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[54] **METHOD FOR PRODUCING CARBON FIBERS**

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[57] **ABSTRACT**

A carbon fiber is prepared by forming a melt of a mixture of novolac and a pyrogenous residue, fiberizing the melt to form a fusible fiber, curing the fusible fiber by reacting with an aldehyde to render the fiber infusible, and carbonizing the infusible fiber to produce a carbon fiber.

7 Claims, No Drawings

METHOD FOR PRODUCING CARBON FIBERS

BACKGROUND OF THE INVENTION

The present invention relates to a process for the production of carbon fibers.

Methods of the prior art for producing carbon fibers include carbonizing filaments of organic substances such as cellulose filaments and acrylonitirle filaments while the filaments are retained in their original form. These methods require starting materials of high cost and are often accompanied by certain difficulties such as the susceptibility of the filaments to loss of their original form and insufficient mechanical strength of the carbon filaments. These materials have low yields of carbonization leading to higher costs of carbon filaments. Further, the low carbon yields necessitate precise control of carbonization cycles so that the fiber properties are not adversely affected due to the considerable loss of weight.

A method is disclosed in U.S. Pat. No. 3,595,946 to Joo et al. wherein a treated pitch is spun into filaments and the filaments are oxidized prior to carbonization. The oxidation process renders the fibers sufficiently infusible to permit a subsequent processing. However, this process requires a complex pretreating of the pitch and subsequent oxidizing of the fusible fiber with ozone or air for a long period of time to form an infusible sheath on the fiber. Further, the oxidation treatment for rendering the spun fiber infusible requires precise control of temperature cycles and process conditions so as to make the process extremely complex and tedious.

Heretofore, the preparation of fibers from low cost pyrogenous residues has required an uneconomical time curing process. A simpler and more economical method for utilizing these residues in fiber formation is therefore desirable.

SUMMARY OF THE INVENTION

According to the process of the present invention, a carbon fiber is prepared by forming a melt of a mixture of a novolac and pyrogenous residue, fiberizing the melt to form a fusible fiber, curing said fusible fiber by reacting with an aldehyde to render the fiber infusible, and carbonizing said infusible fiber to produce a carbon fiber.

The process of the present invention permits those pitches which are generally available and most economical to be used as a starting material. The novolac which is added to the pitch improves the spinnability of the material in the molten state. Furthermore, a novolac facilitates the preparation of an infusible fiber which can be carbonized. The spun fiber is rendered infusible by a short curing process. Thus, the process of the present invention has the dual advantage of starting with an inexpensive pitch material and forming the material into a carbonized fiber within a relatively short period of time.

DETAILED DESCRIPTION OF THE INVENTION

The starting pyrogenous residues that can be used in the process of the present invention include a variety of pitches such as coal tar pitches, pitches obtained by distillation of oils, petroleum pitches, pyrogenous asphalts, and a variety of pitch-like substances produced as by-products of various industrial processes such as distillation residues. Preferably, the starting pyrogenous residue as a softening point of about 80° to about 200°C, more preferably from about 100° to about 150°C. Preferably, the pyrogenous residue has a carbon to hydrogen ratio based on weight percent from about 18 to about 25. The content of aromatic and unsaturated components varies depending on the source of the raw material pyrogenous residue.

Preferably, pyrogenous residues used as starting materials have a beta-resin content greater than about 5 percent and preferably greater than 10 percent by weight. The beta-resin is the benzene insoluble content of the pyrogenous residue minus the quinoline insoluble content. In making the determination, there are other solvents, such as toluene, which can be substituted for benzene and pyridine which can be substituted for quinoline. The beta-resin portion of the pyrogenous residue is believed to enhance the binding and adhesive qualities thereof. It is believed that a suitable amount of beta-resin contributes to rendering the fusible fiber infusible by a short curing process. The upper limit of the weight percent of beta-resin in the starting pyrogenous residue is not critical but is generally limited by the type of pitch used and process conditions. Most commercially available pitches have a beta-resin content less than about 30 percent but pitches with a beta-resin content higher than 45 percent may be used in the present invention.

