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(54) Method for continuous production of carbon fiber using calcining furnace.

(57) 1. A method for continuously producing carbon fiber which comprises (1) using a horizontal calcining furnace comprising (i) a heating chamber comprising an inlet introducing fiber to be carbonized and an outlet for carbon fiber produced, at least one inlet introducing an inert gas, and at least one outlet discharging decomposition gas formed from calcining the fiber in the heating chamber, and (ii) at least one gas sealing chamber which is provided at at least one of the fiber inlet and the fiber outlet to and from the heating chamber, and said sealing chamber further comprising an inlet introducing an inert gas; and (2) maintaining pressure within the sealing chamber at a pressure value greater than each of the pressure within the heating chamber and atmospheric pressure.

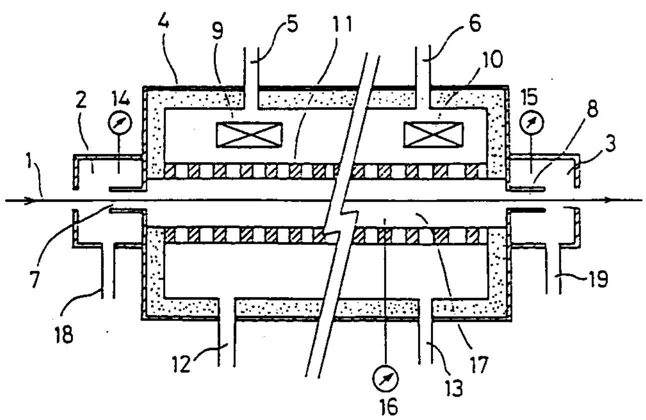

Fig. 1

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FIELD OF THE INVENTION

The present invention relates to a method for continuous production of carbon fiber using a calcining furnace, and more particularly to a method which prevents the exterior air from infiltrating into the furnace, and conversely, also prevents gas from escaping from the furnace to the outside, and also prevents decomposition gas and a tarry material from being deposited on filaments and enables a long-duration operation of the furnace for continuously calcining a large number of strands.

BACKGROUND OF THE INVENTION

A large quantity of carbon fiber has been used in various lightweight structural materials in many fields and particularly the aerospace industry, in recent years because of its excellent mechanical characteristics such as excellent specific strength and specific modulus of elasticity. However, demands have arisen to reduce the manufacturing cost and to improve the quality thereof.

Generally, carbon fiber is formed by using an organic fiber such as cellulose fiber, polyacrylonitrile fiber or pitch fiber as a starting material and calcining it by heat-treatment wherein the final maximum temperature is 1000°C or higher, optionally 2000°C or higher. In the calcination treatment, carbon formed in the fiber is reacted with various gases, such as oxygen. Accordingly, it is necessary that the calcination is carried out in an inert gas atmosphere to prevent carbon from being reacted with the inter-reactive gases. For continuously treating a large number of strands in a high-temperature calcining furnace, the furnace, as a matter of course, must be provided with an inlet for introducing the filaments into the heat chamber of the high-temperature calcining furnace and with an outlet for discharging them from the heat chamber. In general, the inlet and the outlet are provided with a sealing part for preventing the open air from flowing into the calcining furnace through the inlet and the outlet. Suitable sealing methods include a method wherein the outlet is sealed by a gas, or by a liquid as described in JP-B-60-5683 (corresponding to U.S. Patent 4,321,446; the term "JP-B" as used herein means an "examined Japanese patent publication") and a sealing method using a roller as described in JP-B-62-46647. A liquid seal is usually used together with gas seal or roller seal to prevent the liquid from flowing into the heating chamber of the furnace through the inlet. Various proposals for these roller seals and gas seals have been made to prevent the exterior air from being introduced into the furnace or to reduce the amount of inert gas used as disclosed in, for example, JP-A-61-97461 (the term "JP-A" as used herein means an "unexamined published Japanese patent application") and JP-A-62-243831.

