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

(11) Publication number: **0 301 915 A2**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **88307084.9**

(22) Date of filing: **01.08.88**

(51) Int. Cl.^{4}: **D 01 F 9/22**

(30) Priority: **31.07.87 JP 190301/87**

(43) Date of publication of application:
01.02.89 Bulletin 89/05

(84) Designated Contracting States: **DE FR GB**

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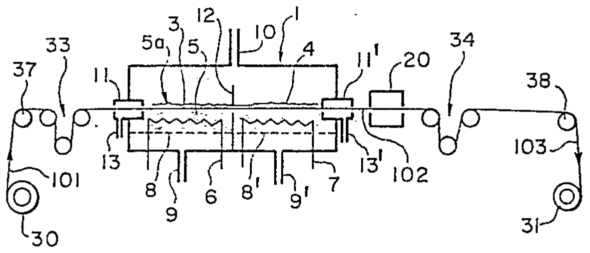
(54) Method for producing oxidized filaments.

(57) In a method for producing oxidized filaments (102) by treating precursor filaments (101) in a bed (5a) fluidized by an oxidizing gas and heat treating the precursor filaments (101) in the fluidized bed (5a), the fluidized bed (5a) is formed with heat-medium particles (5), not less than 80% by weight of which are of solid particles each having a particle diameter of not greater than 10 mesh, and the oxidation is carried out under optimum conditions within an optimum range of the treatment temperatures, an optimum range of depths H of the fluidized bed (5a) and an optimum gas speed of the oxidizing gas. By the method, the period of time required for the oxidation can be greatly shortened and oxidized filaments (102) having excellent characteristics can be obtained Furthermore, where the oxidized filaments thus obtained are carbonized, carbon fibers having excellent mechanical properties can be produced.

FIG. 2



EP 0 301 915 A2

Bundesdruckerei Berlin

Description

METHOD FOR PRODUCING OXIDIZED FILAMENTS

The present invention relates to a method for producing oxidized filaments by oxidizing precursor filaments.

Usually, oxidized filaments are produced by oxidizing precursor filaments, which consist of organic-polymer filaments such as polyacrylonitrile (hereinafter called "PAN") filaments, regenerated cellulose filaments, phenolic filaments, pitch filaments etc., in air or other oxidizing atmosphere at a temperature of about 200-300° C. When oxidizing pitch filaments, this heat treatment is conducted at a higher temperature, for example 450° C, in order to make infusible filaments. The oxidized filaments obtained by the above methods are used, for example, in the manufacture of flameproof material for flameproof clothing, and as a reinforcing material for reinforced cement. In recent developments, oxidized filaments have been used, instead of asbestos, as a heat resisting material or an abrasion resisting material.

The oxidized filaments can be further heat treated in an inert gas atmosphere, such as nitrogen or argon, at a temperature of 800-2000° C after the oxidation to make carbon fibers by carbonizing the oxidized filaments Furthermore, graphite fibers having a higher elastic modulus than that of carbon fibers can be produced by graphitizing the carbonized filaments in an inert gas atmosphere at a temperature of more than 2000° C.

The oxidation of the precursor filaments is a reaction associated with oxidation and cyclization, and the higher the treatment temperature becomes, the faster the rate of the reaction becomes, thereby shortening the period of time required for the oxidation. However, since the oxidation is associated with an exothermic reaction, if the treatment temperature is too high or a plurality of the individual filaments constituting the precursor filaments as a bundle of the plurality of individual filaments are too dense, the heat of the reaction accumulates in the filaments and fusion between the individual filaments and/or breakage of the precursor filaments, or even ignition of the filaments, may occur. Therefore, in order to increase the productivity of the oxidation process, it is necessary to treat the precursor filaments at a temperature as high as possible while eliminating the heat of the reaction as efficiently as possible.

As conventional methods suitable for such a requirement, a method in which hot air is blown onto precursor filaments and a method in which precursor filaments are brought into contact with the surface of a heated solid material, for example, heated rollers, are well known. The oxidation treatment is conducted for 20-120 minutes in the former method and for about 20 minutes in the latter method.

However, there is a problem in the conventional methods in that it is difficult to shorten the period of time for the treatment because there are certain limits to the extent to which the efficiency of heating precursor filaments and the efficiency of eliminating the heat of the reaction from the precursor filaments can be increased. In addition, there is a problem that it is difficult to treat precursor filaments, which are usually in the form of a bundle of filaments having a large total denier, for a relatively short period of time, and to uniformly treat the inside of such a bundle because, when the precursor filaments are present in such a bundle of large denier the inside of the bundle cannot be effectively heated or the heat of the reaction cannot be effectively eliminated from the inside of the bundle. Moreover, in the above method in which hot air is blown onto the precursor filaments, since a fairly large air volume is required to achieve a desired heat treatment and elimination of the heat of the reaction, usually the hot air is circulated from the viewpoint of saving energy and only a part of the hot air used for the treatment is exhausted. However, even if such a hot air circulation system is employed, the capacity of a heater provided in the system and the volume of the hot air to be used for the treatment become fairly great.

As an alternative to the above methods, GB-A-1207152 (JP-B-44-25375) discloses a first oxidation method wherein, in a method for heating filaments of polyacrylonitrile in an oxidizing atmosphere at a temperature of 200-300° C in a first stage and successively carbonizing the oxidized filaments in an inert gas atmosphere at a temperature of about 1000° C in a second stage, the heat treatment in the first stage is performed in a fluidized bed formed by a heat transfer material which is chemically inert to the filaments to be treated. US-A-3615212 (JP-B-47-18896) discloses a second alternative oxidation method including at least one step of etching a polymeric fiber in a fluidized bed.

However, the period of time required for the oxidation in the above first method is 0.5-1 hour, and that required in the second method is about 7 hours in the preoxidation process and 10-15 minutes in the postoxidation process. Accordingly, these methods are not advantageous from the viewpoint of the period of time for oxidation in comparison with the aforementioned method of blowing hot air or the method of bringing the filaments into contact with a heated solid material.

As solid heat-medium particles to be used for a fluidized bed, GB-A-1207152 discloses glass, ceramic or metal beads, and US-A-3615212 discloses glass or hollow alumina ballotini, or silica sand particles. In accordance with the methods described, we have carried out tests to produce oxidized filaments by continuously oxidizing precursor filaments of PAN in a fluidized bed formed with the above particles in a heating furnace. As a result, we have recognized that, unless the size of the heat-medium particles used for the fluidized bed, the depth H in the stationary state of the fluidized bed from the top surface thereof to the bottom thereof and the fluidization gas speed U_f of an oxidizing gas for fluidizing the bed are in adequate ranges, the precursor filaments are relatively easily broken by their heat of reaction during oxidation, fluffs of the oxidized filaments occur or fusion between individual filaments happens, thereby causing deterioration of the quality of the oxidized filaments in comparison with those of the oxidized filaments produced by the aforementioned conventional methods, and, in a case where many yarns of precursor filaments are simultaneously treated, differences between the yarns with respect to the degree of progression of the oxidation occur.

In addition, we have also recognized that, in the strand characteristics of the carbon fibers produced by carbonization successive to the above oxidation, the mechanical properties such as strength, modulus of elasticity, etc. of the carbon fibers are greatly decreased unless the above H and U_f are in the adequate ranges. Particularly, in a case where the oxidized filaments are continuously carbonized immediately successive to the oxidation, the mechanical properties of the carbon fibers obtained are greatly decreased as compared with those of the carbon fibers produced by the aforementioned conventional methods, as long as the heat-medium particles disclosed in the above GB-A-1207152 or US-A-3615212 are employed for the fluidized bed.

Furthermore, there is another problem in addition to the above, associated with the oxidation treatment using a fluidized bed.

Since the treatment in the oxidation process is associated with an exothermic reaction as aforementioned, usually an oil is supplied to the precursor filaments before the treatment in order to prevent a plurality of individual filaments constituting a bundle of the filaments from fusing to each other in the oxidation process. This oil serves to prevent the fusion of the individual filaments, and functions to increase the aggregation of the filaments constituting the bundle, thereby increasing the ease of handling of the filaments by preventing the filaments from being held by guide rollers or from entangling with each other. As this oil, a non-silicone oil, for example, a higher alcohol oil or higher fatty acid oil, is usually used.

However, there is the following problem in the oxidation wherein such a non-silicone oil is supplied to the precursor filaments and the filaments are oxidized in the fluidized bed of heat-medium particles at a high temperature for a short period of time.

