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(54) **Mesophase pitch, processes for its production and fibers produced therefrom.**

(57) There is disclosed a mesophase pitch containing at least about 70% by weight mesophase produced by physical operations without chemical operations on a carbonaceous precursor pitch. The mesophase pitch features a molecular weight distribution wherein at least 75% of the molecules have a molecular weight in the range of from about 600 to about 1300; less than about 10% of the molecules have a molecular weight less than about 600; and less than about 15% of the molecules have a molecular weight more than about 1300. There are also disclosed processes for the production of such a mesophase pitch. The mesophase pitch is useful in producing carbon filter and fibers produced from the pitch of the invention are also disclosed.

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DESCRIPTION

MESOPHASE PITCH, PROCESSES FOR ITS PRODUCTION AND FIBERS PRODUCED THEREFROM

The invention relates to a mesophase pitch and particularly relates to a mesophase pitch containing at least about 70% by weight mesophase and a process for producing the mesophase pitch and carbon fibers from the mesophase pitch.

Mesophase pitch has been known to be suitable for producing carbon fibers having excellent properties suitable for commercial exploitation. It is known that mesophase derived carbon fibers are lightweight, strong, stiff, electrically conductive and both chemically and thermally inert. The mesophase derived carbon fibers perform well as reinforcements in composites and have found use in aerospace applications and quality sporting equipment.

Generally, carbon fibers have been primarily made from three types of precursor materials: rayon, polyacrylonitrile (PAN), and pitch. The use of pitch as a precursor is attractive economically.

Low cost carbon fibers produced from ordinary pitch exhibit little preferred molecular orientation and relatively poor mechanical properties.

In contrast, carbon fibers produced from mesophase pitch exhibit high preferred molecular orientation and relatively excellent mechanical properties.

As used herein, the term "pitch" is to be understood as used in the instant art and generally refers to a carbonaceous residue consisting of a complex mixture of primarily aromatic organic compounds which are solid at room temperature and exhibit a relatively broad

melting or softening temperature range. When cooled from the melt, the pitches behave as glasses.

As used herein, the term "mesophase" is to be understood as used in the instant art and generally is synonymous with liquid crystal. That is, a state of matter which is intermediate between crystalline solid and a normal liquid. Ordinarily, a material in the mesophase state exhibits both anisotropic and liquid properties.

As used herein, the term "mesophase-containing pitch" is a pitch containing less than about 40% by weight mesophase and the non-mesophase portion or isotropic phase is the continuous phase.

As used herein, the term "mesophase pitch" is a pitch containing more than about 40% by weight mesophase and is capable of forming a continuous anisotropic phase when dispersed by agitation or the like in accordance with the prior art.

The conventional method for preparing mesophase pitch from a precursor pitch includes heat treating at a temperature greater than 350°C to effect thermal polymerization. This process produces large molecular weight molecules capable of forming mesophase.

A typical conventional method is carried out using reactors maintained at about 400°C for about 20 hours. The properties of the final material can be controlled by the reaction temperature, heat-treatment time, and volatilization rate. The presence

of the high molecular weight fraction results in a melting point of the mesophase pitch of at least 330°C. An even higher temperature is needed to transform the mesophase pitch into fibers. This is termed "spinning" in the art.

The following patents are representative of the prior art and are incorporated herein by reference: U.S. patent no. 4,005,183 to Singer, U.S. patent no. 3,919,387 to Singer, U.S. patent no. 4,032,430, U.S. patent no. 3,976,729 to Lewis et al., U.S. patent no. 3,995,014 to Lewis, and especially British patent 2,005,298 to Chwastiak.

The amount of mesophase in pitch can be evaluated by known methods using polarized light microscopy. The presence of homogeneous bulk mesophase regions can be visually observed by polarized light microscopy and quantitatively determined by the method disclosed in the aforementioned Chwastiak patent. Previously, the criteria of insolubility in certain organic solvents such as quinoline and pyridine was used to estimate mesophase content. There could, however, be present in the precursor pitch certain non-mesophase insolubles and it is a common practice to remove these insolubles before treating the precursor pitch.