When a roller seal or gas seal is used in a method for sealing a continuous calcining furnace for production of carbon fiber, a tarry material formed from filaments during calcination undesirably is deposited and accumulated on the sealing part, and hence imposes a limit on long-term continuous operation. That is, it is necessary that the calcining operation is periodically stopped so that the tarry material which had accumulated on the sealing part could be removed. This is one of several factors which lower productivity in post operations. Further, since the tarry material deposited on the sealing part is brought into contact with and transferred to the filaments, this phenomenon is one of factors which lower mechanical characteristics otherwise inherent to carbon fiber.

SUMMARY OF THE INVENTION

A first object of the present invention is to provide a method for continuous production of carbon fiber using a calcining furnace.

A second object of the present invention is to provide a method to prevent exterior air from infiltrating into a calcining furnace used for production of carbon fiber and to concurrently prevent the gas in the furnace from escaping to the outside.

A third object of the present invention is to provide a method to prevent the accumulation of decomposition gas and tarry material in a calcining furnace used for production of carbon fiber and, thus, prevent deposition of tarry materials on filaments in the furnace and to thereby produce carbon fiber having a high quality.

A fourth object of the present invention is to provide a method for production of carbon fiber which can be operated for long duration without troubles of accumulation of tarry residues on the calcining furnace for continuous production of carbon fiber.

These and other objects can be achieved with a method for continuously producing carbon fiber which comprises (1) using a horizontal calcining furnace comprising (i) a heating chamber having an inlet introducing fiber to be carbonized, an outlet for exiting carbon fiber produced, at least one inlet introducing an inert gas, and at least one outlet discharging decomposition gas formed from the calcining the fiber in the heating chamber, and (ii) at least one gas sealing chamber which is provided at at least one of the fiber inlet and the fiber outlet to and from heating chamber and said sealing chamber has an inlet introducing an inert gas; (2) and maintaining the pressure within the sealing chamber at a pressure higher than each of the pressure within the heating chamber and atmospheric pressure.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic vertical sectional view of a high-temperature calcining furnace for preparing carbon fiber, which shows an embodiment of the present invention.

Fig. 2 is a sectional view of the sealing chamber, which additionally shows the flow of gas to illustrate in more detail the effect of the present invention.

Fig. 3 is a graph showing the carbonizing temperature with respect to the residence time of the fiber in the furnace.

DETAILED DESCRIPTION OF THE INVENTION

According to the present invention, carbon fiber having excellent characteristics can be prepared by preventing air from infiltrating into the high-temperature calcining furnace, preventing the tarry material from being deposited and accumulated on the sealing part, enabling uninterrupted long-duration stable operation to be made and preventing the fibrous materials from being brought into contact with tarry residues.

The term "carbon fiber" as used herein refers also to graphite fiber, and refers to fiber obtained from an organic fiber such as cellulose fiber, polyacrylonitrile fiber or pitch fiber by calcining it at a temperature of not lower than 500°C, but not higher than the highest sublimation temperature of carbon. Usually, a pretreatment is carried out before the calcination is conducted although such is not required to practice the present invention. As one example of a suitable pretreatment, polyacrylonitrile fiber comprised of a homopolymer or a copolymer of acrylonitrile is subjected to preoxidation which is conducted at a temperature of 200 to 300°C in an oxidizing atmosphere to render the fiber inflammable. Methods with respect to preheating of these fibers are exemplified in, for example, U.S. Patent 4,891,267.

The term "a filament" as used herein refers to "continuous single fiber".

The term "calcining furnace" as used herein refers to a treating furnace which is used for heat-treating the above-described organic fiber or pretreated fiber in an inert gas, such as argon, helium and hydrogen, to continuously form carbon fiber (inclusive of graphite fiber) and is provided with a sealing chamber at an inlet for introducing the filaments into the furnace and/or at an outlet for discharging the carbon fiber produced in the furnace.

The term "gas sealing chamber" as used herein refers to a chamber which prevents introduction or infiltration of air from the inlet and/or outlet of the fiber into the heating chamber of the furnace providing an inert gas in the sealing chamber.

Although any one of the inlet and the outlet provided to the heating chamber may be provided with the gas sealing chamber, it is preferred that at least the inlet is provided with the gas sealing chamber, and it is more preferred that both the inlet and the outlet for the fiber are provided with the gas sealing chamber. For example, a calcining furnace having such a structure wherein the outlet for discharging the fiber is provided with a liquid seal and only the inlet for introducing the fiber is provided with the gas sealing chamber can be used.