Namely, since the non-silicone oil has a poor heat resistance, the oil cannot prevent the individual filaments of the precursor filaments from fusing to each other in the fluidized bed having a high temperature. As a result, the strength and modulus of elasticity of the carbon fibers obtained by carbonization successive to the oxidation become lower than those of the carbon fibers obtained by the aforementioned conventional methods. Although the treatment using a fluidized bed has a great advantage that the oxidation at a high temperature for a short period of time becomes possible because the bed has a high ability to eliminate the heat from the filaments, the treatment temperature cannot but be lowered because the oil has a poor heat resistance as mentioned above. Thus the supply of the oil has been an obstruction to realization of the advantage of the treatment using a fluidized bed.

JP-B-60-47382 discloses a silicone oil having a high heat resistance, but does not disclose use of the oil for the oxidation using a fluidized bed of heat-medium particles.

Furthermore, as a technology relating to the present invention, JP-A-55-128020 and JP-B-62-8521 disclose a method for using a solution in which carbon black particles are dispersed as a sizing solution for spinning or as an assistant solution for thermosetting of pitch filaments. In this method, however, although fusion between individual filaments when the precursor filaments of pitch filaments are converted to infusible filaments can be prevented by actively supplying carbon particles into the filaments, the same defect occurs with this method as occurs with the methods of GB-A-1207152 and US-A-3615212 described above, namely that the mechanical properties deteriorate as a result of generation of fluffs etc. of the oxidized filaments.

The present invention provides a method for producing oxidized filaments which can produce oxidized filaments having desired qualities for a short period of treatment time and capable of producing carbon fibers having excellent mechanical properties by subjecting the obtained oxidized filaments to a carbonization process.

The present invention provides a method for continuously producing oxidized filaments by passing precursor filaments through a bed fluidized by an oxidizing gas and heat treating the precursor filaments in the fluidized bed, the fluidized bed being formed on a means for dispersing the oxidizing gas and supplying the dispersed gas into the fluidized bed, the method including the steps of:

(a) forming the fluidized bed with heat-medium particles, not less than 80% by weight of which are of solid particles each having a particle diameter not greater than 10 mesh; and

(b) conducting the heat treatment of the precursor filaments at a temperature of 200-550°C under the conditions where a depth H(m) in the stationary state of the bed from the top surface of the bed to the dispersing means is in a range given by equation (1) and a fluidization gas speed U_f (Ncm/S) of the oxidizing gas for fluidizing the bed is in a range given by equation (2).

$$20\ M_f/(\rho_p\ C_p\ A)\ <\ H\ <\ 500/\rho_p \qquad (1)$$

$$0.3(dp^2\rho_p/\mu)^{0.538}\ <\ U_f\ <\ 2.4(dp^2\rho_p/\mu^{0.538} \qquad (2)$$

where,

M_f = weight of the precursor filaments existing in the fluidized bed (Kg),

ρ_p = bulk density of the heat-medium particles (Kg/m^3),

C_p = specific heat of the heat-medium particles (Kcal/Kg°C),

A = fluidization area of the fluidized bed (m^2),

U_f = fluidization gas speed determined by dividing a normal flow rate of the oxidizing gas at a temperature for the heat treatment by the fluidization area A (Ncm/S),

dp = average particle diameter of heat-medium particles based on weight distribution of the heat-medium

particles (m),
μ = coefficient of viscosity of air at a temperature for the heat treatment (Kg S/m^2),
and equations (1) and (2) are calculated by using the above dimensions.

The precursor filaments treated in accordance with the method of the present invention may be in the form of, for example, a continuous or discontinuous yarn comprising the filaments, a strand or a tow obtained by spinning an organic polymer typified by polyacrylonitrile, regenerated cellulose, phenol and pitch or a spun yarn, a woven or knitted fabric or a cloth thereof, and thus the configuration of the precursor filaments is not restricted to any particular type. The precursor filaments are preferably constructed of a plurality of individual filaments each individual filament of which has a denier in the range of 0.5-5 deniers, and the total denier of the precursor filaments which take the form of a bundle of individual filaments is preferably in the range of 500-500,000 deniers.

The fluidized bed used in a method according to the present invention provides a means for heat treatment under conditions where solid heat-medium particles are fluidized by an oxidizing gas. The heat-medium particles are fluidized by the oxidizing gas and the particles are heated to 200-550°C, preferably 240-500°C, in the fluidized bed.

In the method of the present invention, the oxidizing gas may be any gas generating a reaction of oxidation on the precursor filaments, such as a gas containing sulfur, and may be other than air.

The heat-medium particles, according to the present invention, are solid particles to be used in the state that they are fluidized by a gas. The heat-medium particles have a property of heat resistance capable of resisting against a temperature required for the oxidation, that is, preferably more than 350°C, more preferably more than 400°C. As such heat-medium particles, inorganic particles, such as ceramics or glass comprising, for example, carbon, alumina, silicon carbide, zirconia or silica as the sole or as the main component, can be used.

The particle diameter of not less than 80% by weight of the heat-medium particles is not greater than 10 mesh (Tyler system) as measured according to a sieving test defined in JIS japanese Industrial Standard)-Z-8815 (this Standard corresponds to ISO-3310/1 and ISO-3310/2.), using a standard sieve defined in JIS-Z-8801, preferably not greater than 28 mesh. If the particle diameter is greater than the above value, a large volume or pressure of the oxidizing gas is required for fluidizing the bed, and since the energy of the heat-medium particles, when the particles collide with the precursor filaments, becomes greater, physical damage such as the formation of fluffs is liable to occur in the filaments. On the contrary, if the particle diameter is small, the gas volume required for the fluidization decreases and damage to the filaments also decreases.

The shape of the heat-medium particle is not restricted to a particular one. However, a shape without sharp edge portions, for example, a near spherical shape is preferable because physical damage to the precursor filaments is suppressed so that little damages occurs.

The particle diameter of the heat-medium particles is preferably greater than a certain value, because the particles having a diameter which is not too small adhere to the filaments only with difficulty and can be easily eliminated from the filaments even if the particles do adhere to the filaments The lower limit of the particle diameter satisfying such a requirement is preferably 400 mesh, more preferably 200 mesh. Namely, the heat-medium particles are preferably solid particles, not less than 80% by weight of which have a particle diameter not greater than 28 mesh and not less than 400 mesh. The upper limit is chosen so as not to cause damage to the filaments taking into account the fluidization gas speed U_f. The lower limit is chosen so as to suppress the number of the particles adhering to the oxidized filaments to a small value. If the particle diameter is smaller than the lower limit, the number of particles adhering to the oxidized filaments becomes radically large, it becomes difficult to sufficiently eliminate the adhering particles and damage to the oxidized filaments is liable to occur by pressing or scratching at the positions of rollers or guides. In a case where the oxidized filaments are produced by use of heat-medium particles other than carbon particles and successively the oxidized filaments are carbonized to produce carbon fibers, any metal components in the heat-medium particles adhering to the oxidized filaments react with the carbon fibers in the carbonization process and the reaction impairs the mechanical properties of the carbon fibers as described later. Thus, in this case in particular, it becomes necessary to decrease the number of the adhering particles to an even a smaller extent.

The bulk density ρ_p of the heat-medium particles in the method of the present invention is determined by measuring the volume of heat-medium particles by use of a volumetric analysis meter defined in JIS-R-3505 and by measuring the weight of the heat-medium particles. The bulk density of the heat-medium particles ρ_p is preferably in the range of 0.3-2.5 g/cm^3 from the viewpoint of ensuring ease of fluidization and a large heat capacity for sufficiently eliminating the heat of the reaction.

The depth H, in the stationary state of the fluidized bed, from the top surface of the bed to the dispersing means which is disposed at the bottom of the bed and supplies the oxidizing gas uniformly into the bed, must be in a range given by the following equation (1), because, the deeper the bed becomes, the higher the gas pressure required for fluidizing the bed becomes, and damage to the precursor filaments is liable to occur on account of the increase of the energy of the particles due to the increase of the gas pressure.

Firstly, the equivalent hydrostatic pressure ΔP (kg/m^2) of the bed of the heat-medium particles is defined by the following equation.

$\Delta P = W_p/A = \rho_p H$ (3)

Here,
W_p = total weight of the heat-medium particles in the fluidized bed (Kg),

A = fluidization area (sectional area of the fluidized bed through which the fluidizing gas passes) (m^2),
ρ_p = bulk density of the heat-medium particles (Kg/m^3),
H = depth of the fluidized bed in the stationary state thereof (m).

The pressure ΔP is desirably in a range given by the following equation so as not to cause damage to the precursor filaments.

$\Delta P < 500\ (Kg/m^2)$ (4)

This ΔP is also a pressure loss of the fluidized bed at the starting point of the fluidization.

Then, a heat capacity sufficient to eliminate the heat of the reaction of the precursor filaments is required for the fluidized bed.

