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PROCESS FOR THE PRODUCTION OF CARBON FILAMENTS FROM COAL TAR PITCH

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ABSTRACT OF THE DISCLOSURE

Carbon filaments are made from specially treated high temperature coal tar pitch. The pitch is filtered, heat treated and its low molecular weight components are removed by distillation. The treated pitch is spun into filaments, the filaments partially oxidized and then carbonized under carefully regulated conditions to yield filamentary carbon having a tensile strength of more than 100,000 p.s.i. The filaments may be graphitized.

Carbon fibers have been produced from organic polymer fibers such as rayon or polyacrylonitrile by subjecting the latter to a regulated carbonization, preceded, in the case of fusible polymers, by a controlled oxidation to an infusible state. A difficulty with this type of approach has been the low yield of carbon available from synthetic polymers.

Satisfactory carbon fibers have also been made from molten decomposition products of synthetic polymeric materials such as polyvinylchloride, polyvinyl acetate, and from fusible carbon-yielding materials like blown asphalt and petroleum pitch. In this type of process, the fusible material is spun into fibers, oxidized and carbonized to yield carbon fibers possessing strengths of over 100,000 p.s.i. In some cases, it has been found necessary to condition the starting material by heat treatment to raise its molecular weight and render it more amenable to the further transformations just mentioned. In the case of coal tar pitch however, these measures have failed and the art does not provide any successful method for the satisfactory spinning of pitches of coal tar origin and for their subsequent conversion into useful carbon fibers having properties comparable to those possessed by carbon fibers from other raw materials.

It is an object of this invention to provide easily spinnable materials from coal tar pitches capable of being transformed into useful carbon fibers. It is a further object to provide a method by which said modified coal tar pitches can be oxidized and carbonized satisfactorily. Still another object is to provide from common industrial coal tar pitches carbon fibers with tensile strengths in the class of 100,000 p.s.i. and which also possess to a sufficient degree the other desirable properties generally associated with such refractory material.

SUMMARY OF THE PROCESS

These and other objects which shall become evident from the detailed description of the invention, have been accomplished by removing from a coal tar pitch substantially all of the material therein which is insoluble and remains as a second phase at the spinning temperature. Before or after this operation, the pitch is heat treated and distilled in order to increase its average molecular weight by polymerization and by removal of low molecular weight components formed or already present in the pitch. Various oxidizing, dehydrogenating and polymerizing agents may be employed in a number of manners to expedite this process. The treated pitch is then melted and spun into air, the resulting filament being stretched

and wound continuously in conventional textile manner. The pitch filament is oxidized in one or more stages in an oxidizing medium and then carbonized at a temperature in the vicinity of 1000° C. in an inert atmosphere. If desired, the resulting carbon filament may be graphitized by heating in an inert atmosphere at elevated temperatures.

DETAILED DESCRIPTION

The raw materials from which the fibers of the invention are spun consist of commercially available high temperature coal tar pitches having a ring-and-ball softening point (A.S.T.M. method) within the range of 70 to 250° C. Incidentally, all softening points in the text of this application are ring-and-ball softening points and all percentages are on a weight basis. Among the usable coal tar pitches, those preferred have a softening point within the range of 90 to 200° C.

A critical operation in the transformation process of the invention is the removal of the quinoline insolubles from the coal tar pitch selected. Quinoline insolubles represent material which is not soluble in the pitch at spinning temperature or, in other words, which forms an undesirable second phase. This removal is generally done before heat treating and distilling the pitch. This sequence of operations however is not binding, especially when a pitch of low quinoline insoluble content is employed. To accomplish the removal of the undesirable fraction, the pitch may be diluted in an appropriate solvent, filtered or centrifuged and recovered. The solvents usable for this purpose are generally speaking any aromatic liquid having a boiling point or range between about 200 and 400° C., provided that the major liquifiable portion of the coal tar pitch is soluble in it. Said liquid should also be removable from the filtered pitch solution at temperatures preferably not exceeding 300° C., either at atmospheric pressure or under reduced pressure. Examples of usable liquids which fit these specifications are light creosote oil, anthracene oil, phenanthrene, quinoline, highly aromatic petroleum fractions and the like.

