United States Patent

Shea et al.

[15] **3,668,110**

[45] **June 6, 1972**

[54] PITCH TREATMENT MEANS

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[22] Filed: **Oct. 28, 1970**

[21] Appl. No.: **84,883**

[52] **U.S. Cl.** **208/45**

[51] **Int. Cl.** **C01b 1/07**, C10c 3/08

[58] **Field of Search** 208/45, 6

[56] **References Cited**

UNITED STATES PATENTS

2,871,181	1/1959	Kulik	208/45
2,953,501	9/1960	Mignone	208/45
3,079,326	2/1963	Neuworth	208/45
3,200,062	8/1965	Britton	208/45
3,278,415	10/1966	Doberenz et al.	208/45
3,373,101	3/1968	Folkins et al.	208/45

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[57] **ABSTRACT**

A spinnable pitch, useful in the manufacture of carbon filaments of continuous lengths, is prepared by the multiple solvent extraction of pitch, first by trituration of pitch particles with a low-boiling, aromatic solvent in which the bulk of pitch particles is essentially insoluble — then by dissolution of the pitch in a solubilizing solvent, filtration, and evaporation of the solvent.

6 Claims, No Drawings

PITCH TREATMENT MEANS

BACKGROUND OF THE INVENTION

Carbon fibers have been produced from organic polymer fibers such as rayon or polyacrylonitrile by oxidation and carbonization of the fibers. The same process has been found to be applicable to manufacture carbon fibers from filaments of polyvinyl chloride, polyvinyl acetate, blown asphalt, and petroleum pitch.

Otani, U.S. Pat. No. 3,392,216, July 9, 1968, discloses and claims a method for the heat treatment of several of these pitch-like materials, particularly polyvinyl chloride. The Otani method involves heating the starting material to 300°–400° C. in an inert atmosphere to raise the softening point and improve the molecular weight range of the pitch-like material.

Coal tar pitch is particularly difficult to use because of the presence of an insoluble second-phase material which must be removed prior to spinning. If allowed to remain when the fiber is drawn from the spinnerette, the particles of second-phase material will form stress points in the filament which tend to lower the strength of the filament. Nodules on the surface of the filament will render the filament unacceptable for use in certain applications.

More recently a method has been devised for treating a coal tar pitch to enable the pitch to be spun into continuous lengths capable of being oxidized and carbonized into commercially acceptable carbon fibers. Such treatment includes (1) dilution of the pitch with quinoline or light creosote oil, (2) filtration, (3) evaporation of the diluent, and (4) heat treatment of the pitch within the range of about 280°–305° C. until a softening point of 230°–260° C. has been attained, usually from 40 to 140 hours. The pitch can then be spun, oxidized, and carbonized as in the prior art. This method leads to a relatively clean pitch of about 80 percent carbon yield after appropriate processing of the spun filament which will form 0.5–10 mil continuous filament.

These carbonized filaments have a tensile strength of 80,000 to 130,000 psi, a volume resistivity of 1,280–1,600 micro-ohm inches, and an apparent density of about 1.65 g./cc. They are useful as substrates for boron deposition, and as fillers for carbon-carbon, carbon-resin, carbon-metal composites and other similar applications where filamentary carbon is conven-tionally and advantageously employed.

This invention relates to an improved method of preparing a spinnable pitch-like material from pitches of petroleum, coal tar, and the pyrolysis of organic polymers origin.

More particularly this invention relates to a method of preparing such pitch-like material without subjecting the pitch precursor to heat treatment to raise the softening point, thus avoiding the potential for second phase carbon formations.

Fibers prepared from the pitch and oxidized and carbonized in the usual manner have improved characteristics.