Pressure within the sealing chamber must be higher than the internal pressure of the heating chamber. When pressure within the sealing chamber is lower than the internal pressure of the heating chamber, the gas containing decomposition gas in the heating chamber flows into the sealing chamber where the gas cools, and the tarry material is converted into mist which is then undesirably deposited on the filaments and the sealing part (boundary part between the sealing chamber and the heating chamber). As a result, coalescence, fluffing and breakage of the fiber product are caused thereby, and an uninterrupted long-duration operation of the furnace cannot be performed.

The difference in pressure between the sealing chamber and the heating chamber is preferably 0.1 to 15 mmH_2O, and more preferably 0.5 to 5 mmH_2O with the sealing chamber pressure being greater, and the pressure difference is particularly preferably at most 3 mmH_2O. Although when the difference in pressure is more than 3 mmH_2O, the effect of the present invention can also be obtained, a large amount of inert gas is required in the sealing chamber, and no increased benefits can be obtained from the viewpoint of an economical advantage. It is most preferred that the difference in pressure is 2 mmH_2O or below. Unless indicated otherwise, all pressure amounts in the present invention are gauge pressures.

Pressure within the sealing chamber also must be settled to be higher than atmospheric pressure, i.e., ambient pressure outside the furnace, whereby the air can be prevented from infiltrating into the sealing chamber from outside the furnace. It is preferred that a difference in pressure is 0.1 to 15 mmH_2O, more preferably 0.3 to 5 mmH_2O with the sealing chamber pressure being higher. Although the difference in pressure can be more than 5 mmH_2O, no increased benefits can be obtained from the viewpoint of an economical advantage for the same reason as mentioned above.

Pressure control within the sealing chamber may be effected by controlling the amount of inert gas fed to the sealing chamber. The gas fed to the sealing chamber is an inert gas. Usually, inert gas having the same composition as that of inert gas fed to the heating chamber is used. Example of the gas which is usually used include helium, argon, nitrogen, chlorine and sulfur dioxide gases.

The heating chamber has a mechanism for discharging a decomposition gas containing the tarry material produced from the fiber to be carbonized to the outside of the calcining furnace by means of a gas carrier stream which usually comprises the same type of gas component as the inert gas fed to the sealing chamber. For this purpose the heating chamber has at least one outlet discharging the gas and has at least one inlet for the inert gas.

The pressure control within the sealing chamber may also be effected by controlling the flow rates of inert gas fed to the sealing chamber and the heating chamber.

Alternatively, pressure control within the sealing chamber is effected by controlling the amount of gas discharged from the heating chamber.

A difference in pressure between the sealing chamber and the inside of the heating chamber can be maintained by controlling the amount of the gas to be introduced to the sealing chamber and to be discharged from the heating chamber.

Usually, the amount of the gas to be discharged from the heating chamber is preferably in the range of 1 to 2 times (by volume) the sum total of the amount of gas to be fed to the heating chamber of the calcining furnace, the inert gas infiltrated from the sealing chamber into the heating chamber through the fiber inlet, and that of gas produced from the fiber, and is adjusted by controlling gas which flows from the sealing chamber into the heating chamber.

The inert gas introduced into the sealing chamber flows to the outside from the fiber inlet at the sealing chamber. This flow is effective to remove air contained in the fiber strand to be fed into the sealing chamber.

The temperature in the furnace is gradually raised as the carbonization proceeds in the heating chamber.

The temperature for calcination is usually not lower than 500 °C and preferably not lower than 700 °C, and the maximum temperature for calcination usually is from about 1,000 to 1,800 °C, and preferably not higher than 1,600 °C. Furthermore, for graphitization the fiber the maximum temperature for calcination is preferably from about 2,000 to 3,000 °C.

It is preferred that the temperature of the sealing chamber should be lower than the temperature within the furnace and preferably it is not higher than 500 °C, particularly preferably not higher than 400 °C and not lower than 200 °C. When the temperature of the sealing chamber is lower than 200 °C, a difference in temperature between the sealing chamber and the inside of the calcining furnace is too great, and it is preferred to provide a temperature buffering zone between the sealing chamber and the heating chamber of the calcining furnace. Hence, the equipment is made complicated and hence such a temperature is not preferred from the viewpoint of the mechanism of the apparatus. On the other hand, when the temperature of the sealing chamber is higher than 500 °C, the filaments are damaged by a very small amount of air contained in the filaments and hence such a temperature is not preferred.