The dilution of the pitch and the subsequent filtration can be carried out at any temperature within a range going from the softening point of the pitch to about 300° C. Proportions of solvents to pitch vary with the viscosity of the substrate at the temperatures selected. In general, a dilution of 1:1 at a temperature of about 200° C. has been found convenient. The diluted pitch is then filtered to remove the undissolved material. This may be accomplished in a number of manners with known equipment, provided of course that the foraminous member of this equipment can withstand the filtration conditions. Fritted glass and porous stainless steel septums having openings of about 10 microns in average diameter are satisfactory. The filtration process may be facilitated and improved in a conventional manner by additions of known filter aids to the pitch liquid. The number of actual filtrations and their timing may vary according to several factors such as viscosity of the pitch liquid, amount and nature of undissolved solids, temperature, pressure and the like. Suffice it to say here that at least one filtration is required for the purpose of this invention and that it may be carried out on liquid solvent diluted or undiluted pitch at any stage before the actual passage of the pitch through the filament-forming spinneret. After completion of the filtration, the solvent is removed by evaporation preferably under reduced pressure at about 150° C., in any event, at a temperature not exceeding 300° C. As mentioned previously, the separation of the undesirable second phase may be accomplished by centrifugation rather than filtration, although the latter technique is preferred in most instances.

The coal tar pitch to be used for spinning filaments is

heat treated and distilled to improve its molecular weight range. Either or both of these treatments may be carried out, as indicated earlier, before, after or between filtrations. The pitch is distilled at a temperature within the range of about 280 to 305° to remove its lower molecular weight components. This may be accomplished by any conventional method including distillation under reduced pressure, steam distillation and so on, using any conventional equipment such as a molecular still and the like, provided the temperature limits are respected. The pitch is heat soaked at similar temperatures for a period of about 10 to 100 hours or more under pressures which may range from less than one atmosphere to more than one atmosphere. The actual length of this heat treatment depends of course on the nature of the pitch components as well as on other factors. Polymerization can also be favored by incorporating within the pitch various oxidizing, dehydrogenating and polymerizing agents which may shorten the heat treatment or lower the operating temperature. Among suitable materials which may accomplish these ends are included organic and inorganic peroxides and high boiling nitro-aromatic compounds such as nitronaphthalene and 2,4-dinitrochlorobenzene, and the like. In any event, the heat treatment must be carried in such a manner and under such conditions, within the limits already described, that there is produced a spinnable pitch having a softening point or range within 230 and 320° C., and a quinoline insoluble content of less than 2%. Preferred pitches within these limits are those which soften between 240 and 260° C. and contain no second phase at spinning temperatures or below.

The heat treated coal tar pitch prepared in the manner described is then spun into a continuous filament through a nozzle or spinneret with an internal diameter appropriate for the thickness of filament required. For spinning, the pitch is metled at a temperature between its melting point and about 300° C. and the melt is extruded through the spinneret's orifice by sufficient nitrogen pressure to achieve a satisfactory rate or by other conventional means such as a metering pump, a piston and the like. The actual pressure and temperature used depend on the properties of the heat treated pitch used as well as upon each other. In this respect, it has been found that a pitch of the type prescribed by this invention can be spun satisfactorily under a driving N_2 pressure of about 80 p.s.i. through a perforated stainless steel spectum with pores averaging 10 microns or less and a spinneret orifice of 1.5 mm. in length and 0.3 mm. in diameter. More than one orifice may of course be employed. The filament produced emerges in air and is stretched and taken up on a conventional textile winder at a fixed speed, e.g. at 250 to 300 meters per minute. Filaments with diameters ranging from about 5 microns and higher can thus be produced.

Extrusion of the filament at high temperature initiates an oxidation process which may be intensified by passing the filament through an oxidizing atmosphere for a length of time sufficient to create the infusibility required by the subsequent carbonization treatment. Suitable oxidizing media for this purpose include air; ozone in air; oxygen blended with air, flue gases or inert gases; vapors or mists of nitroaromatic compounds such as nitrobenzene, nitrophenol, alpha-nitronaphthalene, nitrotoluene, nitrochlorobenzene and the like; oxidizing gases such as sulfur dioxide, sulfur trioxide, nitric oxide and the like. Alternately, the filament may be cooled to a temperature below its fusing point and then passed through liquid oxidizing baths of the above mentioned nitroaromatics or of other oxidizing liquids such as nitric acid, sulfuric acid, chromic acid, permanganate solutions and the like.