Generally, commercially available coal tar pitch has a benzene insoluble content of about 20 to about 50 percent by weight and a quinoline insoluble content of about 10 to about 20 percent by weight with a resulting beta-resin content in the range of about 10 to about 30 percent. These pitches are suited for use as a starting material in the process of the present invention without further modification. Petroleum pitches and pyrogenous asphalts often have beta-resin contents less than about 5 percent. This is generally due to a low percentage of benzene insolubles which is generally less than about 10 percent. In such a case, while the fusible fiber of pyrogenous residue and novolac can be rendered infusible by reacting with formaldehyde, the curing process is comparatively slow. Alternatively, it is possible to upgrade the pitch by increasing the beta-resin content. Such upgrading can be done by reacting the pitch or asphalt with an aldehyde and phenolic compound in the presence of an acid catalyst at a temperature sufficiently high to effect condensation between the pitch or asphalt, aldehyde and phenolic compound. Such a method is described in British specification No. 1,080,866 and U.S. Pat. No. 3,301,803 which are incorporated into the present case by reference. The amount of aldehyde and phenolic compound that is employed can vary widely depending on the degree of upgrading necessary. The reaction is carried out at a temperature from about 150° to about 600°F for a suitable period of time.

The amount of quinoline insolubles in the starting pyrogenous residue should be less than about 20 percent by weight and preferably less than about 10 percent. As the percentage of quinoline insolubles in the starting pyrogenous residue is decreased, the ease of fiberization of the melt is increased and the uniformity of the fibers is enhanced. The most preferred starting pyrogenous residue contains no or a very low percentage of quinoline insoluble. The quinoline insolubles represent material which is not soluble in the pyrogenous residue at the spinning temperature and which forms an unde-

sirable second phase. Removal of the quinoline insolubles can be accomplished by diluting the pitch in an appropriate solvent and filtering or centrifuging to remove the insolubles. Such a method is described in U.S. Pat. No. 3,595,946.

A wide variety of novolac resins may be used as starting materials in the process of the present invention. The term novolac refers to a condensation product of the phenolic compound with formaldehyde, the condensation being carried out in the presence of a catalyst to form a novolac resin wherein there are virtually no methylol groups such as present in resoles and wherein the molecules of the phenolic compounds are linked together by a methylene group. The phenolic compound may be phenol, or phenol wherein one or more of the non-hydroxylic hydrogens are replaced by any of various substituents attached to the benzene ring, a few examples of which are the cresoles, phenyl phenols, 3,5-dialkylphenols, chlorophenols, resorcinol, hydroquinone, chloroglucinol and the like. The phenolic compound may instead be naphthyl or hydroxyphenanthrene or another hydroxyl derivative of a compound having a condensed ring system.

For purposes of the present invention, any fusible novolac which is capable of further polymerization with a suitable aldehyde may be employed for the production of fibers. Stated another way, the novolac molecules must have two or more available sites for further polymerization. Apart from this limitation, any novolac might be employed, including modified novolacs, i.e., those in which a non-phenolic compound is also included in the molecule, such as the diphenyl oxide or bisphenol-A modified phenol formaldehyde novolac. Mixtures of novolacs may be employed or novolacs containing more than one species of phenolic compounds may be employed.

Novolacs generally have a number-average molecular weight in the range from about 500 to about 1200, although an exceptional case in which the molecular weight may be as low as 300 or as high as 2000 or more may occur. Unmodified phenol formaldehyde novolacs usually have a number-average weight in the range from about 500 to about 900, most of the commercially available materials falling within this range. Preferably, novolacs with a molecular weight from about 500 to about 1200 are employed in the method of the present invention. When a very low molecular weight novolac is used, the temperature at which such novolacs soften and become tacky is usually comparatively low. Therefore, it is necessary to cure the fiberized novolac at a very low temperature to avoid adherence and/or deformation of the fibers. It is usually undesirable to employ such low curing temperatures since the curing rate increases dramatically with the increase in temperature and low curing entails the practical disadvantage of a prolonged curing cycle. It is generally preferred to employ a novolac having a moderately high molecular weight for the type of novolac under consideration to permit curing in a reasonable time without adherence and/or deformation but to avoid the extreme upper end of the molecular weight range to minimize problems in fiberizing due to gelling.

A mixture of pyrogenous residue and novolac may be formed by any convenient technique such as dry blending or melting the pyrogenous residue and novolac by heating together to form a homogenous mixture. Mixtures containing from about 5 to about 40 percent by weight novolac may be used for preparing the fibers of the present invention. Since the pyrogenous residue is the most economically available component of the mixture, it is preferred to employ less than about 35 percent novolac by weight. It is preferable that the novolac content be at least about 10 percent and more preferably that it be at least about 25 percent in the mixture so that the spinnability of the fiber is enhanced and the curing time can be sufficiently reduced. Preferably, the mixture consists essentially of the pyrogenous residue and novolac.

