United States Patent Office

3,784,679

Patented Jan. 8, 1974

3,784,679

PROCESS FOR PRODUCING CARBON FIBRES

Pierre Chiche, Verneuil-en-Halatte, France, assignors to Charbonnages de France, Paris, France

No Drawing. Filed Apr. 27, 1971, Ser. No. 137,976
Claims priority, application France, May 19, 1970, 7018171
Int. Cl. C01b *31/07*
U.S. Cl. 423—447 11 Claims

ABSTRACT OF THE DISCLOSURE

A process for the production of carbon fibres from coal tar pitch or from other strongly aromatic distillation residues subjected to heat treatment at a moderate temperature wherein a hydrocarbon polymer is added to the starting material before or during said heat treatment which is followed by spinning, oxidizing, and carbonizing. Polyethylene, polypropylene, polystyrene, polybicyclo[2,2,1]-heptene-2, and rubber are preferred polymers.

The present invention concerns a process for producing carbon fibres from coal-tar pitch or from other strongly aromatic distillation residues.

Carbon fibres have already been obtained from coal-tar pitch by subjecting the said pitch to a heat treatment at a moderate temperature and possibly to other treatments or conditioning, and thereafter spinning the pitch so treated at a temperature of the order of 300° C. The fibres so obtained were subjected to oxidation to render them infusible, and then carbonized in air. However, these processes result in fibres of a much inferior quality, and mechanical properties to those produced from textile (e.g. rayon or poly-acrylonitrile) filaments but the latter are generally expensive to produce.

An object of the present invention is to provide a process which allows an improvement in the quality of the fibres obtained from coal-tar pitch or from another strongly aromatic substance like coal-tar pitch.

Another object of the present invention is to provide improved fibres obtained from this process.

According to the process of this invention, there is provided a process for the production of carbon fibres from a strongly aromatic distillation residue comprising subjecting the said residue to a heat treatment at a moderate temperature, a hydrocarbon polymer being added to the said residue, before or during the heat treatment, the product of the heat treatment being thereafter spun into fibres which are then oxidized and carbonized.

Among the preferred polymers embodied in this invention and giving good results, one can mention natural or synthetic polymers such as polyethylene, polypropylene, polystyrene, polybicyclo[2,2,1]-heptene-2, rubbers, etc.

According to a preferred embodiment, the filtered strongly aromatic pitch is heated, before spinning under conditions of temperature, and for a length of time, as well as with agitation, such that the obtained material contains no or only a little anisotropic material; in other words, the heat treatment is stopped at the latest at the beginning of the onset of the anisotropic phase. The presence of anisotripic material can easily be evidenced by examination with a polarized light optical microscope (M. Ihnatowicz, P. Chiche, J. Deduit; S. Pregermain and R. Tournant, "Carbon," 4, 41 (1966)). This heat treatment can be achieved in a reactor provided with an agitation or stirring system and means for scavenging gases.

One may alternatively heat the mixture to a distinctly lower temperature but the reduced "de-volatilization" or the volatilizing-off of the material so obtained renders the oxidation treatments, necessary for making the filaments infusible before carbonization, more difficult.

The scope of this invention includes carbon fibres made by the process as set forth above.

The following examples will serve better to throw into relief the advantages of this invention.

EXAMPLE 1

A high temperature coal-tar pitch with the following characteristics was utilized:

Kraemer-Sarnow point	° C.	80
Density	g./cm.^{3}	1.32
Index of volatile materials (according to the standard ATIC–02–60)	percent	64.3
Elemental analysis in percentage by weight:		
Carbon		93.02
Hydrogen		4.45
Oxygen		1.5
Nitrogen		0.7
Sulphur		0.3

This pitch was previously filtered at 190° C. over a bronze filter with mean pore size of 2μ in order to separate out the solid and pseudo-solid particles that the pitch contains naturally.

After adding 10% by weight of melt-index 4, high densiy polyethylene, this mixture was heated to 420° C. under constant agitation at a heating rate of 3° C./minute; the generated volatile materials were entrained in a stream of nitrogen flowing at 3 l./min.

The resulting product was spun at 204° C. at a drawing speed of 450 m./minute.