In accordance with the prior art, "% Q. I." refers to quinoline insolubles of a pitch quinoline extracted at 75°C. Also, "% P. I." refers to pyridine insolubles of a pitch by Soxhlet extraction in boiling pyridine at about 115°C.

Softening point or softening temperature of a pitch, is related to its molecular weight constitution, the presence of a large amount of high molecular weight components generally tends to raise the softening temperature. It is a common practice in the art to characterize in part a precursor pitch by its softening point. For mesophase pitches, the softening point is used to determine suitable spinning temperature. Generally, the spinning temperature is about 40°C or more higher than the softening temperature.

Generally, there are several methods for determining the softening temperature and the temperatures measured by these different methods vary somewhat from each other.

Generally, the Mettler softening point procedure is widely accepted as the standard for evaluating precursor pitches. This procedure can be adapted for use on mesophase pitches.

The softening temperature of a mesophase pitch can also be determined by hot stage microscopy. In this method, the mesophase pitch is heated on a microscope hot stage in an inert atmosphere under polarized light. The temperature of the mesophase pitch is raised under a controlled rate and the temperature at which the mesophase pitch commences to deform is noted as the softening temperature.

As used herein, softening point or softening temperature will refer to the temperature determined by the Mettler procedure for both precursor and mesophase pitches.

According to the present invention there is provided a mesophase pitch containing at least about 70% by weight mesophase produced from physical operations without chemical operations on a carbonaceous precursor pitch so that the mesophase pitch possesses a molecular weight distribution wherein at least about 75% of the molecules have a molecular weight in the range of from about 600 to about 1300, less than about 10% of the molecules have a molecular weight less than about 600; and less than about 15% of the molecules have a molecular weight more than about 1300.

Preferably the mesophase pitch of the invention possesses x-ray properites of interlayer spacing Co/2 of less than about 3.60 Angstroms and an apparent stack height Lc of greater than about 20 Angstroms.

Preferably, the mesophase pitch of the invention contains at least about 90% by weight mesophase and more preferably about 100% by weight mesophase.

The physical operations which can be used on the carbonaceous precursor pitch include devolatilizing, solvent extraction, a sequence of solvent extraction; chromatographic separation such as gel permeation chromatography, vacuum sublimation, blending of different pitches any one of which might have been subjected to the same operation, and combinations of the foregoing.

According to another aspect of the present invention there is provided a pitch fiber formed from the mesophase pitch. The pitch fibre may be formed without any chemical operations e.g. by spinning. Preferably, the spinning is at a temperature less than about 370°C. Conventional spinning does not subject the pitch to a chemical change for a temperature below about 370°C. for the period of time the mesophase pitch is at that elevated temperature.

Thus, the instant invention allows the formation of a pitch fiber from a carbonaceous pitch without any chemical operations.

Generally, the solvents suitable for treating the carbonaceous pitch include toluene, benzene, N, N-dimethyl formamide, a mixture of toluene and petroleum ether, and carbon disulfide, of course, numerous other solvents are suitable, particulary among conventional pitch solvents. In any event, the suitability of a solvent can be determined easily in accordance with the instant disclosure. Some solvents which were found unacceptable for obtaining at least about 70% by weight mesophase for certain pitches include nitromethane, acetonitrile, ethylacetate, and methyl ethyl ketone. It appears that the solubility parameter of the solvents is not indicative of the suitability of the solvent.

In the conventional thermal mesophase process, the carbonaceous precursor pitch is heated to effect polymerization. The resultant mesophase pitch is characterized by a molecular weight distribution which contains two major peaks. The low molecular weight peak corresponds

to components of the precursor pitch and the high molecular weight peak corresponds to the molecules produced by the thermal polymerization.

In contrast, the instant mesophase pitch possesses a molecular weight distribution having a single major peak generally positioned between the two peaks which would have arisen if the thermal polymerization had been carried out.

In carrying the invention into effect, certain embodiments have been selected for illustration in the tables and for description in this specification.

Illustrative, non-limiting examples of the invention are set out below. Numerous other examples can readily be evolved in the light of the guiding principles and teaching herein. The examples given herein are intended to illustrate the invention and not in any sense to limit the manner in which the invention can be practiced. The parts and percentages recited herein, unless specifically stated otherwise, refer to parts by weight and percentages by weight.