The fiberization may be performed by any convenient method such as drawing a continuous filament downwardly from an orifice in the bottom of the vessel containing a molten mixture of pitch and novolac. The filament is wound and collected on a revolving take-up spool mounted below the orifice. The take-up spool also serves to attenuate the filament as it is drawn from the orifice before it cools and solidifies upon contacting the atmosphere between the orifice and the spool. The melt can also be formed into short staple fibers by methods known in the prior art such as blowing the melt through a fiberizing nozzle and collecting the cooled fibers for blowing a thin stream of melt into the path of a hot blast of gas. These methods produce a staple consisting of a multiplicity of fusible uncured pitch-novolac fibers of variable length and diameter. The diameter of the fibers can vary from 0.1 micron to about 300 microns.

When producing a continuous filament having a uniform diameter by melt spinning, preferably the fibers have diameters from about 10 to about 30 microns. The filament diameter depends primarily upon two factors, the drawing rate and the flow rate of the melt through the orifice. The fiber diameter decreases as the drawing is increased and increases as the flow rate of the melt is increased. The flow rate of the melt depends primarily upon the diameter and length of the orifice and the viscosity of the melt, increasing as the orifice diameter is increased, decreasing as the length of the orifice is increased, and increasing as the viscosity of the melt is decreased. An increase of flow rate may also be effected, if desired, by applying pressure to the melt to force it through the orifice. Curing of the fusible fiber to render it infusible is effected by heating the uncured fusible fiber in a liquid or gaseous formaldehyde environment. It appears that the curing mechanism involves the diffusion of the formaldehyde into the fiber and reaction of the novolac and formaldehyde to bring about polymerization of the novolac and pyrogenous residue mixture.

It is preferred to effect curing by heating the uncured fusible fibers in an environment containing paraformaldehyde in the presence of a catalyst. The environment may be gaseous, but is preferably liquid as in a solution of the catalyst and formaldehyde. Liquid is preferred because of the greater rapidity of heat and material transport to the fibers, expecially the fibers in the interior portions of a bundle of fibers being cured, and also because higher concentrations of formaldehyde and catalysts may be achieved by employing a solution thereof. Any of a wide variety of acids or bases may be used as the catalysts, any of the mineral acids or bases such as hydrochloric, sulfuric, phosphoric, ammonia hydroxide, potassium hydroxide, sodium hydroxide and organic acids or bases such as oxalic acid, or dimethylamine.

When a solution is employed for the curing step, water is the choice of solvent although other liquids may be employed provided that they do not adversely affect the fiber and are capable of dissolving the formaldehyde in a solution containing the catalyst. Preferably, the solution contains from about 12 to about 18 percent formaldehyde. When an acid catalyst is used, it is preferred that the solution contain from about 12 to about 18 percent acid, and when a base catalyst is used, from about 1 to about 10 percent base. Lower concentrations of catalysts or formaldehyde in the solution generally require longer curing times. Higher concentrations of formaldehyde or catalysts do not appear to offer any advantage.

When curing is carried out in a gaseous environment, any gaseous catalyst such as hydrogen bromide, hydrogen chloride or ammonia may be employed. The formaldehyde may conveniently be generated by heating paraformaldehyde. The gaseous atmosphere may contain as little as about 10 percent formaldehyde up to as much as 99 percent, by volume, and from about 1 percent to about 90 percent, by volume, of the acid. If desired, the atmosphere may also contain a diluent such as nitrogen or other inert gas, but air should be excluded to minimize the possibility of side reactions taking place.

In either a gaseous or liquid environment, the rate of curing increases with increasing temperature. It is possible to cure the pitch-novolac fibers at room temperature (25°C) but is highly impractical to do so because of the time required. In the interest of minimizing the curing time, it is preferred to cure the fibers at the highest temperature at which adherence and/or deformation of these fibers does not occur. In general, the lower the molecular weight of the mixed resin, the lower the temperature at which these occur. Therefore, it is usually preferred not to use extremely low molecular weight resins, thereby avoiding the need for low curing temperatures and the attendent slow curing rates. It is usually desirable to carry out the curing cycle at gradually increasing temperatures. Initially, a temperature is employed at which adherence and/or deformation does not occur. At this stage, the outer portion of the fiber begins to cure, forming a shell, and thereupon, the temperature may be raised as necessary to complete the cure, the shell eliminating problems due to fusion which might otherwise occur.

