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(54) **Process for producing non-woven fabrics of high bulk density carbon fibers.**

(57) A process for producing non-woven fabrics having a high bulk density, uniform porosity and little characteristic of so-called interlayer detachment are provided by subjecting an infusiblized sheet of pitch fibers to a heat treatment at a temperature higher than the softening temperature of the pitch fibers and lower than the softening temperature plus 300 °C, while applying a pressure to the surface of said sheet substantially in the vertical direction thereof.

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Process for producing non-woven fabrics of high bulk density carbon fibers

Background of the Invention

This invention relates to a method for producing high bulk density non-woven fabrics of carbon fibers.

The non-woven fabrics of carbon fibers produced according to the method of the present invention have high bulk density and uniform porosity. The said fabrics exhibit superior properties when they are used in filtration materials, packing materials, break-lining materials, electrode materials, catalyst carrier, shielding materials from electromagnetic waves, heat-sustaining vessels, reinforcement materials for fiber composite materials, etc.

The production of the non-woven fabrics from pitch-based carbon fibers is carried out, as in case of other kind of carbon fibers, by cutting carbonized fibers and through the same steps with those of common synthetic fibers. As a special process for pitch-based carbon fibers, a process in which melt spun pitch fibers are im mediately caught in a non-woven fabric form is also used. Such a method in which pitch-based fibers after melt-spinning are directly caught in the non-woven fabric form is nearly the same process which have been widely used hitherto as a spun-bond process of synthetic fibers and as a production process of glass wool (glass short fibers) and rock wool. In the spun-bond process of synthetic fibers, melt-spun fibers are immediately stretched or pulled at such an extent of velocity as being capable of performing orientation and crystallization to stabilize the fiber structure.And then they are piled up in sheet form of non-woven fabrics on a porous belt such as a net conveyor or a porous drum by such an operation as suction. In case of non-woven fabrics of glass short fibers or rock wool, the melt solution of extruded glass is finely divided by gas stream or centrifugal force, piled up on a porous belt or porous drum by suction with gas stream or by gravity to form into sheet.

In case of synthetic fibers, melted solution is pulled and finely divided by gas stream to turn into non-woven fabrics as in case of glass short fibers. This is known as a melt blow process.

In case of the non-woven fabrics of pitch based carbon fibers, the application of spun bond process, centrifugal spinning process or melt blow process has been investigated. For centrifugal spinning process, the art is disclosed in Japanese patent publication No. Sho 47-32148, etc. and for melt blow process, the art is disclosed in laid open Japanese patent application No. Sho 62-90320, etc.

The common problem to these arts is that only a stationary state infusiblization or carbonization is disclosed and there is no disclosure about what kind of non-woven fabrics are made by treatment in other states.

On the other hand, the non-woven fabrics produced by immediately collecting melt-spun pitch fibers have drawbacks in the points that interlocking of fibers in the direction of thickness is extremely weak and interlayer detachment is liable to occur, and bulkiness-increasing process by forming curl, twist or looseness, etc. onto fibers is difficult. Further it is difficult to give variation of bulkiness due to the fact that compacting process by way of entanglement, shrinkage, etc. is almost impossible.

It is an object of the present invention to provide non-woven fabrics having a high bulk density by overcoming the liability of interlayer detachment due to extremely few entanglement in the direction of thickness as well as the difficulty to give variation of bulkiness by bulkiness-increasing processing or compacting processing.

Summary of the Invention

A method for producing high bulk density non-woven fabrics of carbon fibers which is characterized in subjecting an infusiblized sheet of pitch based fibers to heat treatment at a temperature higher than the softening temperature of the pitch fibers and lower than the softening temperature plus 300°C, while applying pressure to the surface of said sheet substantially in the vertical direction thereof, and thereafter subjecting to carbonization.

Description of the detailed explanation

In the present invention, the application of pressure to a sheet at the time of carbonization treatment is carried out under a static load or by clamping with a number of pressing rollers.

The application of pressure under a static load is carried out by applying pressure with a weight, a fluid pressure of a hydraulic equipment, a screw, etc. In case of static load, not only a vertical pressing to a sheet, utilization of an isotropic pressing is also possible. A pressure application under a static load is 0.1 g - 10 kg/cm^2, preferably 1 - 1000 g/cm^2. If the application of pressure is too strong, damage may be caused to pitch fibers and if it is too weak, an efficiency of increasing bulk density becomes poor.