Generally, the carbonaceous precursor pitch suitable for carrying out the invention should be a precursor pitch capable of forming a large-domained mesophase pitch by

conventional thermal porcesses as set forth in the aforementioned Singer patent no. 4,005,183. The suitability of any carbonaceous pitch can be determined in a straight forward manner in accordance with the teachings herein.

There is, of course, an interrelationship between the carbonaceous precursor pitch and the physical operations suitable and preferable for producing the mesophase pitch. The teachings herein provide the guidelines for selecting and optimizing the physical operations for a particular carbonaceous pitch.

Example 1

A commercially available petroleum pitch was used in a solvent extraction operation. The petroleum pitch had a softening temperature of about 130°C and had 0% P.I. and contained no mesophase.

Ten grams of the pitch were stirred with 200 ml of toluene at room temperature for about one hour and then filtered by vacuum filtration. The dried insolubles or yield was about 8% by weight. The yield had a softening point of about 319°C, exhibited 47% P.I., and contained about 40% by weight mesophase.

Example 2

The Example 1 was repeated except that boiling toluene was used. The yield was 6% by weight and the mesophase content was about 100% by weight.

Example 3

A commercially available petroleum pitch different from the Example 1 was selected. The petroleum pitch

had a softening temperature of about 123°C and had about 0% P.I. and contained no mesophase.

The operations of the Example 1 were repeated except that the solvent was a 1:2 mixture of petroleum ether and toluene. About 14% by weight yield was obtained and the yield had a softening temperature of about 239°C and had about 3% P.I. and contained about 100% by weight mesophase.

Example 4

The Example 3 was repeated except that the solvent was a 1:1 mixture of petroleum ether and toluene. The yield was about 32% and contained about 50% by weight mesophase.

Example 5

The mesophase pitch of the Example 3 was spun into fibers on a monofilament spinning machine at about 290°C. The fibers had a diameter of about 20 microns and were thermoset by heating them in air at 2°C per minute to about 375°C. The thermoset fibers were examined by polarized light microscopy and were determined to contain about 100% anisotropic state. The thermoset fibers were carbonized to 1700°C in an inert atmosphere in accordance with conventional methods and tests on the carbonized fibers exhibited a modulus of about 25 x 10^6 psi (172 GPa) and 250,000 psi (1.72 GPa) tensile strength.

The methods for making carbonized fibers from mesophase pitch are well known in the art and particular reference is had to the aforementioned Singer patent no. 4,005,183 and Chwastiak patent no. 2,005,298.

Example 6

A third type of commercially available petroleum pitch was selected. The petroleum pitch had a softening temperature of about 130°C. In accordance with the preferable embodiment, the pitch was first distilled and the new softening temperature was about 201°C with about 3% P.I. and 3% by weight mesophase.

Next, the pitch was solvent extracted as in the Example 1 to give a yield of about 36% by weight, 41% P.I., and about 90% by weight mesophase. The softening temperature of the mesophase pitch was about 343°C.

Example 7

The Example 6 was repeated except that the solvent extraction was carried out with boiling toluene. About 30% by weight yield was obtained with a softening temperature of about 360°C. The yield had about 69% P.I. and contained about 100% by weight mesophase.

Example 8

The Example 7 was repeated except that the solvent extraction was carried out with benzene at a temperature of about 80°C. The yield was about 30% by weight and had about 55% P.I. and contained about 100% by weight mesophase. The softening temperature was about 360°C.

Example 9

An air-blown petroleum pitch having a softening temperature of about 152°C was solvent extracted with toluene at room temperature and gave a yield of about 34% by weight. The yield contained no mesophase. A similar result was obtained for a pitch derived from pyrolysis tar.

Both of these pitches do not yield large domain mesophase when heat treated in accordance with conventional methods. This shows that such pitches do not appear suitable for the invention.

Example 10

The petroleum pitch of the Example 6 was heated at a temperature of about 390°C under an inert gas purge for about one hour to remove the lowest molecular weight components. About 21% by weight was distilled off and the remaining pitch had a softening temperature of about 162°C, exhibited 0% P.I., and contained no mesophase.

