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PROCESS FOR PREPARING BINDER PITCHES

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ABSTRACT OF THE DISCLOSURE

A process for the production of a petroleum-derived electrode binder pitch which comprises non-catalytically thermally cracking at a temperature of 1350 to 1550° F. a wide boiling range naturally-occurring petroleum condensate having an initial boiling point within the range of 20 to 150° F., at least 30% by weight boiling below 400° F. and a final boiling point in excess of 700° F., said condensate having an A.P.I. gravity of no less than 40 to 45 and containing 55 to 70% by weight paraffins, 20 to 30% by weight naphthenic hydrocarbons and 4 to 15% by weight aromatic hydrocarbons, under conditions such that the conversion of the petroleum condensate to C_3 and lighter hydrocarbons is greater than 45%, separating from the cracked products of said thermal cracking substantially all materials boiling below 500 to 575° F. to thereby produce a high-boiling cracked residue, subjecting said high-boiling cracked residue to a thermal soak at a temperature of 600 to 1000° F. and recovering a heavy aromatic oil as an overhead fraction from said thermal soak and a thermal residue as a bottoms fraction from said thermal soak, said thermal residue having a softening point of 185 to 215° F., a carbon to hydrogen atomic ratio of greater than 1.5 and a sulfur content of less than 0.5% by weight and possessing the properties of an electrode binder pitch.

BACKGROUND OF THE INVENTION

This application is a continuation-in-part of application Ser. No. 477,960 filed Aug. 6, 1965, now abandoned.

The present invention relates to a process for preparing electrode binder pitches. More particularly, the present invention relates to a process for the preparation of petroleum-derived carbonaceous materials useful as binders in the production of carbon electrodes. The present invention further relates to a petroleum-derived composition useful as a binding material for carbon electrodes.

Calcined coke, either of petroleum or coal origin, is generally used as the starting material in the production of carbon electrodes. This calcined coke has no natural adhesiveness and, therefore, must be bound into the desired molded shape by means of a binding material. In preparing the carbon electrode, the binder material generally is first mixed with the coke. In preparing pre-baked electrodes, this mixture is then formed into the desired shape and baked to carbonize the binding material, while in preparing Soderberg electrodes, the mixture of coke and binding material is usually briquetted for future use.

The binding material used in the preparation of carbon electrodes should be relatively stable material of uniform consistency and quality and should be substantially free of contaminants. The binder material should be sufficiently fluid at the temperatures at which it is mixed with the coke to completely wet and penetrate the coke. In addition, the binder material should have a relatively high content of benzene insoluble resinous materials which yield coke when carbonized at relatively low temperatures.

In the past, coal tar pitch has been used almost exclusively as binding material for carbon electrodes. Recently, however, some petroleum-derived materials have been found to possess some utility as binders for carbon electrodes. These petroleum-derived materials have been obtained by such methods as processing selected fractions through several steps including cracking and heat treating followed by blending the final product of such processing with other materials. In addition, the selected fractions from which these petroleum-derived materials are obtained are rather narrowly limited and as such more difficult and costly to obtain which, of course, increases the cost of producing the petroleum-derived binder. Another method which has been proposed for producing a petroleum-derived pitch suitable for electrode binders is that of thermally cracking a selected high boiling fraction obtained by catalytically cracking a particular hydrocarbon fraction, the residue of the thermal cracking then being heat soaked at high temperatures and at elevated pressures. Such a method is somewhat costly in requiring the two cracking steps plus all of the intermediate steps associated therewith.

It is an object of the present invention to provide a process for the preparation of a binder pitch for carbon electrodes. Another object of the present invention is to provide a process for the preparation of a petroleum-derived pitch suitable for use as a binder in carbon electrodes. It is also an object of the present invention to provide a new and novel composition derived from petroleum, said composition having particular utility as a binding material in carbon electrodes. Additional objects will become apparent from the following description of the invention herein disclosed.

SUMMARY OF THE INVENTION

In fulfillment of these and other objects, it has been found that a composition particularly suitable for use as a binding material in the manufacture of carbon electrodes is produced by a process which comprises non-catalytically thermally cracking at a temperature of 1350 to 1550° F. a wide boiling range naturally-occurring petroleum condensate having an initial boiling point within the range of 20 to 150° F., at least 30% by weight boiling below 400° F. and a final boiling point in excess of 700° F., said condensate having an A.P.I. gravity of no less than 40 to 45 and containing 55 to 70% by weight paraffin hydrocarbons, 20 to 30% by weight naphthenic hydrocarbons and 4 to 15% by weight aromatic hydrocarbons, under conditions such that the conversion of the petroleum condensate to C_3 and lighter hydrocarbons is greater than 45%, separating from the cracked products of said thermal cracking substantially all materials boiling below 500 to 575° F. to thereby produce a high-boiling cracked residue, subjecting said high-boiling cracked residue to a thermal soak at a temperature of 600 to 1000° F. and recovering an aromatic oil as an overhead fraction from said thermal soak and a thermal residue as a bottoms fraction from said thermal soak, said thermal residue having a softening point of 185 to 215° F., a carbon to hydrogen atomic ratio of greater than 1.5 and a sulfur content of less than 0.5 and possessing the properties of an electrode binder pitch.