$W_p\ C_p\ \Delta T > Q\ M_f$ (5)

Here,
C_p = specific heat of the heat-medium particles (Kcal/Kg°C),
M_f = weight of the precursor filaments existing in the fluidized bed (Kg),

Q (Kcal/Kg) is the heat of the reaction per unit weight of the precursor filaments due to the oxidation, and Q is in the range of 200-1000 (Kcal/Kg). ΔT is an acceptable increase of temperature due to the exothermic reaction such as not to cause breakage or ignition of the precursor filaments. When this ΔT is set at 10°C, the following equation is derived from equation (5).

$W_p > Q\ M_f/(C_p\ \Delta T) = 20\ M_f/C_p$ (6)

From the equations (3), (4) and (6), the following equation for W_p (Kg) can be derived.

$20\ M_f/C_p < W_p < 500A$ (7)

Therefore, the depth H (m) of the fluidized bed can be expressed as follows.

$20\ M_f/\rho_p\ C_p\ A) < H < 500/\rho_p$ (1)

In the range of $H < 20\ M_f/(\rho_p\ C_p\ A)$, the heat capacity of the heat-medium particles is too small and breakage of the filaments due to the heat of the reaction is liable to occur. In the range of $H > 500/\rho_p$, the gas pressure required for the fluidization is too high and fluffs of the filaments are liable to occur.

Next, the fluidization gas speed U_f determined by tests is explained. The tests were carried out as follows.

As the heat-medium particles, solid particles such as graphite, alumina, silica or alumina-silica having the shape of a block, sphere (bead) or hollow bead were selected. At least 80% by weight of the particles had a particle diameter not greater than 10 mesh. A fluidized bed of which the depth H was in the range given by equation (1) was formed. The fluidized bed was fluidized by compressed air at 260°C under conditions of various gas speeds. As precursor filaments, PAN filaments, as a bundle of 12,000 individual filaments each individual filament of which has a size of 0.73 denier, were selected, and the precursor filaments were allowed to remain in the fluidized bed for 20 minutes under a tension of 800g. Thus oxidized filaments were obtained. For each gas speed, the value of $dp^2\ \rho_p/\mu$ was calculated from the dp and ρ_p of the heat-medium particles used and μ of air at 260°C. The relationship between the calculated $dp^2\rho_p/\mu$ (m/s) and fluidization gas speeds U_f (Ncm/s) is shown in FIG.1, where it is represented by a double logarithmic graph. A key to the symbols used in FIG.1 is given by Table 7.

Table 7

Shape of Particles	Good	Defect A	Defect B
Block	△	▲	⨻
Sphere	○	●	⊗
Hollow sphere	◎	◉	⦻

Referring to the graph, when U_f was in the range given by the following equation,

$U_f < 0.3\ (dp^2\rho_p/\mu)^{0.538}$ (8)

the following defects (referred to generally above as "defect B") occurred, namely breakage of the filaments on account of lack of elimination of the heat of the reaction due to a poor fluidization of the heat-medium particles, and non-uniformity of the degree of progress of oxidization of the filaments due to non-uniformity of temperature in the fluidized bed. When U_f was in the range given by the following equation,

$U_f > 2.4\ (dp^2\ \rho_p/\mu)^{0.538}$ (9)

fluffs of the oxidized filaments thus obtained greatly increased (defect A above).

Where U_f was in the medium area, that is, in the range given by the equation

$0.3\ (dp^2\ \rho_p/\mu^{0.538} < U_f < 2.4\ (dp^2\ \rho_p/\mu)^{0.538}$ (2)

breakage of the filaments did not occur, and uniformity of the degree of oxidation of the oxidized filaments thus obtained was achieved because non-uniformity of temperature in the fluidized bed was very small ("good" area referred to above and shown in FIG.1). When the oxidized filaments thus obtained were successively carbonized at 1350°C, carbon fibers having a good quality were obtained.

Thus, in the present invention, the oxidized filaments are produced by a method wherein the heat-medium particles are small-sized solid particles not less than 80% by weight of which have respective particle diameters not greater than 10 mesh, preferably not greater than 28 mesh, measured according to the method of JIS-Z-8815 using a standard sieve defined in JIS-Z-8801, the bed of the heat-medium particles has the depth H in the stationary state in the range given by equation (1), the bed is fluidized by the oxidizing gas with a fluidization gas speed U_f in the range given equation (2), and the precursor filaments are oxidized by the heat treatment in thus fluidized bed.

The oxidized filaments obtained can be converted to carbon fibers by heat treating the filaments in an inert gas atmosphere such as N_2 or Ar at 800-2000°C, and if required, can be converted to graphite fibers by graphitizing the filaments in the inert gas atmosphere at a temperature of more than 2000°C.

When the carbon fibers are produced from the oxidized filaments obtained by the method according to the present invention, so-called carbon particles whose main component is carbon are preferable as heat-medium particles used for the oxidation process.

Typical of such carbon particles are carbon black, thermal black, hollow carbon, activated carbon powder, activated carbon bead, glassy carbon powder, mesophase pitch bead, artificial graphite powder, granulated graphite powder, and natural graphite powder. The carbon particles have a carbon component of more than 50%, preferably more than 90%. In such carbon particles, even if the particles adhering to the oxidized filaments are brought into the carbonization process, in practice the particles do not impair to any significant extent the properties of the carbon fibers because any metal components contained in the carbon particles merely react with the carbon in the particles themselves in the carbonization process. Since the carbon particles enter between the individual filaments of the precursor filaments in oxidation and the presence of such particles between the individual filaments can prevent fusion between the individual filaments, the particle diameter of the carbon particles is not restricted to a smaller size.

In inorganic particles other than carbon particles, any metal components of the particles, which react with carbon in the carbonization process, that is, in the inert gas atmosphere at 800-2000°C, for example Fe, Ca, Mg, Mn, Cu, Zn, Cr, Ni, etc., are deleterious when the oxidized filaments are carbonized, because the metal components react with the carbon fibers themselves and cause deterioration of the mechanical properties of the carbon fibers. Thus, if desired carbon fibers are to be produced, the total weight of such metal components in particles other than carbon particles is preferably not greater than 1.0 wt.%. When using particles other than carbon particles which contain metal components in an amount greater than the above value, even if special separate means are provided for eliminating about 80% of the particles adhering to the oxidized filaments, it is still inevitable that the mechanical properties of the carbon fibers deteriorate as a result of the reaction between the metal components and the carbon fibers during carbonization.

Furthermore, in a case where heat-medium particles for the oxidation process are inorganic particles other than carbon particles or are a mixture of the inorganic particles other than carbon particles and carbon particles, and the oxidized filaments are carbonized successively to the oxidation process, the amount of the heat-medium particles adhering to the oxidized filaments is preferably suppressed to an extent such that the total amount of any metal components available for reaction with carbon in the carbonization process, such as Fe, Ca, Mg, Mn, Cu, Zn, Cr, Ni, etc., is not greater than 100 ppm, preferably not greater than 10 ppm. The total amount of the metal components is defined as a total ratio of;

> (the weight of the residual heat-medium particles adhering to the oxidized filaments) x (the weight ratio of the metal components to the total components in the particles)/(the total weight of the oxidized filaments including the residual heat-medium particles adhering to the filaments).

This amounts to a ratio of total weight of metal components in the residual heat-medium particles to the total weight of oxidized filaments and residual heat-medium particles adhering thereto. Carbon fibers having excellent properties can be obtained by maintaining the quantity of metal components within the above range.

The metal components in the residual heat-medium particles adhering to the oxidized filaments are detected and determined as follows. After a sample of the oxidized filaments including the residual particles is subjected to heat incineration in air at 600°C for 4 hours, the sample is dissolved in hydrochloric acid and the metal components are detected and determined from the solution by an atomic absorption method using an atomic absorption photometer, for example, a Hitachi 170-30 type atomic absorption photometer.

The weight of the residual heat-medium particles adhering to the oxidized filaments is determined from the ratio between (a) the weight of the metal components in the residual heat-medium particles, which weight is determined from the difference between the weight of the metal components determined from the sample of the oxidized filaments having the residual heat-medium particles by the above atomic absorption method and the weight of the metal components determined from a sample of only the precursor filaments by the same method, and (b) the weight ratio of the metal components to total components in the heat-medium particles.

With respect to the adhesion of the heat-medium particles to the oxidized filaments, in a case where the precursor filaments are formed as a tow or a fabric, it is better to dispose the width direction of the tow or the fabric in a vertical plane in the fluidized bed than to dispose it in a horizontal plane, because the precursor material passing through the fluidized bed in such a state does not hinder the heat-medium particles from being fluidized and the amount of the particles adhering to the oxidized filaments becomes small.