Solvent extraction was carried out at room temperature by stirring 2400 ml of toluene with 120 grams of ground up pitch. After filtering through a sintered glass filter using vacuum suction, the yield was about 19% by weight. The yield had a softening temperature of about 320°C, exhibited about 39% P.I., and contained about 80% by weight mesophase.

Example 11

The Example 10 was repeated except that the solvent extraction was carried out at about 110°C.

The yield was about 7% by weight. The yield had a softening temperature of about 370°C, exhibited about 64% P.I., and contained about 100% by weight mesophase.

Example 12

The distilled pitch of the Example 6 was solvent extracted with boiling benzene by refluxing 50 grams of the powdered pitch with 1000 ml for about two hours.

The hot solution was filtered on a sintered glass funnel and the yield was about 30% by weight. The yield had a softening temperature of about 360°C, exhibited about 55% P.I., and contained about 100% by weight mesophase.

Example 13

The Example 6 was repeated except that there was no prior distillation. No insolubles were obtained.

Example 14

The petroleum pitch of the Example 3 was solvent extracted with petroleum ether. The yield was about 77% by weight and contained no mesophase. Further solvent extraction with toluene in accordance with the Example 3 produced about 1% by weight yield which contained about 100% by weight mesophase.

Example 15

Solvent extraction was carried out on a coal tar pitch having a softening temperature of about 125°C, and about 0% mesophase. At room temperature, 60 grams of pitch was stirred with 1200 ml of toluene for about two hours. The yield was about 47% by weight. The yield had a softening temperature of about 318°C, exhibited about 53% P.I., and contained about 60% by weight mesophase.

Example 16

The coal tar pitch of the Example 15 was solvent extracted by refluxing 29.5 grams of the pitch with 500 ml of toluene at a temperature of about 110°C for about two hours. A 40% by weight yield contained about 85% by weight mesophase.

Example 17

Tests were carried out to determine mesophase content as a function of blending soluble and insoluble portions of the solvent extracted pitch.

For a naphthalene pitch solvent extracted at room temperature with toluene, it was determined that there was a substantially linear relationship between mesophase content by weight and insoluble content by weight for the range of from about 10% to about 100% by weight mesophase which corresponded to the range of from about 35% to about 82% by weight of insolubles.

This relationship was substantially the same when blending experiments were performed using the soluble and insoluble portions from the naphthalene pitch with the corresponding fractions from the Example 3. For example replacing a given weight of insolubles for the naphthalene pitch with the same weight of insolubles from the Example 3 produced the same mesophase content. This is an unexpected result in view of the differences in the chemical compositions of the precursor pitches.

Example 18

Tests were conducted to determine the effect of repeated solvent extraction.

It has been found that the exhaustive solvent extraction with toluene at room temperature results in a diminishing yield and virtually no measurable mesophase.

Thus, this is an additional guideline for the practice of the invention.

Example 19

Tests were carried out on the various yields from the examples to determine the characteristics of both the molecular weight distributions and x-ray diffraction.

Using gel permeation chromatography, the values were determined for number average molecular weight ($\overline{M}n$), weight average molecular weight ($\overline{M}w$), and z-average molecular weight ($\overline{M}_z$). Also, the quantitative distribution of molecular weights was determined.

In addition, x-ray diffraction measurements were made to determine the values of Co/2 and Lc.

Table 1 shows the results of these tests for mesophase pitches of various examples.

The molecular weight distribution data was obtained in accordance with the aforementioned Lewis et al. patent no. 3,976,729 and Chwastiak British patent 2,005,298. The solvent employed in the gel permeation chromatographic procedure was quinoline.