The structure of the sealing chamber may be a single chamber structure, but a multi-chamber structure with a mechanism for cushioning the difference of pressure is preferred because such a structure does much less damage to the filaments. A typical structure of the cushioning mechanism is a labyrinth mechanism as disclosed, for example, in JP-A-62-238986 and JP-A-62-243831.

When the filaments are passed through the boundary between the sealing chamber and the air (outside the chamber) or between the sealing chamber and the heating chamber of the calcining furnace, it is preferred that the filaments do not contact any portion of the boundaries. Particularly, when the boundary between the sealing chamber and the heating part is in the form of a contact type mechanism, for example, a roller, there may be caused problems that the contact part damages the filaments, or the filaments twist around the roller. Accordingly, although the contact type mechanism can be used, it is not preferred in the present invention.

In order to form a gas seal at the boundary between the sealing chamber and the air or between the sealing chamber and the heating chamber, it is preferred to provide a so-called nose at the boundary.

Through the nose the fiber strand or a sheet composed of a large number of fiber strands passes in a non-contacting manner. The nose is made to jut out into the inside of the sealing chamber or into the heating chamber at the boundary. The inside of the nose may be composed of a labyrinth mechanism. It is further preferred to pass an inert gas through the nose at a right angle direction with respect to the fiber traveling direction.

There is no particular limitation with regard to the temperature of the inert gas which is fed to the heating chamber, so long as the temperature does not have an adverse effect on the heating devices, pipes, etc. However, the temperature is usually controlled to a temperature of not higher than 600 ° C.

The present invention will be illustrated by referring to the accompanying drawings.

Fig. 1 shows diagrammatically an embodiment of the present invention and is a schematic vertical sectional view of a high-temperature calcining furnace for preparing carbon fiber, which is provided with a sealing chamber at each of the inlet and the outlet. In Fig. 1, numeral 1 shows the fiber traveling in the direction from left to right shown by an arrow, 2 and 3 each represents the sealing chamber, and 4 shows the heating chamber of the high-temperature calcining furnace. Element 17 designates a calcination chamber for carbonizing or graphitizing the fiber, which is provided within the heating chamber of the calcining furnace. The fiber are introduced into the sealing chamber 2 provided at the inlet of the high-temperature calcining furnace, passed through the calcination chamber 17, discharged through the outlet sealing chamber 3 and fed to a subsequent stage, for example, a heating treatment at a higher temperature, an eleclrolytical surface treatment, a sizing treatment, or washing, if desired. There is no particular limitation with regard to the size of the high-temperature calcining furnace when the furnace has such a size that the fibrous materials take at least one minute to pass therethrough. An inert gas (nitrogen gas, argon gas or other inert gas) preheated by an external heating device is introduced through pipes 18 and 19 into each of the sealing chambers. Through pipe 20 the inert gas is discharged. A preheated inert gas is introduced through pipes 5 and 6 passing through walls of the calcining furnace into the interior of the heating chamber, and the temperature of the inert gas is controlled and maintained at a predetermined temperature by means of internal heaters 9 and 10 provided in the heating chamber and then passes through a flow regulating plate 11 before entering the calcination chamber 17 itself.

Decomposition gas and a tarry material, which are produced from the fiber, are discharged through effluent pipes 12 and 13 from displacement by freshincoming inert gas being introduced into the heating chamber. In a preferred embodiment of the present invention, pressure sensors 14, 15 and 16 are provided.

Numerals 7 and 8 show sealing parts (nose). Each sealing part is usually composed of two parallel plates as depicted in the Figures. The space between these parallel plates is set to 20 mm or less, preferably 10 mm or less to provide a saving in the amount of inert gas to be used. A labyrinth seal (not depicted) can be used in place of the parallel plates without detriment to the effect of the present invention. A material for the sealing part is preferably a metal or graphite.

