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

(11) Publication number: **0 340 475 A2**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **89106179.8**

(51) Int. Cl.[4]: **D01F 9/14**

(22) Date of filing: **07.04.89**

(30) Priority: **12.04.88 JP 88154/88**

(43) Date of publication of application:
08.11.89 Bulletin 89/45

(84) Designated Contracting States:
DE FR

(71) Applicant: **NIPPON OIL CO. LTD.**
3-12, 1-chome Nishi-Shinbashi
Minato-ku Tokyo 105(JP)

(72) Inventor: **Harakawa, Michiharu**
338-104, Iwai-cho Hodogaya-ku
Yokohama-shi Kanagawa-ken(JP)
Inventor: **Sohda, Yoshio**
2-235-638, Kosugi-cho Nakahara-ku
Kawasaki-shi Kanagawa-ken(JP)
Inventor: **Katoh, Kenji**
1-1006-A-402, Kosugigotenmachi
Nakahara-ku
Kawasaki-shi Kanagawa-ken(JP)

(74) Representative: **Kraus, Walter, Dr. et al**
Patentanwälte Kraus, Weisert & Partner
Thomas-Wimmer-Ring 15
D-8000 München 22(DE)

(54) Process for producing pitch-derived carbon fibers.

(57) A process for producing pitch-derived carbon fibers from pitch fibers produced by melt-spinning a carbonaceous pitch, which comprises adding a polyoxyethylene alkyl ether of the following formula [I]:

$$R\text{-}O\text{-}(\text{-}CH_2CH_2O\text{-})_n\text{-}H \quad [I]$$

wherein R represents an aliphatic hydrocarbon having 8 to 12 carbon atoms and n represents an integer of 3 to 9,

as an emulsifier in an amount of 1 to 12 wt. %, based on an amino-modified silicone oil, to this oil having a molecular weight of 500 to 5,000 and an amine value of 2 to 15 to obtain an aqueous silicone emulsion and then applying the thus obtained emulsion to the pitch fibers when or before bundling the pitch fibers thereby adhering said oil to the pitch fibers in an amount of 0.01 to 0.8 wt. % based on the fibers.

EP 0 340 475 A2

PROCESS FOR PRODUCING PITCH-DERIVED CARBON FIBERS

BACKGROUND OF THE INVENTION

1. Filed of the Invention

The present invention relates to a process for producing carbon fibers from pitch fibers. In particular, the present invention relates to a process for producing pitch-derived carbon fibers having a high quality by using a specified treating agent in the step of forming the pitch-derived carbon fibers to facilitate the handling of the fibers and to solve the problems of fiber break, fluffing and fusion bond of the fibers with each other.

2. Prior Art

Pitch-derived carbon fibers are produced by melt-spinning a carbonaceous pitch and then subjecting the pitch fibers thus obtained to infusibilization (rendering infusible), carbonization and, if necessary, graphitization treatments.

The pitch fibers cannot be easily handled in the infusibilization and carbonization steps, since they are quite fragile. In these steps, they have problems such as fluffing, winding around the guide roller, fiber break. damage and fusion bond of the fibers with each other. As a result, the separability of the resulting carbon fibers into single fibers in reduced and the physical properties of them are impaired.

For solving these problems, there was reported a process wherein the pitch fibers are bundled with a silicone oil before the infusibilization and carbonization treatments (refer to Japanese Patent Laid-Open No. 223315/1984).

However, the process wherein the silicone oil is used has defects that a static electricity is produced to make stable spinning impossible and that the production apparatus is seriously stained by compounds derived from the silicone oil in the firing steps such as the infusibilization and carbonization steps.

Other processes wherein a silicone emulsion is used as the bundling agent were also reported (refer to Japanese Patent Laid-Open Nos. 199872/1984, 70017/1986 and 191582/1987).

In the process of the Japanese Patent Laid-Open No. 199872/1984, a polyoxyethylene nonylphenyl ether as a surfactant and further a polyol are added to the silicone oil to obtain an intended effect. In the process of the Japanese Patent Laid-Open No. 70017/1986, an emulsifier such as a sorbitan fatty acid ester is added to the silicone oil. In this process, a large amount of the silicone oil adheres to the fibers and, therefore, the handleability of them is not yet sufficiently improved. In the process of the Japanese Patent Laid-Open No. 191582/1987, the amount of an alkali metal in the aqueous silicone emulsion is controlled to be below a certain level in order tc prevent the decomposition and deterioration of the oil.