TABLE 1

Solvent	Example 1 Toluene, 25°C	Example 3 1:2 Petroleum Ether, Toluene, 25°C	Example 6 Toluene, 25°C	Example 8 Benzene, 80°C
Yield %	8	14	47	30
% Mesophase	40	100	90	100
% P.I.	47	3	41	55
Soft. Temp. °C	319	239	343	360
$\overline{M}n$	--	805	954	973
$\overline{M}w$	--	841	1029	1049
$\overline{M}z$	--	878	1096	1115
Dw = $\overline{M}w/\overline{M}n$	--	1.044	1.079	1.078
Dz = $\overline{M}z/\overline{M}n$	--	1.091	1.149	1.146
% Molecules, MW <600	--	10	6	6
% Molecules MW >1300	--	0.2	12.5	14
% Molecules Between 600-1300	--	90	82.5	80
Co/2, Å	--	3.56	3.58	358
Lc, Å	--	23	20	20

TABLE 1 - Continued

Solvent	Example 10 Toluene, 25°C	Example 11 Toluene, 110°C	Example 15 Toluene, 25°C	Example 16 Toluene, 110°C
Yield	19	7	47	40
% Mesophase	80	100	60	85
% P.I.	39	64	53	
Soft. Temp. °C	320	370	318	350
$\bar{M}n$	935	--		
$\bar{M}w$	1016	--		
$\bar{M}z$	1016	--		
$Dn = \bar{M}w/\bar{M}n$	1.087	--		
$Dz = \bar{M}z/\bar{M}n$	1.168	--		
% Molecules <600MW	8	--		
% Molecules >1300 MW	12	--		
% Molecules Between 600 - 1300	80	--		
Co/2, Å	3.60		3.60	3.55
Lc, Å		--	16	23

For comparison, Table 2 shows mesophase pitches produced by conventional thermal processes for pitches used in various examples.

TABLE 2

	Precursor Pitch Ex. 3	Precursor Pitch Ex. 6 to 14	Precursor Pitch Ex. 15, 17
Yield, %	46	46	55
% Mesophase	100	100	100
% P I	47	61	65
Soft. Temp. °C	309	350	348
$\bar{M}n$	732	880	975
$\bar{M}w$	832	1026	1105
$\bar{M}_z$	954	1169	1215
$Dw = \bar{M}w/\bar{M}n$	1.137	1.166	1.133
$Dz = \bar{M}z/\bar{M}n$	1.303	1.328	1.246
% Molecules, $Mw < 600$	36	21	12
% Molecules, $Mw > 1300$	10	24	29
% Molecules Between 600-1300	54	55	60

For completeness, Table 3 shows x-ray data for precursor pitches prior to any operations.

TABLE 3

	Precursor Pitch Ex. 1	Precursor Pitch Ex. 6	Percursor Pitch Ex. 15	Naphthalene Pitch Ex. 17
Co/2, A^o	4.06	4.11	3.71	4.23
Lc, A^o	8	8	12	7

A comparison between the values for Co/2 and Lc for the precursor pitches as shown in the Table 3 to the values of the instant mesophase pitch shows the instant mesophase pitches exhibit substantial molecular order due to the instant process. In particular, the instant solvent extraction without any applied heat transforms a relatively disordered precursor pitch into a substantially ordered mesophase pitch.

It is interesting to compare the solubility parameter δ of various solvents to the mesophase content of the pitch after treatment. Table 4 shows that the acceptable and unacceptable solvents appear to fall within the same range.

TABLE 4

Solvent	Acceptable Solubility Parameter- ∂	Pitch Used	% Mesophase in Product
Toluene	8.9	Petroleum, Coal tar, Naphthalene Anthracene	up to 100%
Benzene	9.2	Petroleum	up to 100%
N, N-Dimethyl Formamide	12.1	Petroleum	up to 100%
Toluene + Petroleum Ether	8.9 (Toluene) 7 (Petrol-Ether)	Petroleum	up to 100%
Carbon Disulfide	10.0	Petroleum	100%
	Unacceptable		
Nitromethane	12.7	Petroleum	0%
Acetonitrile	11.9	Petroleum	10%
Ethylacetate	9.1	Petroleum	15%
Methylethyl Ketone	9.3	Petroleum	35%

$$\partial = \left(\frac{\Delta Hv - RT}{V}\right)^{\frac{1}{2}}$$

Hv = heat of vaporization
R = molar gas constant
T = temperature in °K
V = molar volume

Example 20

The mesophase pitch of the Example 3 was melted at a temperature of about 300°C and stirred for about 30 minutes in an inert atmosphere in order to remove the solvent. The product was spun into monofilaments at a temperature of about 300°C. The as-spun fibers had a diameter of 15 microns and 25 microns.