Methods for eliminating the heat-medium particles adhering to the oxidized filaments are, for example, ultrasonic cleaning, water washing, chemical cleaning, excitation, suction and air blowing. In these methods, the efficiency of the elimination can be increased by eliminating the particles in a state where the filaments are opened. The method for elimination is desirably a method carried out as statically as possible and is desirably a noncontact method wherein a solid object does not come into contact with the filaments. A method, for instance, of exciting the filament with a contact member is not desirable because damage to the filaments is liable to occur.

Since the amount of the metal components in the particles adhering to the oxidized filaments can be suppressed to less than 100 ppm, preferably 10 ppm, by use of one of the above desirable methods, it becomes possible to produce carbon fibers having excellent mechanical properties in the carbonization process.

In a case where the total amount of the metal components of the heat-medium particles adhering to the oxidized filaments after the oxidation is already within the above range without the elimination, it is not always necessary to eliminate the residual particles on the filaments. The elimination of the residual particles may be carried out in any of the oxidation process and the carbonization process as long as any elimination is carried out before the carbonization of the oxidized filaments.

In the method according to the present invention for producing the oxidized filaments using the fluidized bed, oxidized filaments having an excellent quality without physical damage such as fluffs can be produced stably, in a short period of time for the oxidation and with a high productivity, by setting the particle diameter of the heat-medium particles within the aforementioned range, forming the fluidized bed having the depth H in the range given by equation (1) and setting the fluidization gas speed U_f in the range given by equation (2). Moreover, by adequately selecting the composition of the heat-medium particles and suppressing the amount of the metal components in the residual particles adhering to the oxidized filaments, in the process of producing the oxidized filaments as aforementioned, carbon fibers having excellent mechanical properties can be produced in the carbonization process after the oxidation process.

In the method according to the present invention, since the fluidized solid heat-medium particles conduct their heat intermittently to the precursor filaments via their convection parts (parts of the heat-medium particles brought into contact with the filaments) and remove the thermal boundary layers around the filaments, the efficiency of both heating the filaments and eliminating the heat of reaction from the filaments is extremely high in comparison with the aforementioned conventional methods. Therefore, the temperature for the oxidization can be raised higher than that in the conventional methods, for example, to a temperature of 200-400°C, preferably 240-350°C, for PAN precursor filaments, and 250-550°C, preferably 270-500°C, for pitch precursor filaments. As a result, for example, in a treatment having two temperature stages, the period of time for oxidizing precursor filaments can be shortened to 2.5 minutes for precursor filaments formed as a bundle of 12,000 of 0.73 denier fibers, 4 minutes for a bundle of 24,000 fibers and 9 minutes for a bundle of 48,000 fibers.

There is also a relationship between the outer shape of the precursor filaments and the period of time required for the oxidation. Thus, the period of time can be further shortened by actively flattening the outer shape of the bundle of the filaments and adjusting the ratio (w/d) between the width (w) and the thickness (d) of the outer shape to at least 5. With this flattening, it is possible to set the thickness (d) to a value less than 3 mm,and set the running direction of the precursor filaments in the horizontal direction but with the width direction of the flattened precursor filaments set in the vertical direction. Where such a setting is carried out, it becomes possible to oxidize even precursor filaments of 48,000 individual filaments each of 0.73 denier in less than 5 minutes with 2 stages of the heat treatment. If the number of stages of heat treatment is further increased, the period of time for the oxidation can be further shortened.

The upper limits of heat treatment temperature and the periods of time in the oxidation of PAN precursor filaments with respect to total denier of the bundle of the filaments are summarized in Table 1. Of course, it is possible to lengthen the period of time for the oxidization longer than that in Table 1 by lowering the treatment temperature, but, if it is too long, the quality of the oxidized filaments is impaired, and so this is not desirable. Therefore, it is desirable to set the period of time for the oxidation within 30 minutes.

Table 1

Item	Total Denier		
	12,000	24,000	48,000
Treatment Temperature (°C)	265-320	260-315	240-310
Time for Oxidation (minutes)	0.5-5	2-10	3-20

In the oxidation according to the method of the present invention, it is preferable that the precursor filaments run substantially in a horizontal direction without significantly changing direction in the fluidized bed and the filaments are continuously oxidized. Oxidized filaments having a high quality almost without physical damage can be produced by such a running system. However, outside of the fluidized bed, the running direction of the filaments may be changed significantly, and the filaments can be passed through the fluidized bed several times.

In the method of the invention, a silicone compound is preferably supplied to the precursor filaments before the heat treatment in the fluidized bed. The silicone compound is supplied as an oil, and the silicone oil is preferably, for example, a mixture of an oil containing a higher alcohol oil having at least 18 carbon atoms and/or a higher fatty acid oil, an organic oxidation inhibitor and a straight-chain silicone. More specifically a preferred oil is made by compounding 1-20 wt.% of an organic oxidation inhibitor into 80-99 wt.% of a higher alcohol and/or higher fatty acid oil and compounding 5-50 wt.% of a straight-chain silicone into 50-95 wt.% of the above mixture.

The silicone compound may be supplied by introduction into the raw material polymer prior to the manufacture of the precursor filaments, as shown in JP-A-52-148227. In a case where the silicone compound is supplied in the form of an oil, the straight-chain silicone must be compatible with the higher alcohol and/or fatty acid oil which becomes the matrix for the silicon, and therefore, a silicone material capable of water dispersion is used for incorporation into the silicone oil, for example, a polyether modified polysiloxane, alcohol modified polysiloxane, dimethylpolysiloxane emulsion-polymerized with a little emulsifier, alkyl modified polysiloxane, or an amino modified polysiloxane. Such a silicone material is preferably supplied to the precursor filaments in an amount of 0.1-5% by weight of the weight of the precursor filaments.

Fusion between individual filaments of the precursor filaments can be prevented, and the aforementioned high treatment temperature and the short period of time for the oxidation can be achieved, by supplying such a silicone compound to the precursor filaments.

The production system for producing the oxidized filaments by the method of the present invention may be a batch treatment system or a continuous treatment system. In the case of batch treatment, the precursor filaments can be treated by winding them onto a hank or putting them into a net. In the case of continuous treatment, the precursor filaments can be treated, for example, by running the filaments between rollers and passing the filaments through the fluidized bed. In this case, a system wherein a plurality of the running precursor filaments are arranged in parallel to each other as a plurality of running yarns, or a system having several stages, at which respective treatment temperatures are different from each other, by dividing the fluidized bed or providing a plurality of fluidized beds, can be adopted. However, a system wherein the direction of the precursor filaments is changed in the fluidized bed by rollers, such as that shown in US-A-3615212, is not preferable because physical damage to the precursor filaments due to trapping of the heat-medium particles between the roller and the filaments is liable to occur. Therefore, it is better to run the precursor filaments in a linear direction at least in the fluidized bed with a desirable tension, i.e. without significantly changing the filament direction in the bed.

The above and other objects, features and advantages of the present invention will become apparent and more readily appreciated from the following detailed description of the preferred exemplary embodiments of the invention, taken in conjunction with the accompanying drawings, in which;

FIG.1 is a graph showing the results of tests for deciding upon the fluidization gas speeds to be used in a method embodying the present invention;

FIG.2 is a schematic side view of an oxidized filament producing system for use in a method according to an embodiment of the present invention; and

FIG3. is a schematic side view of a system for producing carbon fibers from the oxidized filaments obtained by the system shown in FIG.2.

A method for producing oxidized filaments and a method for producing carbon fibers from the oxidized filaments, according to a preferred method embodying the present invention, will now be described hereunder with reference to the attached drawings.

In FIG.2, precursor filaments 101 are drawn from a package 30. The precursor filaments 101 are passed through an oxidizing furnace 1 with a fluidized bed 5a of heat-medium particles 5 and oxidized in the bed under a constant tension. Filaments 102 thus oxidized are obtained. Subsequently, if necessary, the oxidized filaments 102 are passed through a means 20 for eliminating the residual heat-medium particles on the filaments so as to obtain oxidized filaments 103 having on them the residual particles in an amount less than a certain level, and the oxidized filaments 103 are wound as a package 31. As the case may be, for instance, depending on the ultimate use of the oxidized filaments 102, the elimination means 20 may not be necessary. In a case where the oxidized filaments are carbonized and the amount of the residual heat-medium particles adhering to the oxidized filaments is more than the value aforementioned, carbon fibers with a high quality can still be obtained by eliminating the residual particles so as to suppress the number of the particles to less than a certain level in the oxidation process as shown in FIG.2 or before carbonizing the oxidized filaments in the carbonization process.