The whole of this was then placed in a furnace and subjected to the following operational conditions:

	Hours
From room temperature to 250° C. in the presence of air at a heating rate of 0.5° C./minute	7.5
From 250° C. to 700° C. in the presence of nitrogen and in the absence of oxygen, at a heating rate of 0.5° C./minute	15
From 700° C. to 1000° C., at a heating rate of 2° C./minute	2.5
Total	25

The furnace was then allowed to cool naturally. The mechanical properties of the resulting carbon fibres were measured with the aid of an Instron press, under the following conditions:

Length of test-tube	mm.	50
Pulling speed	cm./minute	0.05

In this way a mean breaking strength of 55 kg./mm.^{2} was measured as well as a mean Young's modulus of 4200 kg./mm.^{2} and a mean diameter of 30μ.

These values represent the averages taken from 7 readings effected on different filaments. The total yield of the operations comprising the filtering, de-volatilization, spinning, oxidation and carbonization was 65%.

EXAMPLE 2

The operating conditions were identical with those in Example 1, except that the polyethylene was replaced by polybicyclo[2,2,1]-heptene - 2 - (norbornene), see F. W. Michelotti and W. P. Keaveney, J. Polymer Sci., A, 3, (1965), 895.

The resulting carbon fibres were measured to have a mean breaking strength of 150 kg./mm.^{2} and a Young's modulus of 11,960 kg./mm.^{2} for a fibre diameter of 30μ.

The total yield of the operations as described in Example 1 was 66%.

EXAMPLE 3

The operating conditions were identical with those in Example 1, except that the polyethylene was replaced by a polystyrene.

The thus prepared carbon fibres were measured to have a mean breaking strength of 60 kg./mm.^{2} and a Young's modulus of 4600 kg./mm.^{2} for a diameter of 30μ.

The total yield of the operations as described in Example 1 was 64%.

EXAMPLE 4 (NOT ACCORDING TO THIS INVENTION)

The operating conditions were identical with those in Example 1, but here the pitch did not receive any additive.

The carbon fibres prepared in this way were measured to have a mean breaking strength of 24 kg./mm.^{2} and a Young's modulus of 3300 kg./mm.^{2} for a diameter of 30μ.

The total yield of the operations as described in Example 1 was 61%.

The advantages of the invention are thus apparent by comparing these properties with those of the fibres according to the invention described in Examples 1 to 3.

I claim:

1. In a process for the production of carbon fibres from a strongly aromatic distillation residue pitch comprising subjecting said pitch to a heat treatment at a temperature on the order of about 420° C., the product of the heat treatment being thereafter spun into fibres which are then oxidized and carbonized, the improvement comprising adding a hydrocarbon polymer in an amount sufficient to improve the mechanical properties of the carbonized fibres to said pitch no later than during said heat treatment, said hydrocarbon polymer being selected from the group consisting of polyethylene, polypropylene, polystyrene, polybicycle[2,2,1]-heptene-2 and rubber.

2. A process as claimed in claim **1** wherein the said polymer is added before the heat treatment.

3. A process as claimed in claim **1** wherein the said polymer is a polyethylene.

4. A process as claimed in claim **1** wherein the said polymer is a polypropylene.

5. A process as claimed in claim **1** wherein the said polymer is a polystyrene.

6. A process as claimed in claim **1** wherein the said polymer is a polybicyclo[2,2,1]-heptene-2.

7. A process as claimed in claim **1** wherein the said polymer is a natural or synthetic rubber.

8. A process as claimed in claim **1** wherein the heat treatment is stopped before the onset of the anisotropic phase in the pitch.

9. A process as claimed in claim **1** wherein the heat treatment is stopped at the beginning of the onset of the anisotropic phase in the pitch.

10. A process as claimed in claim **1** wherein the said pitch is coal-tar pitch.

11. A process in accordance with claim **1** wherein said hydrocarbon polymer is used in an amount on the order of about 10% by weight.

References Cited

UNITED STATES PATENTS

3,629,379	12/1971	Otani	423—447 X
3,639,953	2/1972	Kimura et al.	423—447
3,607,672	9/1971	Schmitd	423—447
3,392,216	7/1968	Otani	264—29
3,595,946	7/1971	Joo et al.	264—29
3,107,153	10/1963	Boquist	423—448

OTHER REFERENCES

MacKay et al.: "Modern Plastics," vol. 45, No. 2, 1968, pp. 147–150.

EDWARD J. MEROS, Primary Examiner

U.S. Cl. X.R.

264—29