Fig. 2 is a sectional view of the sealing chamber, which additionally shows the flow of gas to illustrate in more detail the effect of the present invention. In Fig. 2, P_0 represents atmospheric pressure, P_1 represents pressure within the sealing chamber and P_2 represents pressure within the heating chamber of the calcining furnace. When the amounts of the inert gas (F_1) introduced into the sealing chamber and the inert gas (F_2) introduced into the heating chamber of the calcining furnace and the amount of gas (E_1) discharged from the heating chamber of the calcining furnace are set so as to allow the relationship of $P_0<P_1>P_2$ to be maintained, gas flows as shown in Fig. 2. Also exterior air can be prevented from flowing into the sealing chamber and also decomposition gas and the tarry material produced in the calcination chamber of the high-temperature calcining furnace can be prevented from being deposited and accumulated on the sealing part.

The amount of the gas to be discharged is decided so that the concentration of the decomposition gas is maintained as low as possible.

The three factors of (1) the flow rate of inert gas from the inert gas inflow pipe provided to the sealing chamber, (2) the flow rate of gas from the gas discharge pipe of the heating chamber provided for discharging decomposition gas containing the tarry material produced in the high-temperature calcining furnace to the outside of the furnace and (3) the flow rate of inert gas fed through the inert gas inflow pipe to the calcining furnace to keep the atmosphere inside the heating chamber as inert relative to the fiber are kept at an appropriate ratio, thereby pressure within the sealing chamber can be kept at a pressure higher than atmospheric pressure, and pressure within the sealing chamber can be kept at a pressure higher than pressure within the heating chamber, whereby air can be prevented from flowing into the calcining furnace, the tarry material can be prevented from being deposited and accumulated on the sealing part, a long-term uninterrupted stable operation can be conducted, and the fibers can be prevented from being brought into contact with the tarry material. Thus, carbon fiber having excellent mechanical characteristics can be obtained in the present invention.

Particularly, the present invention can be applied to the horizontal calcining furnace of a type wherein the inlet and/or the outlet is provided with the sealing chamber, irrespective of the specific mechanism of the sealing part. When each of the inflow pipes and the discharge pipes is provided with an automatic flow rate control valve interlocked with the pressure sensor, the method of the present invention can be very simply applied to a large-size high-temperature calcining furnace on an industrial scale and gives many advantages.

The present invention can be better understood by reference to the following non-limiting examples.

Example 1

Fifty strands (the number of filaments per one strand: 12000) of preoxidized fiber obtained by preoxidizing acrylic fiber at 270 °C (maximum) and which had a density of 1.40 g/cm^3 were put in order in parallel in the form of sheets at intervals of 10 mm (distance between the centers of strands which are adjacent therewith) and introduced into a calcining furnace. The temperature distribution with respect to the residence time of the fiber in the furnace is shown in Fig. 3. Carbonization of the fiber is conducted for 4 minutes.

The calcining furnace used was the furnace of Fig. 1, and the mechanism of the sealing part was a non-contact type slit structure having an opening size of 5 mm.

Pressure within the heating chamber was 0.5 mmH_2O, pressure within each of the sealing chamber at the fiber inlet and outlet was 1.0 mmH_2O, and the temperature of each of the sealing chamber was controlled to 350 °C by nitrogen gas.

The results are shown in Table 1.

Comparative Examples 1 and 2

For comparison, experiment the same as Example 1 were carried out except that the pressure conditions of the heating chamber and the sealing chamber were changed as indicated in Table 1. The results obtained in Comparative Examples 1 and 2 are also shown in Table 1.

Table 1

	Example 1	Comparative Example 1	Comparative Example 2
Heating chamber			
Pressure	0.5 mmH_2O	1 mmH_2O	-1 mmH_2O
Sealing chamber			
Temperature	350°C	350°C	350°C
Pressure	1.0 mmH_2O	0.5 mmH_2O	-0.5 mmH_2O
Fiber tensile strength	400 kg/mm^2	400 kg/mm^2	320 kg/m^2
Remarks	A stable operation could be carried out even after the operation was continuously run for 400 hours.	After 24 hours, tar was deposited on the sealing part and the operation had to be stopped.	Fiber strength was significantly lowered, though the operation could be continuously run for 400 hours.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