The curing time must be sufficiently long to render the uncured fiber infusible. Once such infusibility has been achieved, further curing is unnecessary for purposes of this invention. At a temperature of 80°C, the time is about 10 hours, while at a temperature of about 100°C, the time is about 3 hours. It is generally preferred to carry out the curing by employing an initial room temperature and increasing the temperature to a final curing temperature of about 80° to about 100°C over a period of from about 1 to 3 hours and maintaining the temperature of a final curing temperature from a residence time of about 2 to about 4 hours for a total curing time of from about 3 to about 10 hours. Although the curing step renders the fiber infusible, an additional step of heating or oxidizing the cured fiber can be performed to further produce a non-smoking fiber. It is believed that the additional step promotes the formation of cross links whereby a highly cross-linked polymeric material of insoluble and unmeltable characteristics is further produced. The infusible fiber, after curing by reacting with an aldehyde, visibly smokes when subjected to a flame. The smoking is a volitilization of a small and uncured portion of the pyrogenous residue in the fiber. Non-smoking means that no visible smoke is present when the fiber is subjected to a flame or high temperature.

A carbonized fiber is produced from the infusible fiber by heating the fiber in a non-oxidizing atmosphere to a temperature of about 600° to about 1500°C. As the non-oxidizing atmosphere, there can be used inert gases such as nitrogen, helium, argon or even a vacuum, e.g., 0.001 mm. Also, there can be employed reducing gases such as hydrogen. The infusible fiber is preferably heated from an initial temperature, preferably about room temperature (25°C), to a final temperature within the range of about 600° to about 1500° C at a rate of about 10° to about 200°C per hour, preferably 25° to 100°C per hour. Preferably, the final temperature is within the range of about 700° to about 900°C.

The mechanical properties of carbonized fibers vary with fiber diameter, and the tensile strength and break elongation both increase markedly with increasing diameter. Considering the carbonized fiber with a diameter of 20 to 25 microns, typical properties would be: tensile strength, 50,000 to 80,000 psi; elastic modulus, 5×10^6 psi; and break elongation, 1 to 2 percent. Carbonization of the infusible fibers results in high carbon yields. When the liquid cured fiber is carbonized, carbon yields in the range of 65 to 75 percent is observed. Further, when the liquid cured infusible fiber is heated in air to 200°C at 10°C per hour and then heated to 800°C in nitrogen at 100°C per hour, carbon yields in the range of 70 to 75 percent are observed. Carbon yields of this magnitude are unexpected because the yields are higher than those normally expected from either of the raw materials themselves. An associated and yet unique and novel result is the exceptional dimensional stability of the fiber during carbonization. The infusible fiber showed an average shrinkage of only a few percent and again the shrinkage is lower than that expected from bodies prepared from either of the raw materials.

The invention will further be described partly with reference to the following examples which are intended to illustrate, and not limit, the scope of the invention.

EXAMPLE 1

A starting coal tar pitch (Allied Chemicals Company) has a softening point of 125°C, a beta-resin content of 22 percent, and a quinoline insoluble content of 13.6 percent. The pitch was mixed with a novolac resin (Varcum) having a molecular weight of about 800 to 1000 in the proportion of 70 percent by weight of pitch to 30 percent by weight of resin in the final mixture. The novolac and pitch were heated together to 190°C to form a homogenous mixture and the resulting mixture was poured into a fiberization vessel. The vessel was a cylinder having an orifice at the bottom and a plunger at the top for forcing liquid through the orifice. The vessel was mounted on the fiberization equipment which included a spool attached to the shaft of a variable speed electric motor mounted beneath the vessel for gathering the fibers. The vessel was surrounded by an electrical heating coil connected to an adjustable source of electricity whereby a controlled amount of heat was imparted to the vessel and its contents. The fibers were spun through the orifice which was about

1.5 mm in length and had a diameter of about 0.3 mm. The vessel containing the mixture of resin was maintained at a temperature of about 120°C while the bottom portion with the orifice was maintained at about 150°C. The mixture of pitch and novolac was driven through the orifice by a ram at a pressure of about 110 psi. The resulting mixed pitch-novolac filament had an average diameter of about 15 to 25 microns and was taken up on a graphite cylindrical cone at the rate of 500 rpm. The fiber bundle obtained was cured by hanging the graphite cone containing the fiber on a graphite support and immersing it in a curing solution. The solution was prepared by mixing equal portions of an aqueous solution containing about an 18 percent concentration of hydrochloric acid and paraformaldehyde, respectively. The curing solution with the graphite cone containing the fiber immersed therein was heated from room temperature to 100°C by increasing the temperature from 25° to 50°C over a period of 1 hour, increasing the temperature from 50° to 100°C over a period of half hour and maintaining the temperature at 100°C for 4 hours for a total residence time of about 6 hours. The resulting cured infusible fibers were then placed in a graphite container and heated in an atmosphere of nitrogen at 100°C per hour to a temperature of 800°C from room temperature (25°C). The resulting carbonized monofilament was tested on an Instron tester at a cross head speed of 0.2 inch per minute using a 1.0 inch gauge length. The fibers were found to possess an average tensile strength of 80,000 psi and a modulus of elasticity of 5×10^6 psi. These latter measurements are averages of at least ten independent determinations. The carbon monofilament had an average diameter of 20 to 25 microns. As measured on 0.125 inch long samples, the filaments had a volume resistivity of about 0.1400 micro ohms inch with a variation of 5 percent. During carbonization to 800°C, a carbon yield of 65 to 70 percent was observed. The fibers were exceptionally dimensionally stable during carbonization. Therefore, high yields of carbon fibers were obtained. Because of the high yield, the fibers showed on an average a shrinkage of only a few percent and this is lower than that normally expected from either of the raw materials.