These various oxidizing treatments may be carried out in a continuous manner on the filament emerging from the spinning machine or they may be applied to batches of filament wound into packages. In such an eventuality, the support of the filament package must be of such nature and/or construction that it yields or collapses as the

wound filament contracts during the oxidation process. Paper cylinders have been found useful in this function.

The oxidation of filament wound in packages must follow a fairly critical heating regime if the superimposed and adjacent loops of filament are not to fuse together. This regime will naturally vary with the pitch, its previous oxidation history and the type and quality of additive present, if any. The best heating rates and soaking temperatures for a given material are naturally difficult to determine since the fusion temperature of the pitch changes as the oxidation proceeds. Nevertheless, it has been established that a heat treated pitch of the type preferred, as described earlier, will yield filaments that are successfully oxidized by raising the temperature to 100° C. in less than 15 minutes, a non-critical step; holding the filament at 100° for about 20 hours; raising the temperatures from 100 to 195° C., at a preferred rate of about 5° C./hour; holding the filament at the later temperature for a period within the range of about 60 to about 120 hours, the upper part of that range being preferred. It should be noted that with certain materials temperature increase rates of up to 10° C./hour may be tolerated. In any event, the temperature at any time during the oxidation treatment should preferably be not higher than 10° C. below the softening point of the pitch at the given time. This batch type oxidation is best carried out in a circulating oven through which passes a constant flow of air or oxygen containing gas, both fresh and recycle, pre-heated at the desired temperature.

The oxidized filament may then be cooled to room temperature or subjected immediately to carbonization. If cooling is elected, it should be gradual, the 195 to 100° C. step being accomplished at about the same rate as the reverse step previously carried out, with the last 100° to room temperature adjustment taking about three hours.

The oxidized pitch filament is then converted to a carbon filament. This is accomplished in an oven or kiln provided with means for allowing sweeping of the reaction area with an inert gas, e.g. nitrogen scoured through hot coke. When wound filament in packages is treated, the packages are placed in a sagger and, as the inert gas is allowed to sweep the package for example from bottom to top, the temperature of the kiln is raised according to the following typical cycle: from 30 to 100° C., when necessary, at the rate of 10°/hour; from 100 to 500° C. at 5°/hour and from 500 to 1100° C. at 10°/hour. Cooling to room temperature also should be gradual, e.g. from 1100° to 30° C. in about 36 hours. As the 100 to 500° C. temperature range is the most critical in the carbonization process, special care need be exerted in controlling the heating rate through that range. As to the top carbonization temperature, it must be noted that useful carbon fibers may be produced from 700° C. for amorphous carbon filaments to as high as 2800+° C. if graphitic filaments are desired. Heating rates and holding times are no longer critical about 1100° C.

A graphite filament may be conveniently prepared by heating a carbon filament for about one hour in argon at above 1500° C.

Carbon filaments (1100° C.) of conventional textile lengths may be produced from coal tar pitch by the method just described, having a tensile strength of 80,000 to 130,000 p.s.i., a modulus of elasticity within the range of 4.5 to 5.2×10^6 p.s.i., a volume resistivity in μohm-inch of 1200 to 1600 and an apparent density of about 1.65 g./cc. Such filaments, and their graphitic counterparts, are eminently suited as substrate in vapor phase depositions such as manufacture of boron filaments, heat resistant reinforcement in fiber-matrix composites, as well as in other similar applications where filamentary carbon is conventionally and advantageously employed.

A better understanding of the process of the invention may be obtained from the following example. This embodiment is provided for illustrative purposes only and

must not be construed as limiting the invention beyond the scope of the claims that follow this specification.