Several advantages obtain from the process of the present invention and the electrode binder composition produced thereby. Of particular note is the fact the present invention permits preparation of an electrode binder pitch directly from a naturally-occurring petroleum composition with a fewer number of treating steps than are required of many prior art processes which begin with a synthetic petroleum fraction obtained from prerefining of the petroleum. Further, since the process of the present invention provides for the production, pri-

marily of C_3 and lighter compounds, i.e., ethylene and propylene, in the thermal cracking step, the present process is economically more attractive than similar prior art processes. Yet, another advantage resulting from the present invention is that of the thermal residue being usable directly as a binder pitch without additional treatment or blending with other petroleum or coal derived fractions. In addition to the above advantages, the binder composition prepared by the process of the present invention is superior to many prior art binder compositions with regard to several properties desirable for electrode binder pitches. Particularly, the binder compositions of the present invention are high in benzene insoluble materials.

DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE PRESENT INVENTION

To demonstrate the herein described process for preparing an electrode binder pitch and the usefulness of the compositions so prepared as an electrode binder pitch, the following experiment was carried out.

A petroleum condensate cracking feed having an initial boiling point of about 20° F., a final boiling point in excess of 700° F. and having a 50% boiling point of approximately 400° F. and an A.P.I. gravity of greater than 50 was thermally cracked in a tubular furnace in the absence of a catalyst at a temperature of 1350 to 1475° F. The cracking was carried out in the presence of steam. The weight ratio of steam to cracking feed was about 0.25. A pressure ranging from an inlet pressure of 5 p.s.i.g. to an outlet pressure of about 45 p.s.i.g. was maintained in the cracking zone.

The cracked product was subjected to distillation and the components boiling below about 550° F. removed as overhead. Analysis of the overhead from the distillation column indicated that the conversion of the petroleum condensate to normally gaseous hydrocarbons was in excess of 50%.

The cracked residue from the distillation was continuously passed through a preheater which heated the residue to a temperature of about 550° F. From the preheater, the heated cracked residue was passed into a tubular soaking coil having a three-inch internal diameter and a length of 452 feet. The temperature at the exit end of the soaking coil was about 950° F. and the pressure about 250 p.s.i.g. Residence time within the soaking coil was about 10 minutes. The heat soaked cracked residue was passed to a flash column and quenched to a temperature of 890° F. and the pressure lowered to 80 p.s.i.g. As a result of the lowering in pressure, an aromatic oil was flashed overhead leaving behind a thermal residue as a bottoms fraction. The aromatic oil had an initial boiling point of about 247° F. and a 90% boiling point of about 706° F. The thermal residue bottoms fraction had the physical properties shown in the following table.

Softening point, ° F.	203
Specific gravity	1.246
Benzene insolubles, wt. percent	26.2
Quinoline insolubles, wt. percent	1.8
Conradson carbon, percent	55
Sulfur content, wt. percent	0.09
Ash, wt. percent	<0.1
Carbon to hydrogen atomic ratio	1.54

To demonstrate the utility of the thermal residue as an electrode binder pitch, a portion of the thermal residue was heated and intimately mixed with a calcined coke. The mixture was molded under pressure and heated to a high temperature sufficient to carbonize or coke the binder. The resulting electrodes were tested as to crushing strength, electrical resistivity, and apparent density, three of the more important properties of finished electrodes. Crushing strength was found to be good while both the electrical resistivity and apparent density were acceptable. These ratings were based on comparison with

a conventional electrode prepared with well accepted coal tar pitch as the binding material. Therefore, the petroleum-derived binder pitch compositions of the present invention may be readily substituted for the more expensive, conventional coal tar pitch binder.

To further demonstrate the utility of the thermal residue of the present invention as an electrode binder pitch, it was tested in a Soderberg electrode. As a result, it was found that thermal residue was acceptable in such electrodes as a substitute for coal tar pitch. This is a particularly advantageous result since Soderberg electrodes usually require larger quantities of binder than pre-baked electrodes.