The oxidizing furnace 1 is divided by a partition 12 in the running direction of the precursor filaments 101. The fluidized bed thus divided comprises two heating areas 3 and 4 having respective heaters 6 and 7. Oxidizing gas, for example, compressed air, is supplied to each heating area via respective gas supply pipes 9 and 9′. The air is dispersed by dispersion plates 8 and 8′ constructed, for example of a sintered wire mesh, sintered metal, or porous or perforated plate, and then passes through the bed, where it fluidizes the bed. The used air is thereafter exhausted through an exhaust duct 10. In order to prevent the heat-medium particles 5 and/or the hot air from flowing out of the furnace through the entrance and exit openings provided for the introduction and departure of the filaments, sealing means, for example, pressurized sealing chambers 11 and 11′ are provided, sealing gas being supplied to the chambers via supply pipes 13 and 13′ at a pressure higher than the pressure of the atmosphere in the furnace so as to prevent the heat-medium particles or the hot air from escaping. Of course, other sealing means, for example, an ejector for directing gas flow toward the inside of the furnace, may be adopted, and as the case may be, a system wherein the heat-medium particles flow out of the furnace and are stored without sealing, the stored particles being automatically returned to the fluidized bed by a returning means such as a screw feeder, can be employed.

The following matters are desirable and important in any sealing method. Firstly, it is desirable to project the nozzles for introducing and drawing the filaments into and from the furnace respectively up to the inside of the fluidized bed. Secondly, in the entry region of the furnace at which the filaments are introduced into the furnace, an inert gas, or an oxidizing gas at a temperature lower than the temperature causing a breakage of the precursor filaments, is desirably supplied as the sealing gas. In such a method, damage to the filaments due to abrasion between the filaments and the stagnated particles, or breakage of the filaments in the entry region due to fusion between individual filaments or due to the exothermic nature of the filaments themselves, can be prevented.

Although the furnace 1 is divided into two heating areas by the partition 12 in the embodiment, the heating areas can be divided further, or a plurality of furnaces can be provided and the treatment temperatures of the plurality of furnaces can be set to respective values different from each other.

The oxidized filaments 102 or 103 produced by the method according to the present invention, if required, can be subsequently carbonized using a carbonizing furnace 2 as shown in FIG.2. The oxidized filaments are carbonized to make carbon fibers 104 and the carbon fibers are wound as a package 32. The oxidized filaments may be carbonized in a batch system.

Resistance heating or induction heating can be adopted as a method for heating the carbonizing furnace 2, but the heating method is not particularly restricted as long as it can be carried out in an inert gas atmosphere such as N_2, Ar, or He and it can achieve a required temperature.

Although the oxidation and the carbonization are carried out separately in the embodiment shown in FIGS. 2 and 3, alternatively the carbon fibers 104 can be obtained by carbonizing the oxidized filaments 102 or 103 continuously after the oxidation.

Numerals 37, 38, 39 and 40 show guide rollers, respectively, and numerals 33, 34, 35 and 36 show drive rollers, respectively, in FIGS. 2 and 3.

In the above oxidation process, silicone compound is pre-supplied (i.e. during manufacture) to the precursor filaments 101, or supplied before the filaments reach the fluidized bed 5a in the furnace 1.

Examples 1 and 4:

PAN filaments, of which each individual filament was 0.73 denier and which were formed as a bundle of 12,000 of the individual filaments, were used as precursor filaments. The fluidized bed was divided into two heating areas, each area having an effective length of 0.45m, by a partition, as shown in FIG.2. High purity alumina beads having 99.8 wt.% alumina component (E in Table 2) and graphite powder having 99.9 wt.% carbon component (A in Table 2) were selected as heat-medium particles of the fluidized bed in Examples 1 and 4, respectively. The bed was fluidized by compressed air. 10 yarns of the precursor filaments, which were spaced from each other by 10mm and ran parallel with each other, were introduced to the bed at a running speed of 0.095m/min. and drawn from the bed at a running speed of 0.09m/min. The withdrawal speed is slower than the speed of introduction because heat contraction of the treated filaments in the fluidized bed occurs. The precursor filaments were continuously oxidized in the bed for 10 minutes under a certain tension at 275° C. The residual heat-medium particles adhering to the oxidized filaments thus obtained were eliminated to a certain extent by the compressed air blown from an air nozzle, and the oxidized filaments were wound as a package. The quality of the oxidized filaments thus obtained, as measured for example by the number of fluffs, and the amount of fusion between filaments, was of the same grade as that of the oxidized filaments obtained in the conventional method using hot air. The amounts of deleterious metal components were determined by the aforementioned method. The results are shown in Table 3.

Next, the oxidized filaments were carbonized in N_2 gas atmosphere at 1350° C with the running speed of 1m/min. The strand characteristics of a obtained carbon fibers are shown in Table 3 (Examples 1 and 4).

Examples 2 and 3:

The same precursor filaments and the same fluidized bed-containing oxidizing furnace as those used in Examples 1 and 4 were used in these Examples. The particles shown as E and F in Table 2 were used as heat-medium particles, respectively, and the particles were fluidized and heated under the conditions shown in Table 3. The filaments were oxidized at two stages at respective different treatment temperatures with a running speed twice that in Examples 1 and 4, for 5 minutes. After the oxidation, the residual particles adhering to the oxidized filaments were eliminated and the ratios of the metal components in the residual particles as hereinbefore defined were suppressed to the values shown in Table 3. The oxidized filaments thus obtained were wound as a package. The qualities of the oxidized filaments obtained were of the same grade as those of the oxidized filaments obtained in Examples 1 and 4.

Next, the oxidized filaments were carbonized under the same conditions as those in Examples 1 and 4. The strand characteristics of the carbon fibers thus obtained are shown in Table 3.

Examples 5, 6 and 7:

The same precursor filaments and the same fluidized bed-containing oxidizing furnace as those of Example 1 were used, and the graphite powder shown as A in Table 2 as used as heat-medium particles of the fluidized bed. The precursor filaments were heat treated and oxidized at 2 stages at respective different treatment temperatures as shown in Table 3 for 5 minutes The residual particles adhering to the oxidized filaments were eliminated so that the ratio of the metal components was suppressed to the value shown in Table 3, and after that the oxidized filaments were wound as a package. The quality of the oxidized filaments obtained was better than that of the filaments obtained using other heat-medium particles.

Next, the oxidized filaments were carbonized under the same conditions as those in Example 1. The strand characteristics of the carbon fibers thus obtained are shown in Table 3.

Example 8:

The same precursor filaments and the same fluidized bed-containing oxidizing furnace as those of Example 1 were used, and the graphite powder shown as A in Table 2 was used as heat-medium particles of the fluidized bed. The precursor filaments were heat treated and oxidized at 2 stages at respective different treatment temperatures lower than those in Examples 5-7, under the conditions shown in Table 3 for 10 minutes. The quality of the oxidized filaments thus obtained was of the same grade as those in Examples 5-7 when measured by observation.

Next, the oxidized filaments were carbonized under the same conditions as those in Example 1. The strand characteristics of the carbon fibers thus obtained are shown in Table 3.

Example 9:

PAN filaments, of which each individual filament had a size of 0.73 denier and which were formed as a bundle of 12,000 of the individual filaments, were used as precursor filaments. Silicone oil containing 1.6 wt.% hydrocarbon surface active agent and 0.4 wt.% amino modified silicone oil was supplied to the precursor filaments, and the precursor filaments were oxidized in a fluidized bed of alumina powder (B in Table 2) fluidized by compressed air, under the conditions shown in Table 4. The oxidized filaments thus obtained were wound as a package. Samples were cut from the oxidized filaments to a length of 2-3 mm, and immersed in 100 cc of an aqueous solution containing 0.1% Noigen SS (produced by Daiichi Kogyo Seiyaku Kabushiki Kaisha: Japanese company), after which the solution was dispersed for one minute by a stirrer, filtered under reduced pressure to deposit the cut filaments on a filter paper, and the degree of the fusion between individual filaments was observed and classified into 5 grades. As a result, it was found that the grade was as good as that of the oxidized filaments obtained by a conventional method using hot air.

Next, the oxidized filaments were carbonized under the same conditions as those in Example 1. The strand characteristics of the carbon fibers thus obtained are shown in Table 4.

Example 10:

PAN filaments, of which each individual filament was 1 denier in size and which were formed as a bundle of 6,000 of the individual filaments, were used as precursor filaments. Silicone oil containing 1.6 wt.% hydrocarbon surface active agent and 0.4 wt.% silicone oil with ethylene glycol was supplied to the precursor filaments, and the precursor filaments were oxidized in a fluidized bed of graphite powder (A in Table 2) under the conditions shown in Table 4. The grade of the fusion between individual filaments of the oxidized filaments thus obtained was determined in the same manner as in Example 9. As a result, the determined grade was found to be of the same level as in Example 9 or of a slightly lower grade than that in Example 9.

Next, the oxidized filaments were carbonized under the same conditions as those in Example 9. The strand characteristics of the carbon fibers thus obtained are shown in Table 4.