EXAMPLE

A coal tar pitch having a softening point of 187° C., Allied Chemicals Company's CP–275 grade 350, was dissolved at 180° C. in as equal weight of a light creosote oil fraction having a boiling range of 270 to 315° C. for 88% of its content. The solution was filtered with 10% Dicalite "Speedplus"® diatomaceous earth through a coarse 40 to 60μ fritted glass plate, then through a 4.5 to 5.5μ fritted glass plate. The filtrate was stripped to 130° C. under a pressure of 3 mm. Hg. The soluble pitch fraction was heat treated for 20 hours at 280 to 305° C. pot temperature, under a —50° C. condenser in which about 17% of low melting solid fraction was collected at 2 mm. Hg. The heat treated soluble pitch remaining after this treatment had a softening point of approximately 256° C.

The modified coal tar pitch just described was spun through a spinneret having an orifice of 1.5 mm. in length and a diameter of 0.3 mm. The molten pitch at 287° C. was driven through the spinneret by a nitrogen pressure of 110 p.s.i. The resulting pitch filament had a final diameter of about 30 microns, when stretched and taken up on a paper cylinder at the rate of 256 meters per minute.

The wound filament paper packages were then hung on graphite supports in an oven through which fresh and recycled air in a ratio of about 1:1 was constantly circulated while the temperature was raised and lowered in the following manner:

	Hours
40 to 100° C.	0.25
100° C.	24.0
100° to 196° C., 3.5° C./hour	28.0
196° C.	96.0
196° to 100° C., 3.5° C./hour	28.0
100° to 40° C.	2.0

The total residence in the oxidizing oven was thus 178.25 hours.

The oxidized filament packages were then placed in a stainless steel sagger on the same type of graphite hangers as used in the oxidation step, and subjected to the following time-temperature regime while being constantly swept by nitrogen previously scoured through coke at process temperature:

	Hours
40° to 100° C., 10°/hour	6
100° to 500° C., 5°/hour	80
500° to 1100 C., 10°/hour	60
1100° to ambient temperature	36

The resulting carbon monofilament was tested on an Instron tester at a crosshead speed of 0.2 in./min., using 1" gauge lengths. It was found to possess a tensile strength of 127,400 p.s.i., an elongation at break of 2% and a modulus of elasticity of 5.1×10^6 p.s.i.—all these measurements being averages of at least 6 independent determinations.

The carbon monofilament had an average diameter of 25 microns and, as measured on 0.125 inch long samples, a volume resistivity of 1419 μohm-inch with a variation of $\pm 5.0\%$.

There was thus produced by the method of this invention a carbon filament from coal tar pitch, that has excellent mechanical and electrical properties as compared to what was heretofore taught by the art. It is evident that these properties may be maximized by the man skilled in the art while remaining within the scope of the invention as described in the foregoing specification and defined by the following claims.

What is claimed is:

1. A method for producing carbon filaments from a coal tar pitch having a softening point within the range of 70° to 250° C. which comprises:

(a) filtering the pitch at a temperature less than about 300° C. to remove substantially all of the second phase quinoline insoluble material,

(b) heating the filtered pitch within the range of 280 to 305° C. for about 10 to about 100 hours to produce a product having less than 2% by weight of quinoline insolubles and a softening point within the range of 230° to 260° C.,

(c) removing the volatile materials during at least a portion of step (b);

(d) melting the product from (c) by heating it to a temperature within the range of above its softening point to about 300° C. and extruding and stretching it into a continuous filament,

(e) contacting the filament from (d) with an oxidizing gas at a temperature of from about 100° C. to not higher than 10° C. below the softening point of the product from step (b), and

(f) carbonizing the filament from step (e) by heating it in an inert atmosphere through the temperature range of 100° to 500° C. at a rate not greater than 5° C. per hour and then through the range of 500° to 1100° C. at a rate not greater than 10° C. per hour.

2. The process of claim **1** wherein the pitch is diluted before filtration with an aromatic solvent boiling above 200° C. and removable after filtration at a temperature not exceeding about 300° C.

3. The process of claim **2** wherein the solvent is a light creosote oil fraction of coal tar distillation.

4. The process of claim **1** wherein the heating of step (b) is done under reduced pressure at a temperature ranging from about 280° to about 300° C.

5. The process of claim **1** wherein the pitch filaments from (d) are oxidized in air for a period of about 60 to about 120 hours at a temperature of about 10° C. below the melting point of the preconditioned pitch and wherein the heating in (f) is carried out at a rate of about 3 to about 10° C. per hour.

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