The 25 micron fibers were crushed to a powder and examined by x-ray. The Co/2 was measured as 3.54 Angstrom and Lc was measured as 34 Angstrom. The x-ray data for the mesophase pitch prior to spinning showed Co/2=3.58 Angstroms and Lc of about 25 Angstroms.

The preferred orientation of the as-spun fibers was measured as being about 30°.

By comparison, the as-spun fibers made by conventional processes as disclosed in the aforementioned Singer patent no. 4,032,430 had a Co/2 of from 3.45 to 3.55 Angstroms, Lc of from 30 to 50 Angstroms, and a preferred orientation of from 25° to 30°.

Additionally, the 15 micron fibers were thermoset by heating in air at 2° per minute to about 375°C. The thermoset fibers were examined and contained about 100% anisotropic state. The thermoset fibers were carbonized to 1700°C in an inert atmosphere in accordance with conventional methods and the carbonized fibers exhibited a modulus of about 28 x 10^6 psi (193 GPa) and a tensile strength of 273,000 psi (1.88 GPa).

I wish it to be understood that I do not desire to be limited to the exact details of construction shown and described, for obvious modifications will occur to a person skilled in the art.

CLAIMS

1. A mesophase pitch containing at least about 70% by weight mesophase characterised by being produced from physical operations without chemical operations on a carbonaceous precursor pitch so that the mesophase pitch possesses a molecular weight distribution wherein at least about 75% of the molecules have a molecular weight in the range of from about 600 to about 1300, less than 10% of the molecules have a molecular weight less than about 600, and less than about 15% of the molecules have a molecular weight of more than about 1300.

2. A mesophase pitch as claimed in claim 1, characterised in that the mesophase content is at least about 90% by weight.

3. A mesophase pitch as claimed in claim 1 or 2, characterised in that the mesophase content is about 100% by weight.

4. A mesophase pitch as claimed in any one of the preceding claims, characterised in that the x-ray properties show an interatomis spacing Co/2 of less than about 3.60 Angstroms and an apparent stack height Lc of greater than about 20 Angstroms.

5. A pitch fiber characterised in that it has been formed from the mesophase of any one of the preceding claims.

6. A process for producing a mesophase pitch containing at least about 70% by weight mesophase characterised by applying physical operations to a carbonaceous precursor pitch.

7. A process as claimed in claim 6, characterised in that the physical operations include at least one step of solvent extraction.

8. A process as claimed in claim 6 or 7, characterised in that the physical operations include a sequence of solvent extraction steps.

9. A process as claimed in claim 6, 7 or 8, characterised in that the solvent extraction is preceded by distilling said carbonaceous pitch.

10. A process as claimed in any one of claims 6 to 9, characterised in that solvent extraction is used with a solvent selected from the group consisting of toluene, benzene, N, N-dimethyl formamide, a mixture of toluene and petroleum ether, and carbon disulfide.

11. A process as claimed in any one of claims 6 to 10, characterised in that a mesophase pitch containing a predetermined amount of mesophase is obtained by blending together soluble and insoluble portions resulting from solvent extraction on said carbonaceous precursor pitch.

12. A carbonized fiber made from a mesophase pitch as claimed in any one of claims 1 to 4.

European Patent Office

EUROPEAN SEARCH REPORT

Application number EP 80 30 3384

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
D	US - A - 3 919 387 (L.S. SINGER) * Column 7, line 43 - column 10, line 27 * --	1-3,5-8,10,12
	GB - A - 2 002 024 (EXXON) * Claims 1,7-14 * & FR - A - 2 396 793 & DE - A - 2 829 288 --	6,7,10
P	US - A - 4 219 404 (G'HAZI DICKA-KIAN) * Claims 4-9; column 4, lines 30-38 * ----	6,7,9,10

CLASSIFICATION OF THE APPLICATION (Int. Cl.³)

C 10 C 3/00
D 01 F 9/14

TECHNICAL FIELDS SEARCHED (Int. Cl.³)

C 10 C 3/00
1/00
D 01 F 9/14
9/12

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	08-12-1980	ROTSAERT