SUMMARY OF THE INVENTION

The object of the present invention is to provide a process for producing pitch-derived carbon fibers having an excellent separability into single fibers by improving the handleability of the fibers and preventing not only the fiber break, fluffing and damage of the fibers but also coherence and fusion bond of the fibers with each other.

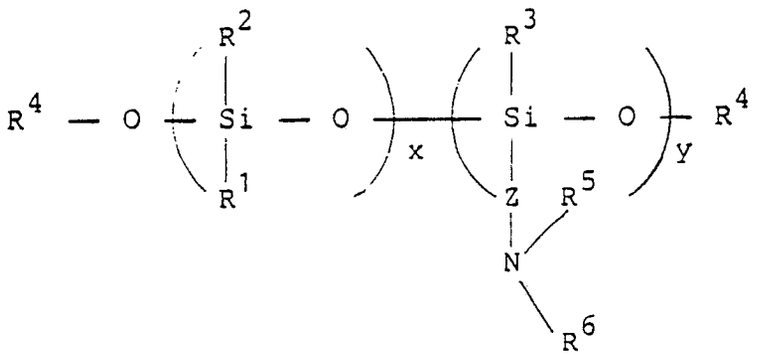
DETAILED DESCRIPTION OF THE INVENTION

The above-described object of the present invention can be attained by using a specified aqueous silicone emulsion as the bundling agent.

The present invention relates to a process for producing carbon fibers from pitch fibers produced by melt-spinning a carbonaceous pitch, the process being characterized in that an aqueous silicone emulsion prepared by adding a polyoxyethylene alkyl ether of the following formula [I]: $R\text{-}O\{CH_2CH_2O\}_n H$ [I] wherein R represents an aliphatic hydrocarbon having 8 to 12 carbon atoms and n represents an interger of 3 to 9,

as an emulsifier in an amount of 1 to 12 wt. %, based on an amino-modified silicone oil, to this oil having a molecular weight of 500 to 5,000 and an amine value of 2 to 15 is applied to the pitch fibers before or when bundling them so that said oil adheres to the pitch fibers in an amount of 0.01 to 0.8 wt. % based on the fibers.

The amino-modified silicone oils usable in the present invention are those shown by the following general formula [II]:



[II]

wherein R^2 and R^3 each represent an alkyl group having 1 to 6 carbon atoms, preferably 1 to 4 carbon atoms; R^1, R^5 and R^6 each represent a hydrogen atom or an alkyl group having 1 to 6 carbon atoms, preferably 1 to 4 carbon atoms; R^4 represents a hydrogen atom or $-SiR^1_3$; Z represents an alkylene group having 1 to 6 carbon atoms, preferably 1 to 4 carbon atoms, and x and y each represent an integer of 1 to 70, preferably 1 to 30.

The amino-modified silicone oils usable in the present invention are those having a molecular weight of 500 to 5,000, preferably 700 to 2,000 and an amine value of 2 to 15, preferably 3 to 8. The amine value is determined according to the method as specified in JIS K 0113.

When the amine value exceeds 15, the fibers are apt to cause fusion bond with each other in the infusibilization step and, on the contrary, when it is less than 2, the stability of the aqueous silicone emulsion is insufficient. When the amount of the emulsifier is increased to stabilize the emulsion in the latter case, undersirable influences are exerted on the fibers in the subsequent infusibilization and carbonization steps.

The polyoxyethylene alkyl ethers used as the emulsifier in the present invention are compounds represented by the above general formula [I].

In the general formula [I], R represents an aliphatic hydrocarbon group, preferably a straight-chain aliphatic hydrocarbon group having 8 to 12 carbon atoms, and n represents an integer of 3 to 9, preferably 5 to 7.

When the number of carbon atoms of R and/or n is excessively high, the compound is apt to be deteriorated by oxidation and the handleability thereof is lowered and, on the other hand, when it is insufficient, the emulsifying capacity thereof is reduced.

The polyoxyethylene alkyl ether is used in an amount of 1 to 12 wt. %, preferably 1 to 6 wt. %, based on the amino-modified silicone oil in the present invention.

In the prior art, the amount of a nonionic surfactant used as the emulsifier was usually in the range of 15 to 30 wt. % based on the base oil.