The application of pressure by way of the pressing rollers, is carried out with a pair of rollers revolving at approximately the same surface velocity. It is possible to apply aprons to the pressing rollers if necessary. Since for the apron, heat-resisting property is required, it is preferable to use metal net made of heat-resisting alloy or fabrics made of carbon fibers. It is preferable that the surface of the pressing roller is of a material superior in heat-resisting property and wear resisting property such as ceramics. For example, it is preferable to use rollers obtained by flame spray coating of ceramics. Compression can be carried out by one step, but in case of the use of rollers, it is preferable to carry out little by little through several steps. Abrupt compression may have an advantage of providing a strong entanglement between fibers. But it is not preferable, because it is liable to give injury to fibers and brings about loss of fibers. Moreover, the surroundings of a production facility is contaminated by floating fibers.

Compression is carried out after a certain extent of infusiblization treatment is finished. The pitch fibers after infusiblization is complete will be referred to as pitch fibers. The pitch fibers which are not subjected to an infusiblization treatment has a low softening point, there is an advantage that the pressure applying effect appears at a low temperature. But since the strength, and the elongation are low, there is a drawback that the compression processing is liable to damage fibers and it is considered to be disadvantageous for increasing bulk density. It is preferable that the infusiblization treatment is carried out to the extent that infusiblized fibers have an oxygen content of 20 - 90 % of the value obtained at the complete infusiblization. Even when the infusiblization is carried out till completely infusiblized state or till the oxygen content which passes the level of completely infusiblized state, the production of high bulk density non-woven carbon fiber fabrics is possible. But as the compression processing requires to be carried out at a higher temperature, there are problems that life of facility becomes shorter and yield of the non-woven carbon fiber fabrics from pitch is lowered.

Compression rate is preferably 50 % - 95 % as a ratio of the roller gap to the thickness of the sheet which is fed to the rollers. When the compression ratio is large, compression effect becomes smaller and when the compression ratio is small, unpreferable tendency that the fibers are damaged is brought about.

As for steps of compression, 3 - 50 steps is preferable, and 5 - 15 steps is mostly preferable. If number of step is too small, compression effect becomes smaller and in addition damage of fibers becomes higher. This is not preferable. If number of step is too large, cost of the facility becomes higher, and in addition, tendency of saturation of effectiveness is brought about. This is not preferable.

A temperature of compression treatment is higher than the softening point of pitch fibers and lower than the softening point + 300 °C. It is preferably in the range of from (softening point + 25) °C to (softening point + 150) °C. Further, it is preferable that this temperature does not go over 500 °C.

When the pressure applying treatment is carried out at 500 - 1400 °C, and that it is carried out continuously from a temperature lower than that temperature, there is a problem that effectiveness is not notable. When the pressure application is started suddenly in this temperature range, there occurs such a problem that compression does not proceed, but only damage of fibers becomes notable. This may or may not be due to the fact that modulus of elasticity has become already great. Further there is a problem that the compression attained by the pressure application in this temperature range is recovered during the carbonization treatment carried out at a high temperature (especially 800 °C or higher). And it is difficult to increase bulk density. The measurement of the softening point of pitch fibers is carried out by seeking for a temperature at which compacting of test piece by plastic deformation is completed at the time of measurement of specific volume under a constant heating rate with a flow tester. As a measuring instrument such as "Koka type flow tester" made by Shimazu Seisakusho is used at the heating rate of 2 °C/min.

As for sheets of pitch fibers used as a raw material in the present invention, it is preferable to be a material produced by directly collecting melt spun pitch fibers.

Concretely, any of the spinning processes, such as a spun bond type spinning process in which melted pitch is spun from an usual spinning nozzle and drawn by gas stream or rollers, melt blow type spinning process in which extruding is carried out from a spinning hole or a slit having an outlet in a high speed gas stream, or a centrifugal spinning process in which a pitch is scattered from a pot revolving at a high speed and turned into liquid stream, can be adopted, but especially the melt blow process is preferable.

In case of the melt blow process, there has been known a process in which spinning holes are arranged in one row or slits are provided in a discharging slit of high velocity gas stream or a process in which one or several spinning holes are provided in a discharging hole of high velocity gas stream. For the present invention, any of the above-mentioned processes can be used.

The pitch used in the present invention is a high softening point pith which is capable of being subjected to melt spinning and infusiblization treatment. Preferably it is an optically anisotropic pitch, most preferably a substantially 100 % optically anisotropic pitch.

The pitch used in the present invention can be one kind or 2 kinds or more. It is possible to provide a high electric conductivity by highly carbonizing for the non-woven carbon fiber fabrics produced according to the present invention. The non-woven carbon fiber fabrics having a high electric conductivity can be used in shielding materials for electromagnetic waves, surface heat-generator, electrode materials, catalyst carriers etc.

The non-woven fabrics produced according to the present invention can contain metal nets, carbon fiber fabrics ceramics fiber products, etc. in the inside or on the surface in order to improve electric conductivity, shape stability, etc. Further, they can contain adhesives layer or binder layer, in order to stick to other material. Further, fiber implanting, flocking, resin coating, laminating with film, etc. can be conducted.