1. A method for continuously producing carbon fiber which comprises (1) using a horizontal calcining furnace comprising (i) a heating chamber comprising an inlet introducing fiber to be carbonized and an outlet for carbon fiber produced, at least one inlet introducing an inert gas, and at least one outlet discharging decomposition gas formed from calcining the fiber in the heating chamber, and (ii) at least one gas sealing chamber which is provided at at least one of the fiber inlet and the fiber outlet to and from the heating chamber, and said sealing chamber further comprising an inlet introducing an inert gas; and (2) maintaining pressure within the sealing chamber at a pressure value greater than each of the pressure within the heating chamber and atmospheric pressure.

2. The method as claimed in claim 1, wherein pressure within the sealing chamber is provided as 0.1 to 15 mmH_2O greater than atmospheric pressure and 0.1 to 15 mmH_2O greater than pressure within the heating chamber.

3. The method as claimed in claim 1, wherein pressure control within the sealing chamber is effected by controlling the flow rate of inert gas fed to the sealing chamber.

4. The method as claimed in claim 1, wherein pressure control within the sealing chamber is effected by controlling the flow rate of inert gas fed to the sealing chamber and and the heating chamber.

5. The method as claimed in claim 1, wherein pressure control within the sealing chamber is effected by controlling the amount of gas to be discharged from the heating chamber of the calcining furnace.

6. The method as claimed in claim 1, wherein the difference in pressure between the sealing chamber and the heating chamber is maintained by controlling the amount of the inert gas to be introduced to the sealing chamber and to be discharged from the heating chamber.

7. The method as claimed in claim 1, wherein the amount of the gas discharged from the heating chamber is in the range of 1 to 2 times by volume the sum total amount of gas to be fed to the heating chamber.

8. The method as claimed in claim 1, wherein said fiber to be carbonized is at least one of fiber obtained from fiber selected from the group consisting of cellulose fiber, polyacrylonitrile fiber and pitch fiber.

9. The method as claimed in claim 1, wherein said fiber to be carbonized is obtained by preoxidizing polyacrylonitrile fiber by heating at 200 to 300 °C in an oxidizing atmosphere to render the fiber inflammable.

10. The method as claimed in claim 1, wherein the temperature of the heating chamber is not lower than 500 °C.

11. The method as claimed in claim 1, wherein pressure within the sealing chamber is provided as 0.3 to 5 mmH_2O greater than atmospheric pressure and 0.5 to 5 mmH_2O greater than pressure within the heating chamber.

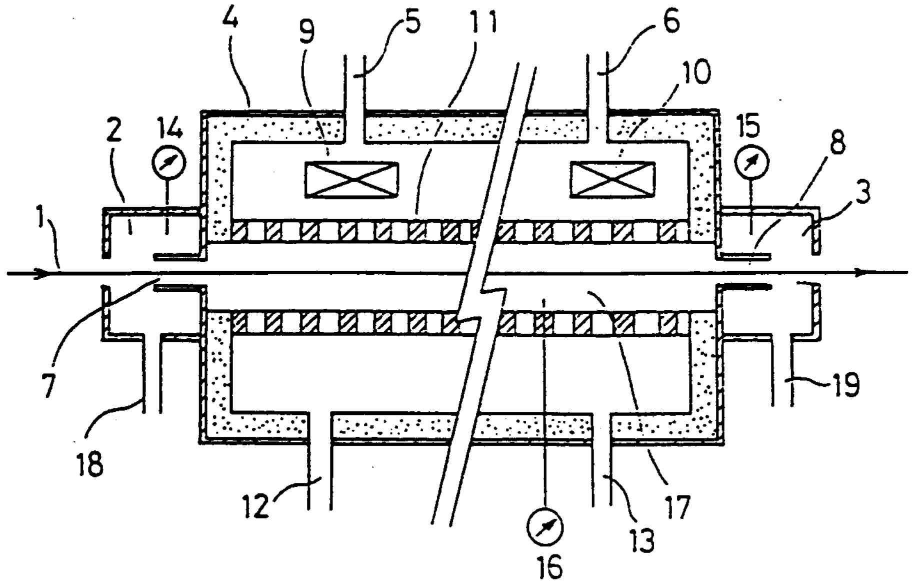
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Fig. 1