EXAMPLE 2

A mixture of pitch and novolac resin prepared according to the procedure of Example 1 was poured into a fiberization vessel equipped with a nozzle. The nozzle was connected to a source of air pressure for forcing a mixture of pitch-novolac in air through the nozzle. In this manner, short staple fibers or blown fibers were collected on a plate after being cooled by falling through the air. The nozzle was maintained at about 250°C and the air pressure used was about 20 psi. The fibers collected in this manner were cured by placing in a graphite container to form a mat and curing in a liquid state in a manner similar to Example 1. The average diameter of the cured fiber was about 2 microns. The resulting fibers were carbonized in a nitrogen atmosphere in a manner similar to the procedure of Example 1. Again, as noted in Example 1, a high carbon yield of 65 to 70 percent was observed for these fibers during carbonization to 800°C.

EXAMPLE 3

The cured fibers of Example 1 or Example 2 were placed in separate graphite containers and each container was heated in air at a heating rate of 10° to 50°C per hour to 200° to 250°C from room temperature. The fibers were maintained at this temperature for 5 minutes to 2 hours. It is believed that this step of heating the fibers in air leads to oxidation which promotes the formation of cross links in the material. The air oxidized fibers were then heated in an atmosphere of nitrogen to 800°C at 100°C per hour to obtain a carbon fiber. The oxidation treatment of the fibers results in a high carbon yield. A carbon yield of 70 to 75 percent was observed during the carbonization of the air cured (air oxidized) fibers. This is indeed an unexpected result because the yield is about 10 percent higher than the yield observed during the carbonization of the liquid cured fibers and much higher than the yield expected from either of the raw materials. An associated and yet unexpected result is the extremely small dimensional change observed during carbonization of these fibers because of the high yield.

EXAMPLE 4

The cured fibers of Example 1 or Example 2 were placed in a graphite container and heated in an oven in nitrogen at a heating rate of 10° to 50°C per hour to 200° to 300°C from room temperature. The fibers were maintained at this temperature for 5 minutes to 2 hours. It is believed that this slow heating of fibers at these temperature ranges promotes the cross linking of the material. The fibers were then heated at 100°C per hour to 800°C to obtain a carbon fiber. An unexpected and novel result of the slow heating rate to 200° to 300°C was the high carbon yield. A carbon yield of 65 to 70 percent was observed during the carbonization of the fibers and this is about 5 percent higher than the yield observed during the carbonization of the fibers in Examples 1 and 2 and much higher than the yield expected from either of the raw materials. An associated and yet unexpected result is the extremely small dimensional change and excellent physical properties observed during the carbonization of these fibers because of the high carbon yield.

While the invention has been described with reference to certain examples and preferred embodiments, it is to be understood that various changes and modifications may be made by those skilled in the art without departing from the broad spirit and scope of the present invention.

What is claimed is:

1. A process for producing a carbon fiber comprising:

a. forming a melt of a mixture of a fusible novolac capable of further polymerization and a pyrogenous residue having a beta-resin content of from 5 to 45 percent;

b. fiberizing the melt to form a fusible fiber;

c. curing said fusible fiber by reacting with an aldehyde to render the fiber infusible; and

d. carbonizing said infusible fiber by heating in a non-oxidizing atmosphere to a temperature of from about 600° to about 1500°C.

2. A process according to claim **1** wherein said heating is at the rate of from about 25° to about 100°C per hour.

3. A process according to claim **2** wherein said pyrogenous residue has a quinoline insoluble content of less than about 20 percent by weight.

4. A process according to claim 2 wherein said melt comprises less than about 40 percent by weight novolac.

5. A process according to claim 2 wherein said melt comprises about 5 to about 35 percent by weight novolac.

6. A process according to claim 2 wherein said novolac has a molecular weight from about 300 to about 2000.

7. A process according to claim 2 wherein said novolac is a phenol-formaldehyde novolac.

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