparative Examples 1-3, 2-2 and 3-2, a copolymer comprising 95 mol% of acrylonitrile, 3 mol% of methacrylic acid and 2 mol% of itaconic acid was obtained through solution polymerization using a dimethylsulfoxide solvent, and was then neutralized with the addition of ammonia in an amount equal to the amount of itaconic acid, thus obtaining a polyacrylonitrile-based copolymer in ammonium salt form, thereby preparing a spinning dope having a copolymer content of 20 wt%, which was then added with a conductive carbon material in a kind and amount as shown in Table 1

and subsequently mixed. The subsequent processes for producing PAN precursor fibers and carbon fibers were performed in the same manner as in Example 1-1.

**[0065]** The polyacrylonitrile-based precursor fibers of the examples and comparative examples were measured for calorific value using a DSC and carbon fiber strength through the following methods. The results are shown in Table 1 below.

#### Calorific value using DSC

**[0066]** To evaluate thermal behavior after flameproofing treatment of the precursor, the calorific value was measured after flameproofing using a DSC (Model DSC 7), made by Perkin Elmer, and the samples were analyzed in an ambient atmosphere at a heating rate of 10/min.

#### Strength

**[0067]** The strength of carbon fibers was measured according to ASTM D4018.

[Table 1]

|          | Conductive carbon material |              | Flameproofing time (min) | Calorific value by DSC after flameproofing (H, J/mol) | Carbon fiber strength (GPa) | Note                                          |
|----------|----------------------------|--------------|--------------------------|-------------------------------------------------------|-----------------------------|-----------------------------------------------|
|          | Kind                       | Amount (wt%) |                          |                                                       |                             |                                               |
| Ex.1-1   | CNT                        | 0.2          | 45                       | 934                                                   | 3.45                        |                                               |
| Ex.1-2   |                            | 0.25         | 45                       | 895                                                   | 3.75                        |                                               |
| Ex.1-3   |                            | 0.30         | 45                       | 760                                                   | 2.95                        |                                               |
| C.Ex.1-1 |                            | 0.005        | 40                       | 1,790                                                 | -                           | Could not be fired                            |
| C.Ex.1-2 |                            | 3.5          | 40                       | 536                                                   | 1.75                        | Poor firing workability                       |
| C.Ex.1-3 |                            | 0.2          | -                        | -                                                     | -                           | Addition of CNT after polymerization          |
| Ex.2-1   | Graphene                   | 0.3          | 35                       | 1,112                                                 | 3.32                        |                                               |
| Ex.2-2   |                            | 0.4          | 35                       | 922                                                   | 3.89                        |                                               |
| Ex.2-3   |                            | 0.5          | 35                       | 716                                                   | 3.13                        |                                               |
| C.Ex.2-1 |                            | 0.01         | 35                       | 1540                                                  | -                           | Could not be fired                            |
| C.Ex.2-2 |                            | 0.2          | -                        | -                                                     | -                           | Addition of graphene after polymerization     |
| Ex.3-1   | CNT/graphene mixed at 1:1  | 0.5          | 35                       | 1,087                                                 | 3.61                        |                                               |
| Ex.3-2   |                            | 0.6          | 35                       | 881                                                   | 3.98                        |                                               |
| Ex.3-3   |                            | 0.7          | 35                       | 743                                                   | 3.45                        |                                               |
| Ex.3-4   |                            | 1.0          | 35                       | 785                                                   | 3.32                        |                                               |
| Ex.3-5   |                            | 1.6          | 35                       | 566                                                   | 2.98                        |                                               |
| C.Ex.3-1 |                            | 0.01         | 35                       | 1930                                                  | -                           | Could not be fired                            |
| C.Ex.3-2 |                            | 1.0          | -                        | -                                                     | -                           | Addition of CNT/graphene after polymerization |

(continued)

|          | Conductive carbon material |              | Flameproofing time (min) | Calorific value by DSC after flameproofing (H, J/mol) | Carbon fiber strength (GPa) | Note               |
|----------|----------------------------|--------------|--------------------------|-------------------------------------------------------|-----------------------------|--------------------|
|          | Kind                       | Amount (wt%) |                          |                                                       |                             |                    |
| Ex.4-1   | Carbon black               | 2.5          | 40                       | 571                                                   | 2.89                        |                    |
| Ex.4-2   |                            | 2.0          | 40                       | 687                                                   | 3.62                        |                    |
| Ex.4-3   |                            | 1.5          | 40                       | 825                                                   | 3.85                        |                    |
| C.Ex.4-1 |                            | 5            | -                        | -                                                     | -                           | Could not be spun  |
| Ex.5-1   | Graphene oxide             | 1.0          | 40                       | 732                                                   | 3.05                        |                    |
| Ex.5-2   |                            | 0.5          | 40                       | 969                                                   | 3.48                        |                    |
| C.Ex.5-1 |                            | 0.01         | 40                       | 1998                                                  | -                           | Could not be fired |
| C.Ex.6   | -                          | 0            | 40                       | 1,840                                                 | -                           | Could not be fired |
| C.Ex.7   | -                          | 0            | 90                       | 1,569                                                 | 3.28                        |                    |