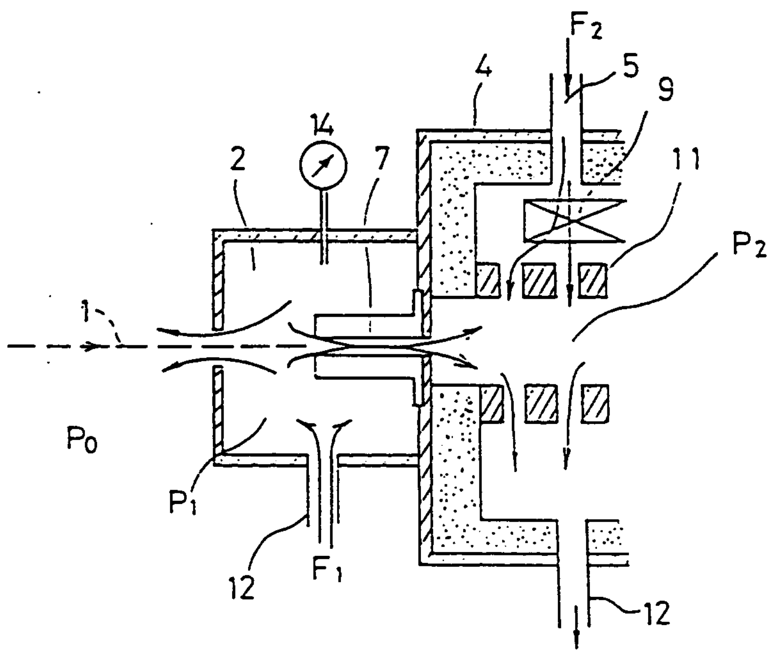
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Fig. 2

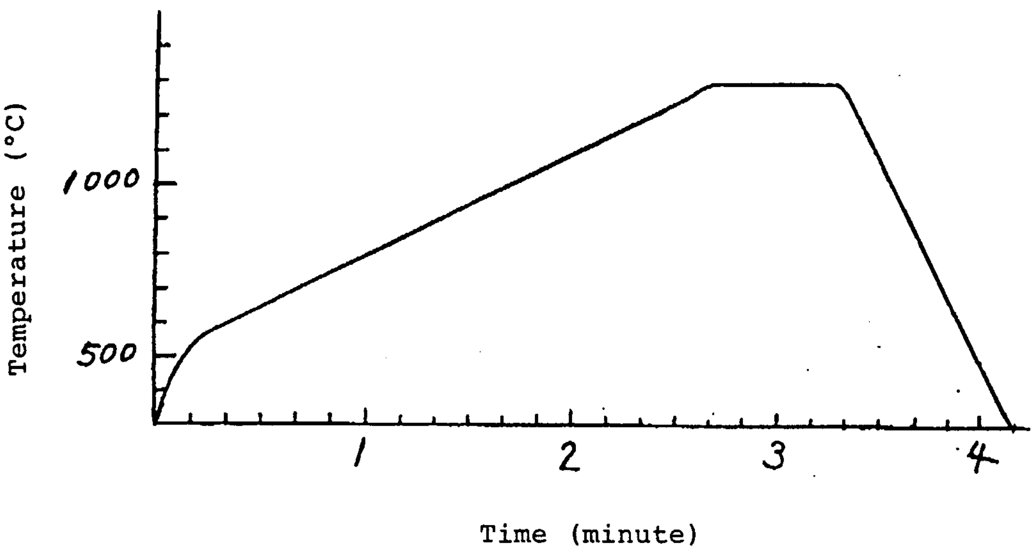

Fig. 3

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 10 8855

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	FR-A-2 543 982 (TOHO BESLON) * Whole document * ---	1	D 01 F 9/32 F 26 B 13/00
A	US-A-4 301 136 (R. YAMAMOTO et al.) * Whole document * ---	1	
A	US-A-4 268 977 (GEIGER) * Whole document * -----	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

D 01 F
F 26 B
F 27 D
C 21 D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	20-08-1992	HELLEMANS W.J.R.

CATEGORY OF CITED DOCUMENTS

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