The present invention is further illustrated by the following non-limitative examples.

Example 1.

A raw material which was a petroleum based pitch having 100 % optically anisotropic proportion and a softening point of 285 °C was melt spun by using a spinneret having spinning holes of a diameter 0.8 mm in which a tubular nozzle for extruding the raw material, having an inside diameter of 0.3 mm and an outside diameter of 0.6 mm, was provided and heated air was ejected from the circumference of the tubular nozzle. Flow rate of the pitch was 12 g/80 holes.min. Pitch temperature was 320 °C. Spinneret temperature was 420 °C. Heated air rate was 0.43 kg/min. And temperature of heated air was 420 °C.

Spun fibers were collected on a belt by suctioning from the backside of a 20 mesh stainless metal net in collecting part. Resulting sheets were subjected to infusiblization treatment under a condition that the resulting sheet had an oxygen content of 75 % of the value obtained at the complete infusiblization treatment and further subjected to a heat treatment while pressing in an inert gas atmosphere furnace. Compression was carried out by 7 step and the compression rate in each step was set to 80 %. Temperature was 250 °C at the first step. Temperature was elevated in each step thereafter by 30 °C and pressing treatment was carried out.

Resulting non-woven carbon fiber fabrics had an apparent specific gravity of 0.22 and weight/unit area of 80 g/cm^2. Resulting non-woven fabrics showed almost no interlayer detachment.

Comparative Example 1.

Fiber sheets spun under the same condition with Example 1 were subjected to infusiblization treatment according to a usual process. And carbonization treatment was conducted under the condition where no pressing was applied. Apparent specific gravity of resulting non-woven carbon fiber fabrics was 0.08. Many interlayer detachment was observed and even light rubbing caused separation into a great number of thin fiber layer.

Example 2.

After application of light infusiblization to fiber sheets spun under the same condition as in Example 1, resulting fiber sheets were subjected to a heat treatment while pressing under various conditions. Apparent specific gravities and interlayer detachment of resulting non-woven carbon fiber fabrics were investigated. The result thereof are shown in Table 1.

Table 1

Pressing condition at the heat treatment and interlayer detachment				
Experiment No.	Pressing condition at the heat treatment		Apparent specific gravity	Extent of interlayer detachment and other
	pressure (g/m^2)	temperature (°C)		
1	0.09	250 - 480	0.02	There is interlayer detachment.
2	0.21	265 - 430	0.12	slight
3	1.8	180 - 420	0.18	almost none
4	7.5	250 - 480	0.23	"
5	15.5	180 - 400	0.26	"
6	20.0	280 - 540	0.27	"
7	75.3	180 - 410	0.29	"
8	180	240 - 450	0.31	"
9	900	240 - 495	0.34	There is damage of fiber.
10	12000	240 - 480	0.42	There is heavy damage of fiber.

Example 3.

A raw material which was a high softening point isotropic petroleum pitch having a softening point of 237°C was melt spun by a spinneret having 3000 spinning holes of 0.15 mm diameter arranged on three straight line form. Immediately after cooling, the spun fibers were sucked through slit form pulling nozzle and were blown into a space holding a vertical angle of 60° between 2 net conveyers to deposit and to collect in sheet form.

After resulting sheets was subjected to an infusiblization treatment according to an ordinary process a heat treatment was conducted under an inert gas atmosphere while being pressed by 7 step rollers. Compression rate was 80 % in each step. Temperature was 150°C at the 1st step and the temperature was elevated by 40°C in every step.

Resulting sheet had an apparent specific gravity of 0.25 and almost no interlayer detachment.

On the other hand in case of carbonization treatment in which no pressing was conducted, the apparent specific gravity of resulting sheet was 0.02. Heavy interlayer detachment occurred.

Function and Effectiveness

The present invention relates to a process for producing non-woven carbon fiber fabrics having a high bulk density. The non-woven carbon fiber fabrics of the present invention have a high bulk density, a uniform porosity and little characteristic of so-called interlayer detachment (i.e. breakage occurs from the place of weak entanglement of fibers during usage).

The non-woven carbon fiber fabrics produced according to the process of the present invention exhibit superior property when these are used in filtration material, packing material, break-lining material, electrode material, catalyst carrier, shielding material from electromagnetic waves, heat-resisting vessel, reinforcement material for fiber composite materials.

Claims

A process for producing high bulk density non-woven fabrics of carbon fibers which comprises subjecting an infusiblized sheet of pitch fibers to heat treatment at a temperature higher than the softening temperature of the pitch fibers and lower than the softening temperature plus 300°C, while applying a pressure to the surface of said sheet substantially in the vertical direction thereof.