**[0068]** As is apparent from Table 1, in Comparative Examples 1-1, 2-1, 3-1, 5-1 and 6, the conductive carbon material was added in small amounts or was not added, whereby flameproofness, resulting from flameproofing treatment for 40 min, was poor, and strength was drastically reduced in the carbonization process, thus causing yarn breakage, making it impossible to produce carbon fibers normally. In Comparative Examples 1-2 and 4-1, the carbon material, i.e. carbon black, was excessively added, and thus drawing could not be performed at a drawing ratio of 8 upon the formation of the polymer.

**[0069]** When the conductive carbon material was dispersed in the spinning solution after polymerization, as in Comparative Examples 1-3, 2-2 and 3-1, dispersibility became non-uniform due to the highly viscous spinning solution. Upon filtering of the spinning solution, a large amount of aggregated conductive carbon material was accumulated, consequently making it impossible to perform spinning.

**[0070]** As shown in Table 1, in the carbon fibers, without the use of conductive carbon material or with the use of conductive carbon material in an amount less than the required level, firing could not be performed attributable to excessive calorific values. On the other hand, in the carbon fibers using an excess of the conductive carbon material, spinning was impossible.

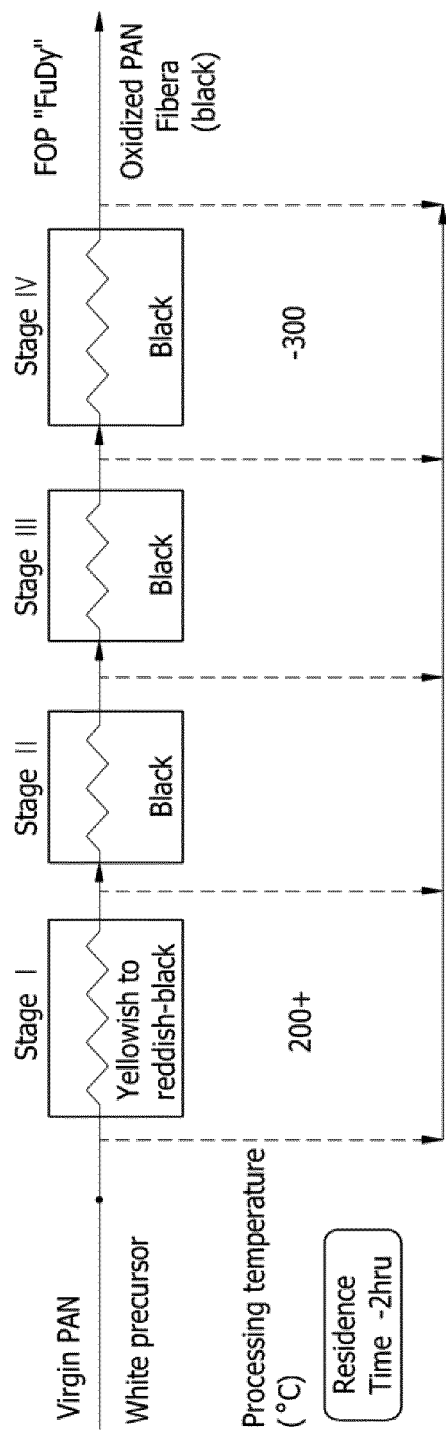
## Claims

1. A polyacrylonitrile-based precursor fiber for a carbon fiber, comprising a conductive carbon material.
2. The polyacrylonitrile-based precursor fiber of claim 1, wherein the conductive carbon material comprises at least one selected from the group consisting of carbon black, carbon nanotubes (CNT), graphene, and graphene oxide.
3. The polyacrylonitrile-based precursor fiber of claim 1, wherein the conductive carbon material is used in an amount of 0.03 to 3.0 wt% based on a total amount of the polyacrylonitrile-based precursor fiber.
4. The polyacrylonitrile-based precursor fiber of claim 1, wherein the conductive carbon material has an electrical resistivity ranging from  $3.5 \times 10^{-5}$  to  $10^3 \Omega\text{-cm}$ , a purity of 95% or more, and a particle diameter of 0.1 to 200 nm.
5. The polyacrylonitrile-based precursor fiber of claim 1, which has a single-yarn fineness of 0.8 to 2.0 denier.
6. A method of producing a polyacrylonitrile-based precursor fiber for a carbon fiber, comprising:
  - preparing a polyacrylonitrile-based polymer solution;
  - spinning a spinning solution including a polyacrylonitrile-based polymer, thus obtaining a spun fiber;
  - extracting a solvent from the spun fiber in a coagulation solution, thus manufacturing a coagulated fiber;
  - washing the coagulated fiber with water;

drawing the coagulated fiber;  
oiling the coagulated fiber; and  
drying the coagulated fiber,  
wherein in the preparing the polyacrylonitrile-based polymer solution, a conductive carbon material is added.

7. The method of claim 6, wherein in the preparing the polyacrylonitrile-based polymer solution, a solution containing monomers for a polyacrylonitrile copolymer is added with the conductive carbon material and then polymerized.
8. The method of claim 7, wherein the conductive carbon material is added in an amount of 0.03 to 3.0 wt% based on a total amount of the polyacrylonitrile-based precursor fiber.