After intensive investigations made for the purpose of reducing the amount of the emulsifier to be used as far as possible without impairing the stability of the aqueous silicone emulsion, the inventors have succeeded in remarkably reducing the amount of the emulsifier by employing a combination of a specified amino-modified silicone oil with a specified polyoxyethylene alkyl ether.

The aqueous silicone emulsion contains usually 0.01 to 10 wt. %, preferably 0.05 to 5 wt. %, based on water, of the amino-modified silicone oil.

The aqueous silicone emulsion used as the bundling agent in the present invention is applied to the pitch fibers so that 0.01 to 0.8 wt. %, preferably 0.05 to 0.5 wt. %, of the amino-modified silicone oil adheres to the pitch fibers.

It is a characteristic feature of the present invention that the amount of the amino-modified silicone oil adhered to the fibers is very small. Namely, the effect of the present invention can be exhibited with such a small amount of the amino-modified silicone oil, while, for example, the adhesion of 1 to 15 wt. % of a silicone oil to the pitch fibers is necessitated in the above-mentioned Japanese Patent Laid-Open No.

70017 1986.

The method of applying the aqueous silicone emulsion (bundling agent) to the pitch fibers is not particularly limited and any known methods can be employed. For example, said emulsion can be applied by spraying, roller coating, immersion, use of a claw-shaped bundling apparatus, or a method comprising a combination of them.

The pitch fibers are produced by melt-spinning a carbonaceous pitch. The carbonaceous pitches include, for example, petroleum and coal pitches, among which optically anisotropic ones are preferred. The melt-spinning is conducted by any known process.

The pitch fibers to which the aqueous silicone emulsion (bundling agent) has been applied are then infusibilized in an oxidizing gas atmosphere. The infusibilization treatment is conducted at a temperature of usually 400 °C or below, preferably 150 to 380 °C and more preferably 200 to 350 °C. When the temperature of the treatment is below this range, a long treatment time is necessitated and, on the contrary, when it is above this range, the pitch fibers are fused to each other or wasted unfavorably. The oxidizing gas is usually oxygen, ozone, air, a nitrogen oxide, sulfur dioxide or a halogen. They can be used either alone or in combination of two or more of them.

The pitch fibers thus infusibilized are then carbonized and, if necessary, further graphitized in an inert gas atomsphere to form carbon fibers. The carbonization is conducted usually at a temperature of 800 to 2,000 °C for 0.1 minute to 10 hours. The graphitization is conducted, if necessary, at a temperature of 2,000 to 3,500 °C for 1 second to 1 hour.

Examples

The following Examples and Comparative Examples will further illustrate the present invention, which by no means limit the invention.

Example 1

A petroleum-derived pitch having an optically anisotropic phase content of 90 vol. % and a softening point of 280 °C was melt-spun through a 1,000-hole spinneret to form pitch fibers each comprising 1,000 filaments having an average diameter of 12 μm.

30 to 50 cc/min of a bundling agent (an aqueous silicone emulsion having a concentration of 0.2 to 0.5 wt. %) was sprayed on the fibers extruded through the spinneret and the fibers were treated with 20 to 30 cc/min of the bundling agent in a claw-shaped bundling apparatus.

The amount of the bundling agent adhered to the pitch fibers was 0.1 to 0.2 wt. % based on the pitch fibers.

An amino-modified dimethylsiloxane having a molecular weight of 1,500 and an amine value of 5 was used as the base oil of the bundling agent, and a straight chain polyoxyethylene alkyl ether of the formula: $C_{12}H_{25}O\{CH_2CH_2O\}_7$ H was used as the emulsifier, with the proviso that said oil and emulsifier were used in a weight ratio of 95:5.

The pitch fibers each comprising 1,000 filaments thus formed were infusibilized at 270 °C in air, precarbonized at 650 °C in a nitrogen atmosphere and graphitized at 2,500 °C in a nitrogen atmosphere to obtain carbon fibers.

The degree of separation of the carbon fibers thus obtained was 98.

The term "degree of separation" herein represents the degree of separability of the carbon fibers into single filaments, which is determined according to the following method:
A fiber comprising 1,000 filaments is cut into a length of 10 mm and gently shaken in a solution such as an alcohol. After allowing to stand, the number of the filaments thus separated is counted (a bundle of filaments not separated being counted as one filament). The number of the filaments thus separated per 1,000 filaments is calculated into the number per 100 filaments and taken as the degree of separation.