SUMMARY OF THE INVENTION

By the process of this invention, a pitch from coal tar or petroleum, petrochemicals and the pyrolysis or organic polymers is (1) fabricated into small particles capable of being acted upon by an appropriate solvent to remove therefrom low boiling, low molecular weight material; (2) the resulting particles are contacted with such an essentially aromatic or equivalent solvent to remove such low boiling, low molecular weight materials at a temperature from about ambient room temperature to about the softening point of the pitch in contact with the solvent; (3) the particles are separated from the solvent; (4) the particles are then extracted with a solubilizing solvent; (5) the resulting suspension is filtered to remove the insoluble solid materials therefrom, and (6) the solvent of the second extraction is evaporated from the resulting filtrate to yield a spinnable pitch. In an obvious alternative, steps 1, 2, and 3 are removed until after the performance of step 6. That is, (1) the raw pitch is extracted in a solubilizing solvent; (2) filtered to remove the solid materials therefrom; (3) the solvent is removed by evaporation; (4) the resulting solid or liquid filtered pitch is ground if necessary; (5) extracted by an appropriate solvent to remove the low-molecular weight components; and (6) separated from the extract. The pitch, when prepared by either of the above methods, need not be subjected to heating over long periods of time and is of a physically more uniform nature with respect to softening point and homogeneity than is a heat treated pitch. The filaments manufactured therefrom when carbonized to 1,200° C. or above are stronger than those prepared from heat treated pitches.

DETAILED DESCRIPTION OF THE INVENTION

Otani, in Japanese patent specification No. 2511/69, discloses a method for the preparation of a spinnable pitch from coal tar. By the method of the patent, coal tar pitch is either melted or solubilized in chloroform and filtered to remove the second-phase material. It is then destructively distilled at a temperature not exceeding 250° C. for several hours and then vacuum distilled at about 300° C. Otani states that the distillation step accomplishes the removal of low molecular weight components.

By the herein-described method, only selected low molecular weight components, only those soluble in benzene or equivalent solvents are removed. Additionally, there is no thermal rearrangement, polymerization, or aromatization of the coal tar pitch generally found as a result of any heat treatment process. This method affords a product particularly suitable for spinning, oxidizing, and carbonizing to yield a superior filamentous product.

The first step of the herein-described method is to mechanically or otherwise form the pitch into small particles, of the order of −100 mesh. This can be done most conveniently by grinding or milling solid pitch or by nebulizing or atomizing a molten pitch and rapidly cooling the droplets to below their softening point so as to prevent coalescence. This nebulization can be accomplished in the presence of the aromatic or equivalent solvent useful for the subsequent process of this invention.

The above-formed pitch particles are then extracted by a selected solvent in such a quantity that from about 10 to about 30 percent of the pitch is extracted into the solvent, the soluble portion of the pitch being the low molecular weight components thereof. The choice of solvent and solvent volume is determined by the desired softening point range of the final pitch product. As for example, a pitch solubilizing solvent, quinoline, used in a solvent to pitch ratio of <1:1 (V/V) is adequate and a non-solubilizing solvent, benzene, in a >1:1 (V/V) ratio is satisfactory to the practice of this invention. It is preferred to use a solid to solvent ratio of about 1:5 (V/V) when benzene is used as a solvent. The extraction can be carried out at from about the freezing point of the solvent to about the softening point of the pitch. Ideally, since the solvent can be recovered and reused, safety and economics dictate the use of a relatively large volume of solvent at or about room temperature. We have found that about 1–10 volumes of benzene per volume of pitch is capable of performing the extraction depending upon the temperature at which the extraction is carried out.

The solvent and solid pitch are then separated by filtration, centrifugation or the like separative means. Preferably, any residual solvent contained in the pitch is removed therefrom prior to further treatment of the pitch such as dissolution of the pitch in the second solvent by the method of this invention. This solvent removal can be effected by the usual vacuum stripping or evaporative techniques carried out at or below atmospheric pressure. It is advantageous to use vacuum removal of the solvent in order to raise the relative vapor pressure thereof.

The resulting solid pitch particles are then dissolved in a sufficient quantity of a pitch solubilizing solvent to dissolve at least 45 percent of the pitch based upon the total quantity of starting pitch. This dissolution can be accomplished at from the freezing point to the reflux temperature of the solvent.