Example 11:

The conditions for oxidation in this Example were the same as in Example 10 other than that the heat treatment temperature was set to 270/290° C and the period of time for oxidation was set to 10 minutes. The grade of the fusion between fibers of the oxidized filaments thus obtained was determined in the same manner as in Example 9. As a result, the determined grade was as good as that of the oxidized filaments produced by a conventional method using hot air.

Next, the oxidized filaments were carbonized under the same conditions as those in Example 9. The strand characteristics of the carbon fibers thus obtained are shown in Table 4.

In the above Examples 1-11, the depth H in the stationary state of the fluidized bed calculated from equation (1) was as follows.

Examples 1-3, 9: $6 \text{ (mm)} < H < 250 \text{ (mm)}$

Examples 4-8, 10, 11: $11 < \text{(mm)}\ H < 550 \text{ (mm)}$

Accordingly, the depth H was within the above range in all Examples. Further, the fluidization gas speed U_f in each Example was within the range determined from equation (2) (shown in Tables 3 and 4).

Table 2

	Particles	Shape of Particles	Composition (wt.%)					Mean Diameter of Particles (mesh)
			Al_2O_3	SiO_2	Fe_2O_3	CaO	Others	
A	graphite powder	block	0.03 -0.035	0.005 -0.01	0.025 -0.035	0.001 -0.005	C:99.9 Mg, Ti etc.	100-200
B	alumina powder	block	99.9	0.03	0.01	-	Na_2O:0.06	120
C	alumina powder	block	99.9	0.03	0.01	-	Na_2O:0.06	60
D	alumina-silica bead	sphere	62.4	35.0	0.78	0.15	TiO_2:0.65 MgO:0.12 Na_2O:0.26	145
E	high purity alumina bead	sphere	99.8	0.07	0.01	0.02	Na_2O:0.04	200-250
F	high purity alumina bead	sphere	99.8	0.02	0.01	0.02	MgO :0.02 Na_2O:0.14 K_2O :0.01	48-60
G	high purity alumina bead	sphere	99.8	0.02	0.01	0.02	MgO :0.02 Na_2O:0.14 K_2O :0.01	8-10
H	high purity alumina bead	sphere	99.8	0.02	0.01	0.02	MgO :0.02 Na_2O:0.14 K_2O :0.01	$<$400
I	glass bead	sphere	4.4	72.8	0.1	6.0	Na_2O:2.9 B_2O_3:11.6 BaO:2.2	100

Table 3

Example No.	Twist of original filaments	Conditions of oxidation						result of treatment*	properties of carbonized filaments		means for eliminating the residual particles	metal compounds (ppm)	U_f calculated value (Ncm/S)
		treatment means	heat-medium particles	H (mm)	U_f (Ncm/S)	treatment temperature (°C)	treatment time (min)		tensile strength (kg/mm^2)	tensile modulus of elasticty (t/mm^2)			
1.	Yes	fluidized bed	E	40	0.8	275	10	o	292	24.1	air nozzle	4.5	0.47-3.8
2.	Yes	fluidized bed	E	40	0.8	275/295	5	o	275	24.4	air nozzle	2.4	0.47-3.8
3.	Yes	fluidized bed	F	40	5.5	275/295	5	o	295	24.3	air nozzle	7.4	2.7-21
4.	Yes	fluidized bed	A	80	1.3	275	10	o	322	26.2	air nozzle	5.4	0.50-4.0
5.	Yes	fluidized bed	A	80	1.3	270/295	5	o	317	26.6	nothing	4.7	0.50-4.0
6.	Yes	fluidized bed	A	80	1.3	270/295	5	o	307	26.0	air nozzle & exitation	2.8	0.50-4.0
7.	No	fluidized bed	A	80	1.3	270/295	5	o	301	22.0	air nozzle & exitation	3.3	0.50-4.0
8.	No	fluidized bed	A	40	1.7	260/280	10	o	440	23.0	nothing	5.7	0.50-4.0

*(Note) o ... good results, i.e. little or no fluffs and fusion as measured by observation

Table 4

Example No.	Twist of original filaments	Conditions of oxidation						result of treatment*	properties of carbonized filaments		means for eliminating the residual particles	metal compounds (ppm)	U_f calculated value (Ncm/S)
		treatment means	heat-medium particles	H (mm)	U_f (Ncm/S)	treatment temperature (°C)	treatment time (min)		tensile strength (kg/mm^2)	tensile modulus of elasticty (t/mm^2)			
9.	No	fluidized bed	B	80	1.5	270/300	5	o	285	21.5	nothing	12.3	1.0-8.0
10.	No	fluidized bed	A	80	1.8	275/297	5	o	234	16.8	nothing	5.8	0.50-4.0
11.	No	fluidized bed	A	80	1.8	270/290	10	o	336	20.0	nothing	6.5	0.50-4.0

*(Note) o ... good results, i.e. little or no fluffs and fusion as measured by observation

Comparison 1:

The same filaments as those of Example 1 were used as precursor filaments to be oxidized in Comparison 1. The precursor filaments were continuously oxidized between rollers at the same temperature (275° C) as that of Example 1 and at a gas speed of 0.5 - 100 Ncm/sec. However, oxidized filaments could not be obtained because of breakage of filaments due to the reaction heat of the filaments themselves.

Comparisons 2 and 14:

The same filaments and the same fluidized bed-containing oxidizing furnace as those of Example 1 were used. Furthermore, alumina beads, shown as G in Table 2, similar to those used in Examples 2 and 3 but having larger average particle diameters, i.e. 8 - 10 mesh, and alumina beads, shown as H in Table 2, having smaller particle diameters, i.e. finer than 400 mesh, were used as heat-medium particles in Comparisons 2 and 14, respectively. The precursor filaments were oxidized according to the oxidation conditions shown in Tables 5 and 6, respectively and were wound up in the form of packages. The obtained oxidized filaments had many fluffs and the strand characteristics of the carbon fibers which were obtained by carbonizing the oxidized filaments G and H were of low grade as shown in Tables 5 and 6, respectively.

Comparisons 3 and 4:

The same filaments and the same fluidized bed-containing oxidizing furnace as Example 1 were used. Furthermore, a bed of alumina beads, shown as E in Table 2, having its depth outside the range H calculated by equation (1) was used. In Comparisons 3 and 4, the fluidization gas speeds U_f were selected so as not to be in the range calculated by equation (2) and shown in Table 5. The precursor filaments were oxidized according to the conditions shown in Table 5. Under the conditions of Comparison 3, it was impossible to oxidize the filaments because of filament breakage. Under the conditions of Comparison 4, the characteristics of the oxidized filaments were of low grade because the filaments had many fluffs, and the carbon fibers obtained from the oxidized filaments were also of low grade.

Comparisons 5, 6 and 7:

The same filaments and the same fluidized bed-containing oxidizing furnace with a heat fluidized bed as that of Example 1 were used. Two kinds of high purity alumina particles, shown as B and C, respectively, in Table 2, which were like blocks in shape and had different average particle diameters, and alumina-silica beads, shown as D in Table 2, which were spherical in shape and included a large quantity of SiO_2 and Fe_2O_3 were used as heat-medium particles in Comparisons 5, 6 and 7, respectively. Those filaments were oxidized according to the conditions shown in Table 5 and were wound up to form packages. The oxidized filaments thus obtained had surfaces which were not greatly inferior, as viewed, to those of the oxidized filaments obtained according to the Examples of the present invention, but when the oxidized filaments were carbonized according to the same conditions as those of the Examples of the present invention, the strand characteristics of the carbon fibers were of low grade as shown in Table 5.

Comparisons 8 and 9:

Precursor filaments were oxidized in the oxidizing furnace with a fluidized bed using the heat-medium particles I of Table 2 according to the conditions of Table 6, as in Examples 2 and 3. The amount of the deleterious metal compounds in the particles adhering to the filaments under the conditions of elimination and non-elimination of the heat-medium particles are shown in Table 6, respectively. Table 6 also shows the strand characteristics of the carbon fibers which were obtained through carbonizing these oxidized filaments.

Comparisons 10 and 11:

Precursor filaments were oxidized under the same conditions as those of Example 5 except that the selected fluidization gas speeds Uf were 0.4 Ncm/sec and 4.5 Ncm/sec in Comparisons 10 and 11, respectively. In Comparison 10, breakage of filaments occurred due to a lack of heat elimination ability. In Comparison 11, the oxidized filaments had a large amount of fluffs and the characteristics of the carbon fibers thus obtained were of low grade. The test results are shown in Table 6.

Comparisons 12 and 13:

Precursor filaments were oxidized under the same conditions as those of Example 2 except that the selected depths of beds of heat-medium particles in their stationary state were 4 mm and 300 mm in Comparisons 12 and 13, respectively. In Comparison 12, even if the gas speed was in the range obtained by equation (2), filament breakages occurred due to a lack of heat elimination, as in Comparison 3. In Comparison

13, little improvement in the characteristics of the carbon fibers was seen as compared with Comparison 4 as shown in Table 6.