Example 2

An amino-modified dimethylsiloxane having a molecular weight of 1,000 and an amine value of 5 was used as the base oil, and a straight-chain polyoxyethylene alkyl ether of the formula: $C_8H_{17}O\{CH_2CH_2O\}_5$ H was used as the emulsifier, with the proviso that said oil and mulsifier were used in a weight ratio of

95:5.

The same procedure as that of Example 1 was repeated except that the bundling agent thus prepared was used to obtain carbon fibers having a degree of separation of 95.

Example 3

An amino-modified silicone having a molecular weight of 3,000 and an amine value of 8 as the base oil, and the same emulsifier as that used in Example 1, were used in a weight ratio of 90:10.

The same procedure as that of Example 1 was repeated except that the bundling agent thus prepared was used to obtain carbon fibers having a degree of separation of 90.

Comparative Example 1

An amino-modified dimethylsiloxane having a molecular weight of 10,000 and an amine value of 5 as the base oil, and the same emulsifier as that used in Example 1, were used in a weight ratio of 85:15, the amount of the emulsifier being controlled to be as small as possible so far as the stability of the emulsion was not impaired.

The same procedure as that of Example 1 was repeated except that the bundling agent thus prepared was used to obtain carbon fibers having a degree of separation of 35.

Comparative Example 2

The same base oil as that used in Example 1, and an ordinarily used polyoxyethylene nonylphenyl ether as the emulsifier, were used in a weight ratio of 85:15, the amount of the emulsifier being controlled to be as small as possible so far as the stability of the emulsion was not impaired.

The same procedure as that of Example 1 was repeated except that the bundling agent thus prepared was used to obtain carbon fibers having a degree of separation of 23.

Comparative Example 3

A dimethylsiloxane having a molecular weight of 1,500 and an amine value of 0 as the base oil, and the same emulsifier as that used in Example 1, were used in a weight ratio of 85:15, the amount of the emulsifier being controlled to be as small as possible so far as the stability of the emulsion was not impaired.

The same procedure as that of Example 1 was repeated except that the bundling agent thus prepared was used to obtain carbon fibers having a degree of separation of 25.

Comparative Example 4

An amino-modified dimethylsiloxane having a molecular weight of 1,500 and an amine value of 30 as the base oil, and the same emulsifier as that used in Example 1, were used in a weight ratio of 95:5.

The same procedure as that of Example 1 was repeated except that the bundling agent thus prepared was used to obtain carbon fibers having an extremely lowered degree of separation of 9 and exhibiting sticking of the filaments to each other.

Comparative Example 5

The same base oil and emulsifier as those used in Example 1 were used in a weight ratio of 80:20.

The same procedure as that of Example 1 was repeated except that the bundling agent thus prepared was used to obtain carbon fibers having a degree of separation of 12.

Comparative Example 6

The procedure of Example 1 was followed except that the bundling agent was used in a 10 % concentration and it was allowed to adhere to the pitch fibers in an amount of 3 wt. % based on the pitch fibers. The carbon fibers thus formed had an extremely lowered degree of separation of 5 and exhibited sticking of the filaments to each other.

[Effect of the Invention]

As described above, the pitch-derived carbon fibers having a high quality, an excellent separability into single filaments and excellent handleability can be formed by preventing fiber break, fluffing, damage and fusion bond of the fibers with each other according to the process of the present invention.

Claims

A process for producing pitch-derived carbon fibers from pitch fibers produced by melt-spinning a carbonaceous pitch, which comprises adding a polyoxyethylene alkyl ether of the following formula [I]:

$$R\text{-}O\text{-}(\text{-}CH_2CH_2O\text{-})_n\text{-}H \quad [I]$$

wherein R represents an aliphatic hydrocarbon having 8 to 12 carbon atoms and n represents an integer of 3 to 9,

as an emulsifier in an amount of 1 to 12 wt. %, based on an amino-modified silicone oil, to this oil having a molecular weight of 500 to 5,000 and an amine value of 2 to 15 to obtain an aqueous silicone emulsion and then applying the thus obtained emulsion to the pitch fibers when or before bundling the pitch fibers thereby adhering said oil to the pitch fibers in an amount of 0.01 to 0.8 wt. % based on the fibers.