9. The method of claim 6, wherein the conductive carbon material comprises at least one selected from the group consisting of carbon black, CNT, graphene, and graphene oxide.
10. The method of claim 6, wherein the conductive carbon material has an electrical resistivity ranging from  $3.5 \times 10^5$  to  $10^3 \Omega\text{-cm}$ , a purity of 95% or more, and a particle diameter of 0.1 to 200 nm.
11. The method of claim 6, wherein the drawing is performed at a drawing ratio of 4 to 20.

Figure 1



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2014/005523

## A. CLASSIFICATION OF SUBJECT MATTER

*D01F 6/18(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)

D01F 6/18; D04H 1/728; B01J 21/06; D01F 6/54; D01G 1/02; D02J 1/22; B01J 23/30; D01F 9/14

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

Korean Utility models and applications for Utility models: IPC as above

Japanese Utility models and applications for Utility models: IPC as above

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

eKOMPASS (KIPO internal) &amp; Keywords: carbon fiber, flame resistance, Polyacrylonitrile(PAN), heatstabilizing, electroconductive material

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                      | Relevant to claim No. |
|-----------|---------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X         | JP 2010-185163 A (TOYOCO CO., LTD. et al.) 26 August 2010<br>See abstract, claims 1-5, paragraphs [0011]-[0013].                                        | 1-11                  |
| A         | KR 10-2013-0027690 A (AMOGREENTECH CO., LTD. et al.) 18 March 2013<br>See abstract, claims 1-3, paragraphs [0028]-[0029].                               | 1-11                  |
| A         | KR 10-2013-0060969 A (INDUSTRY FOUNDATION OF CHONNAM NATIONAL UNIVERSITY) 10 June 2013<br>See abstract, claims 1-2, 4, 10-11, paragraphs [0012]-[0015]. | 1-11                  |
| A         | KR 10-2013-0022960 A (INDUSTRY FOUNDATION OF CHONNAM NATIONAL UNIVERSITY) 07 March 2013<br>See abstract, claims 1-12.                                   | 1-11                  |
| A         | KR 10-2012-0090126 A (KOLON INDUSTRIES, INC.) 17 August 2012<br>See abstract, claims 1-4.                                                               | 1-11                  |

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

\* Special categories of cited documents:

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search

23 SEPTEMBER 2014 (23.09.2014)

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT  
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International application No.

PCT/KR2014/005523

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member | Publication<br>date |
|-------------------------------------------|---------------------|-------------------------|---------------------|
| JP 2010-185163 A                          | 26/08/2010          | JP 5261405 B2           | 14/08/2013          |
| KR 10-2013-0027690 A                      | 18/03/2013          | KR 10-1309074 B1        | 16/09/2013          |
| KR 10-2013-0060969 A                      | 10/06/2013          | KR 10-1348202 B1        | 16/01/2014          |
| KR 10-2013-0022960 A                      | 07/03/2013          | KR 10-1334294 B1        | 28/11/2013          |
| KR 10-2012-0090126 A                      | 17/08/2012          | NONE                    |                     |

Form PCT/ISA/210 (patent family annex) (July 2009)