Comparison 15:

Precursor filaments were oxidized to obtain oxidized filaments under the same conditions as those of Example 9 except that 8 wt.% non-silicone oil containing hydrocarbon itself and hydrocarbon surface active agents was added as an oil for the precursor filaments. On evaluating the degree of the fusion between the individual filaments of the oxidized filaments according to the same evaluation method of Example 9, it was found that the oxidized filaments obtained in Comparison 15 was of the worst grade among the five grades. The strand characteristics of the carbon fibers obtained by carbonizing the oxidized filaments are shown in Table 6.

Comparisons 16 and 17:

Precursor filaments were oxidized under the same conditions as those of Examples 10 and 11 to obtain the oxidized filaments of Comparisons 16 and 17, respectively, except that the same oil as that of Comparison 15 was added. On evaluating the degree of fusion between the individual filaments of the oxidized filaments according to the same evaluation method of Example 9, it was found that the grade thereof was the worst after a five minute oxidation period and the grade thereof was the second worst after a ten minute oxidation period, among the five grades, respectively. The oxidized filaments were carbonized according to the same conditions as those of Examples 10 and 11 to obtain carbon fibers. The characteristics of the carbon fibers thus obtained are shown in Table 6.

The mean particle diameters of Table 2 are those determined on the basis of weight distributions. The gas speeds Uf of Tables 3 - 6 are obtained by dividing the normal gas flow rate of the compressed air used for fluidizing the heat-medium particles by the fluidization area (A).

Table 5

Comparison No.	Twist of original filaments	Conditions of oxidation						result of treatment*	properties of carbonized filaments		means for eliminating the residual particles	metal compounds (ppm)	U_f calculated value (Ncm/S)
		treatment means	heat-medium particles	H (mm)	U_f (Ncm/S)	treatment temperature (°C)	treatment time (min)		tensile strength (kg/mm^2)	tensile modulus of elasticty (t/mm^2)			
1.	Yes	hot air	-	-	0.5-100	275	10	x	-	-	-	-	-
2.	Yes	fluidized bed	G	40	120	275/295	5	△	163	19.2	air nozzle	2.5	23-190
3.	Yes	fluidized bed	E	4	0.4	275/295	5	x	-	-	-	-	0.47-3.8
4.	Yes	fluidized bed	E	300	5.0	275/295	5	△	186	19.4	air nozzle	4.3	0.47-3.8
5.	Yes	fluidized bed	C	80	5.0	270/290	5	△-o	168	19.4	nothing	18.5	2.2-18
6.	Yes	fluidized bed	B	80	1.6	280/290	5	△-o	192	18.2	air nozzle	6.0	1.0-8.0
7.	Yes	fluidized bed	D	40	1.8	285/298	5	o	230	21.2	air nozzle	56	0.77-6.1

*(Note) x ... breakage of filaments occurs.
△ ... fluffs occur.
o ... good results, i.e. little or no fluffs and fusion as measured by observation.

Table 6

Comparison No.	Twist of original filaments	Conditions of oxidation						result of treatment*	properties of carbonized filaments		means for eliminating the residual particles	metal compounds (ppm)	U_f calculated value (Ncm/S)
		treatment means	heat-medium particles	H (nm)	U_f (Ncm/S)	treatment temperature (°C)	treatment time (min)		tensile strength (kg/mm^2)	tensile modulus of elasticty (t/mm^2)			
8.	No	fluidized bed	I	40	1.3	270/295	5	o	124	10.2	nothing	860	1.1-8.6
9.	No	fluidized bed	I	40	1.3	270/295	5	o	102	9.7	exitation & air blow	220	1.1-8.6
10.	Yes	fluidized bed	A	80	0.4	270/295	5	x	-	-	-	-	0.5-4.0
11.	Yes	fluidized bed	A	80	4.5	270/295	5	△	265	20.3	nothing	5.2	0.5-4.0
12.	Yes	fluidized bed	E	4	0.7	275/295	5	x	-	-	-	-	0.47-3.8
13.	Yes	fluidized bed	E	300	0.8	275/295	5	△	204	21.4	air nozzle	4.5	0.47-3.8
14.	Yes	fluidized bed	H	4	0.4	275/295	5	△-O	226	20.1	air nozzle	18.5	0.23-1.8
15.	No	fluidized bed	B	80	1.5	270/300	5	x	180	17.4	nothing	112	1.0-8.0
16.	No	fluidized bed	A	80	1.8	275/295	5	x	160	15.0	nothing	5.2	0.50-4.0
17.	No	fluidized bed	A	80	1.8	270/290	10	x	221	16.3	nothing	6.8	0.50-4.0

*(Note) x ... breakage of filaments occurs.
△ ... fluffs occur.
o ... good results, i.e. little or no fluffs and fusion as measured by observation.

As described above in detail, according to the method of heating precursor filaments in the fluidized bed to obtain oxidized filaments in accordance with the present invention, because physical damage of the precursor filaments and residual heat-medium particles adhering to the oxidized filaments are reduced in amount, because the diameters of heat-medium particles are selected so as to not be accompanied by a large amount of oxidizing gas required for the fluidization, and further because the depth of the bed of heat-medium particles and the gas speeds are selected to be within appropriate, respective range, from the view point of reducing physical damage, gas volume needed in fluidization and increasing heat elimination abilities, it becomes possible to produce high quality oxidized filaments in a short period of time and, further, carbon fibers with excellent mechanical properties, with high in manufacturing efficiency, and at low cost.

Furthermore, because metal components included in the heat-medium particles adhered to the oxidized filaments can be prevented from reacting with the carbon fibers during carbonization by optimum selection of the composition of the heat-medium particles, the mechanical characteristics of the carbon fibers obtained through carbonization of the oxidized filaments are improved to a great extent.

Moreover, because it is possible to oxidize the precursor filaments in a state in which carbon particles of the fluidized bed are interposed between the fibers of the filaments, and because it is possible to oxidize the precursor filaments after providing them with silicone compounds, it is possible to produce oxidized filaments without the occurrence of fusion between individual filaments.

Yet further, because the method of the present invention for producing oxidized filaments is based on the rule of fluidization of the heat-medium particles, the gas speeds within a range of from several centimeters per second to several tens of centimeters per second can be used in the method of the present invention, while in the conventional method gas speeds of at least several meters per second are necessary, this being because the conventional oxidation heat treatment using hot gases is based on a rule of avoiding build up of reaction heat. As a result, in the method of the present invention, the amount of gas to be used is very small, which is naturally accompanied by reduction in furniture and energy.

Accordingly, the present invention can realize a method for producing oxidized filaments to produce high quality oxidized filaments and carbon fibers at low cost and at high efficiency thanks to the merit of oxidizing precursor filaments at high temperatures in a short period of time.

Claims

1. A method for continuously producing oxidized filaments by passing precursor filaments through a bed fluidized by an oxidizing gas and heat treating the precursor filaments in the fluidized bed, said fluidized bed being formed on a means for dispersing the oxidizing gas and supplying the dispersed gas into the fluidized bed, said method including the steps of:

(a) forming the fluidized bed with heat-medium particles, not less than 80% in weight of which are of solid particles each having a particle diameter not greater than 10 mesh; and

(b) conducting said heat treatment of the precursor filaments at a temperature of 200-550°C under conditions where a depth H(m) in the stationary state of the bed from the top surface of the bed to said dispersing means is in a range given by equation (1), and a fluidization gas speed U_f (Ncm/S) of said oxidizing gas for fluidizing the bed is in a range given by equation (2).

$20\,M_f/(\rho_p\,C_p\,A) < H < 500/\rho_p \qquad (1)$

$0.3(dp^2\,\rho_p/\mu)^{0.538} < U_f < 2.4(dp^2\,\rho_p/\mu^{0.538} \qquad (2)$

where,

M_f = weight of the precursor filaments existing in the fluidized bed (Kg),

ρ_p = bulk density of the heat-medium particles (Kg/m^3),

C_p = specific heat of the heat-medium particles (Kcal/Kg°C),

A = fluidization area of the fluidized bed (m^2),

U_f = fluidization gas speed determined by dividing a normal flow rate of the oxidizing gas at a temperature for the heat treatment by the fluidization area A (Ncm/S),

dp = average particle diameter of heat-medium particles based on weight distribution of the heat-medium particles (m),

μ = coefficient of viscosity of air at a temperature for the heat treatment (Kg S/m^2).

2. The method of claim 1, wherein not less than 80% of the weight of said heat-medium particles are inorganic particles having respective particle diameters within a range of from 28-400 mesh inclusive.