The solvent useful for this dissolution can be the same or a different solvent from that used in the first extractive step. If the solvent is the same, it is obvious that a greater quantity of solvent will be necessary and/or a higher temperature will be required to carry out the dissolution at this point. If the solvents are different, the volume and temperature of dissolution are so chosen to provide a pitch of the proper softening range and physical characteristics. For example, if benzene is used as a solvent, a solvent-pitch ratio of 4:1 (V/W) is appropriate for the first extraction at room temperature, and a solvent-pitch ratio of 50:1 (V/W) at reflux temperature is useful for the second extraction to provide a final product having a softening range of 240°–260° C. from a 150° C. softening point starting pitch. The same effect can be accomplished by using a benzene solvent in 5:1 solvent-pitch ratio and a quinoline solvent in 10:1 solvent pitch ratio for the two extractive steps.

The next step in the purification process is the separation of the second-phase insoluble material, commonly called quinoline insolubles, from the pitch-solvent mixture. This separation is carried out by filtration, centrifugation, or similar separation technique.

The filtrate is then stripped of the solvent. The stripping operation is preferably carried out at less than atmospheric pressure in order to avoid heating the pitch to a temperature at which rearrangement and cracking can occur. Thus, for example a quinoline-pitch (10:1) mixture is heated for about 8.5 hours, ultimately attaining a temperature of 235° C. at 0.15 mm. (in.) in order to completely remove the quinoline therefrom.

Solvents useful for the dissolution steps of this invention include acetone, benzene, toluene, o, m, p-xylene, Tetralin, methyl ethyl ketone, quinoline, isoquinoline, indole, pyridine, quinoxaline, pyridine, pyrimidine, pyrazine, α-, and β-methylnaphthylene, dimethyl formamide, dimethyl acetamide, dimethylsulfoxide, dimethylsulfone, and the like, and mixtures thereof in appropriate concentrations to carry out the manipulative steps as required by this invention.

A more complete understanding of the process of this invention can be obtained by reference to the following examples which are illustrative only and not meant to limit the scope thereof which is fully expressed in the hereinafter appended claims.

EXAMPLE 1

A coal tar pitch with a softening point of about 187° C. (ring and ball - A.S.T.M. D–36) is ground to −100 mesh size. Four hundred grams of this pitch is triturated with 2 liters of benzene at room temperature for 10 minutes.

The suspension is filtered, and the filter cake washed with 300 ml. of hexane and dried in vacuo for 4 hours. A residue of 294 g. is obtained which is mixed with 2,940 g. of quinoline for 10 minutes at 60°–70°C. The suspension is filtered using 25 g. of diatomaceous earth as a filter aid.

The filter cake is washed with 400 ml. of quinoline and the quinoline is added to the previous filtrate. The combined filtrates are evaporated in vacuo to yield 195 g. of a pitch suitable for melt spinning. Softening point: 270°–280°C.

EXAMPLE 2

A coal tar pitch of similar origin to that of Example 1 (10 g.) is extracted by stirring with 100 ml. of quinoline at about room temperature for one hour. The mixture is filtered and the residue washed well with 10 ml. of quinoline. The filtrates are combined and the solvent removed therefrom by evaporation in vacuum.

The resulting residue is ground to −100 mesh and extracted by stirring into 4 volumes (W/V) of a mixture of benzenehexane (3:1).

The solvent is removed and the residue dried in a vacuum oven for four hours to yield a spinnable pitch. Softening point: 210°–240°C.

EXAMPLE 3

A polyvinyl chloride pitch of softening point 150°–160° C. is milled to −100 mesh and the resulting powder is extracted with 4 volumes (W/V) of a 10:1 (V/V) mixture of acetone-benzene at the freezing point of the solvent mixture. After stirring the mixture for one hour, the pitch is separated by decantation and the residue dried in vacuo. A second solvent mixture comprising pyridine-benzene, 20:1 (V/V) is added to the solid pitch powder. The mixture is refluxed for 12 hours and then filtered. The filtrate is evaporated to dryness resulting in a spinnable pitch of softening point over 250° C.

EXAMPLE 4

A 52° API light crude naphtha was subjected to catalytic cracking at high pressure in the presence of steam to produce ethylene, other low boiling gases and a resinous residue having the following properties:

Softening point (Ring and Ball), ° C.		45
Specific gravity (at 15°C.) 1.180 Conradson carbon	percent	36.5
Ash	do	0.02
Sulfur	do	.38
Benzene soluble	do	98.0

This residue has a dark brown-black color and a glossy resin-like appearance. In an ASTM (D–20) distillation, 44 percent by weight of the material distilled. An analysis of the overhead showed it to be a highly aromatic material containing substantial amounts of phenanthrene, anthracene, fluorene and various derivatives of these cyclic compounds.

A 100 g. lot of this resin is dissolved in 4 liters of quinoline and filtered through a pre-coat of 25 g. of activated carbon filter aid at 100° C. in a steam jacketed fine porosity metal filter. The quinoline is removed in vacuo. The resulting pitch is mixed with an equal volume of benzene and stirred in an indented flask at the reflux temperature of benzene for 4 hours. The pitch layer is separated by decantation of the benzene layer. A vacuum is pulled on the flask for about 1 hour to remove the last traces of benzene and the pitch is ready for melt spinning.

EXAMPLE 5

A gas-oil fraction is separated from the straight thermal distillation of a mid-Continent crude oil and is catalytically cracked in the presence of a zeolite catalyst at about 500° C. with the separation of gas and gasoline. A side stream of substantially the same boiling range as the gas-oil charging stock is separated and conducted into a second catalytic cracking zone. The side stream of cycle oil therefrom is heated to a temperature of 525° C. in a thermal cracking unit maintained at about 400 psi. The vapors are stripped and recovered for gas and gasoline and the high boiling aromatic cut having the following characteristics is used as starting material.

A.P.I. gravity −20	
Distillation range	
<235° C.	none
<270° C.	16%
<315° C.	34%
<355° C.	44%
Residue	56%

The above-defined starting material, 100 g. is triturated with 2.5 liters of a mixture of benzene-quinoline, 100:1 (V/V), at about 5° C. for 20 minutes. The pitch is separated by decantation of the benzene-quinoline solvent. The pitch is ground to −100 mesh and then added to another benzene-quinoline mixture, 2.5 liters of a 1:50 (V/V) solution at ambient room temperature. The solvent effects essentially complete solution. The solid particles are collected therefrom by adsorption on charcoal and centrifugation of the solids.

The solution is then evaporated to dryness to provide a spinnable pitch.

We claim:

1. A method for the preparation of a spinnable pitch which comprises
a. grinding a pitch into small particles;
b. contacting the particles with an essentially aromatic or equivalent solvent to dissolve a total of about 10 to 30 percent therefrom;
c. separating the solvent and the insoluble particles;
d. extracting the particles with a solubilizing solvent in sufficient quantity to dissolve at least 45 percent of the pitch based upon the original quantity of starting pitch;
e. filtering the resulting mixture and
f. evaporating the solvent from the resulting filtrate.

2. The process of claim 1 wherein the contacting step, b, is carried out at from about the freezing point of the solvent to about the softening point of the pitch in contact with the solvent.

3. The process of claim 1 wherein the extracting step, d, is carried out at from about the freezing point of the solvent to about the reflux temperature of the solvent.

4. A method for the preparation of a spinnable pitch which comprises
a. extracting the pitch with a solubilizing solvent in sufficient quantity to dissolve at least 45 percent of the pitch;
b. filtering the mixture;
c. evaporating the solvent from the resulting filtrate;
d. grinding the resulting pitch into small particles;
e. contacting the particles with an essentially aromatic or equivalent solvent to remove a total of about 10 to 30 percent based upon the original quantity of starting pitch therefrom;
f. separating the solvent and the particles.

5. The process of claim 4 wherein the contacting step is carried out at from about the freezing point of the solvent to about the softening point of the pitch in contact with the solvent.

6. The process of claim 4 wherein the extracting step is carried out at from about the freezing point of the solvent to about the reflux temperature of the solvent.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,668,110 Dated June 6, 1972

Inventor(s) Frederick L. Shea et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

On the cover sheet insert -- [73] Assignee

Great Lakes Carbon Corporation, New York, N. Y. --.

Signed and sealed this 12th day of December 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
* U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334.