3. The method of any preceding claim, wherein said heat-medium particles are carbon particles having a carbon component of not less than 50wt.%.

4. The method of any preceding claim, wherein said heat-medium particles are inorganic particles, in which the total weight of any metal components therein capable of reacting with carbon in a carbonization process after the oxidization process is not greater than 1wt.%.

5. The method of any preceding claim, wherein the bulk density ρ_p of said heat-medium particles is in the range of 0.3-2.5g/m^3.

6. The method of any preceding claim, wherein the period of time for said heat treatment is within 30

minutes.

7. The method of any preceding claim, wherein said precursor filaments extend through the fluidized bed in a substantially horizontal direction without any substantial change of direction.

8. The method of any preceding claim, which method further includes the step of decreasing the number of residual heat-medium particles adhering to the oxidized filaments after the heat treatment so that the ratio of the total weight of any metal components in the residual heat-medium particles capable of reacting with carbon in a carbonization process subsequent to the oxidation process, to the total weight of the oxidized filaments including the residual heat-medium particles, is suppressed to not greater than 100ppm.

9. The method of any preceding claim, which method further includes the step of supplying a silicone compound to the precursor filaments before said heat treatment.

FIG. 1

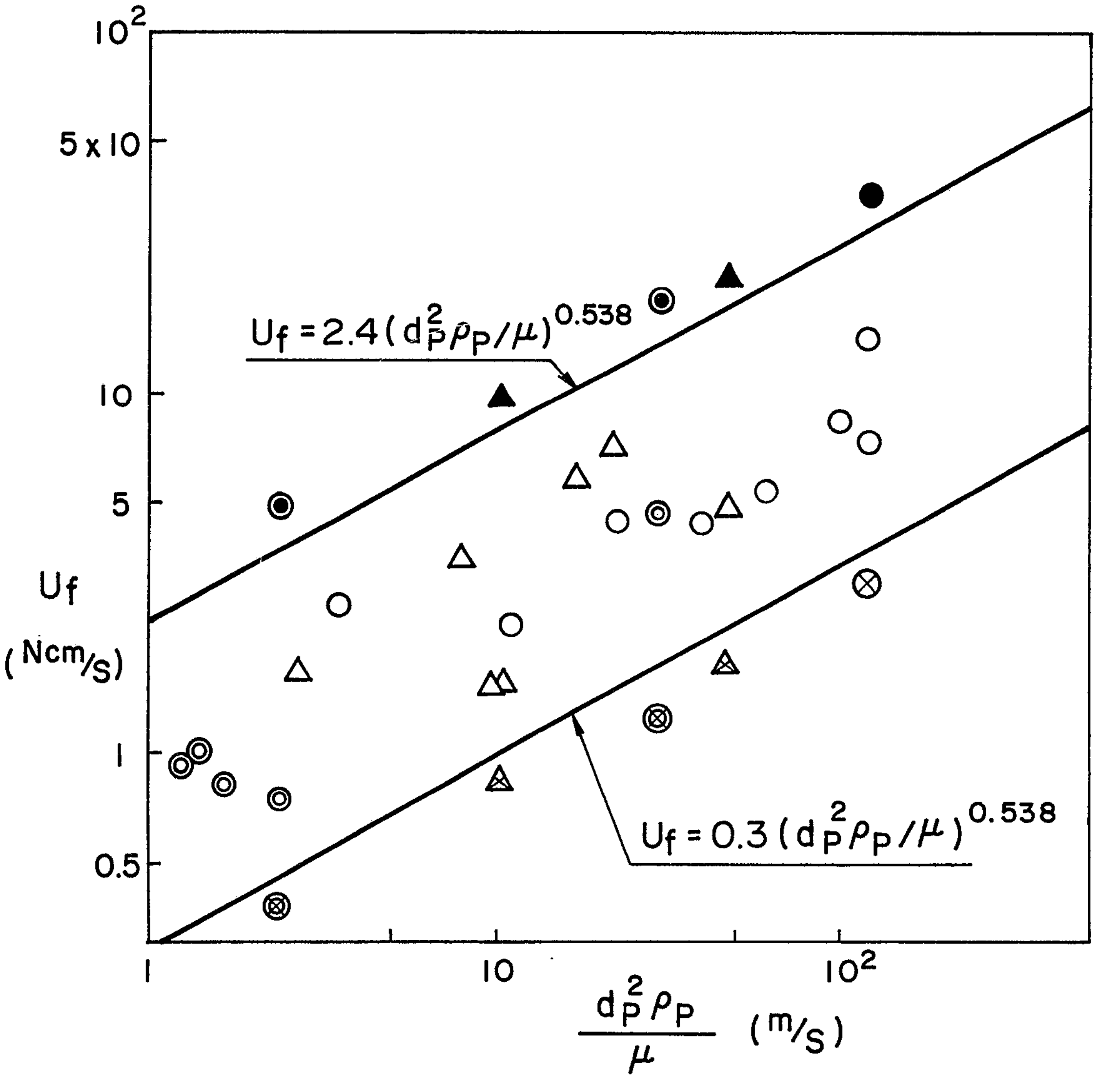
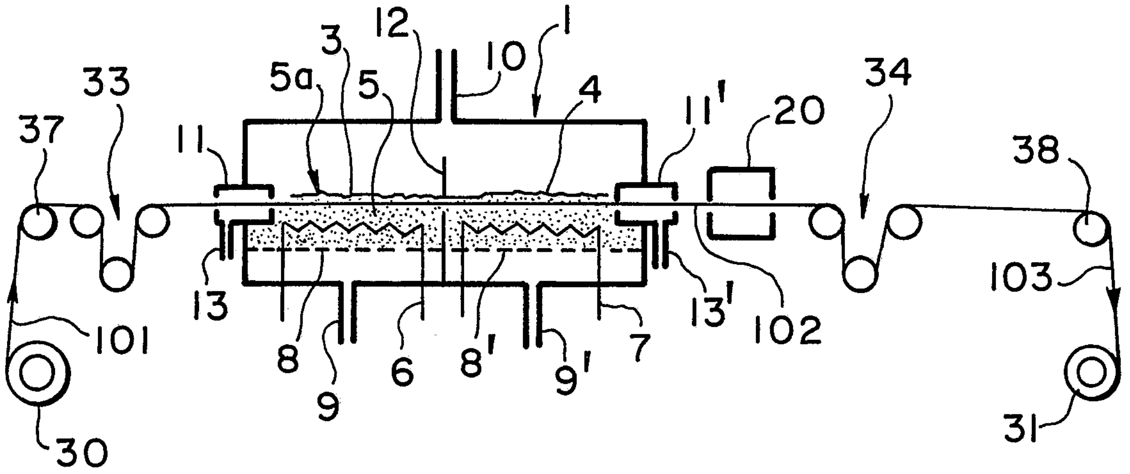

10^2
5×10
10
5
1
0.5
U_f
(Ncm/s)
$U_f = 2.4 (d_p^2 \rho_p / \mu)^{0.538}$
$U_f = 0.3 (d_p^2 \rho_p / \mu)^{0.538}$
1
10
10^2
$\frac{d_p^2 \rho_p}{\mu}$ (m/s)

FIG. 2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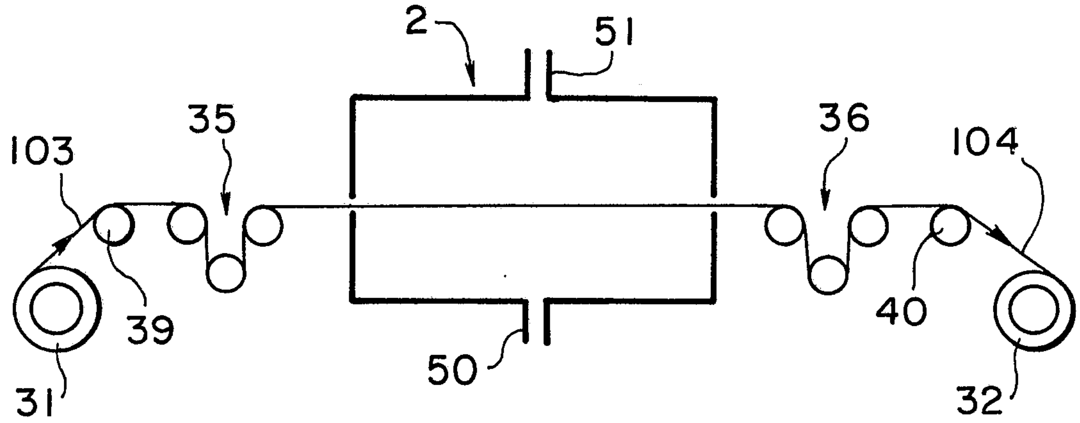
103

FIG. 3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103
104