The wide boiling range naturally-occurring petroleum condensate useful as a feed material to the thermal cracking step of the process of the present invention generally has an initial boiling point within the range of 20 to 150° F. and a final boiling point in excess of 700° F. Petroleum condensates grade from colorless liquids of relatively high A.P.I. gravity to rather dark colored liquids with gravities as low as 40–45° A.P.I. The condensates are substantially the same and include, insofar as properties are concerned, many light crude oils. For the purposes of the present invention, light crude oils meeting the physical property requirements defined herein are included within the term "petroleum condensates." The primary difference between the petroleum condensates and the light crudes of similar physical properties is in their condition in the subterranean reservoir from which they are produced. The condensates are usually vaporized and in admixture with large quantities of methane and are condensed from the methane usually upon reaching the surface of the earth. The light crudes, on the other hand, are usually produced as a liquid by usual production means. The petroleum condensates useful as feeds to the cracking step of the present invention are those having the above initial and final boiling points and in addition have a boiling range such that at least 30% by weght of the condensate boils below 400° F. For the purposes of the present invention, such feed materials are comprised of 55 to 70% by weight paraffinic hydrocarbons, 20 to 30% by weight naphthenic hydrocarbons and 4 to 15% by weight of aromatic hydrocarbons. Preferably, the petroleum condensates have an A.P.I. gravity within the range of 50 to 60. A particularly useful feed material to the cracking step of the process of the present invention is one having an initial boiling point within the range of 90 to 110° F., a final boiling point within the range of 700 to 750° F., and of which at least 40% boils below 400° F. This particularly useful feed usually has an A.P.I. gravity of 50 to 55 and is comprised of 65 to 70% by weight of paraffins, 25 to 30% by weight of naphthenes and 5 to 10% by weight of aromatics.

Thermal cracking, as carried out in the process of the present invention, is non-catalytic, but may be, and most often is, carried out in the presence of a diluent. Among the diluents useful in the cracking step are steam, low molecular weight paraffinic hydrocarbons, hydrogen, carbon monoxide and the like. The most useful of these diluents is steam. In using a diluent in the cracking step, it is preferably used in an amount such as to cause a weight ratio of diluent to cracking feed of 0.15 to 0.40 though both higher and lower ratios may be used.

The temperatures useful in the cracking step of the present invention are those within the range of 1350 to 1550° F. Pressures for the thermal cracking step most often range from atmospheric pressure up to 60 p.s.i.g. and higher with pressures from about 10 to 50 p.s.i.g. preferred. Lower pressures usually are preferred since the production of desired normally gaseous hydrocarbons, particularly C_3 and lighter hydrocarbons such as ethylene and propylene, is thereby favored. In practicing the cracking step of the present invention, the cracking conditions should be adjusted within the above ranges such that the quantity of C_3 and lighter hydrocarbons produced

is such as to represent a conversion of feed to such hydrocarbons in excess of 45% and preferably in excess of 50%. Such conversion maximizes production of such desired materials as ethylene and propylene while producing the relatively high molecular cracked residuum which is thermally soaked to obtain the high quality binder compositions of the present invention.

The cracked products of the thermal cracking are subjected to a separation means, usually distillation, to separate substantially all of the components boiling below 500 to 575° F. at atmospheric pressure from a residue fraction. If distillation is used as the separation means, it may be carried out at subatmospheric, atmospheric, or superatmospheric pressures or a combination of these. Steam distillation also provides a useful method of removing the higher boiling components boiling below the above temperatures. The resulting cracked residue will usually possess the following properties:

Softening point, R&B, ° F.	110–140
Specific gravity	1.14–1.18
Benzene insolubles, wt. percent	0.1–3.0
Quinoline insolubles, wt. percent	<0.5
Sulfur, wt. percent	<0.5
Carbon to hydrogen atomic ratio	1.15–1.30

Distillation, ASTM D-20, ° F.:	Weight percent distillate
455–518	0
518–572	1–5
572–671	30–50

The thermal soak step of the process of the present invention may be carried out as a batch operation or as a continuous or semi-continuous operation. Generally, in either manner, the thermal soak temperatures are within the range of 600 to 1000° F. with residence times in the soaking area ranging from 1 to 90 minutes. The higher temperatures are advantageously used with the lower residence times and, conversely, lower temperatures are more often used with the longer residence times. Pressure seems to have little effect on the products of the thermal soak. Usually, pressures ranging from atmospheric pressure to as high as 300 p.s.i.g. or higher are used. The use or non-use of elevated pressure generally is determined by the mechanical aspects of the thermal soak operations as will be seen from the description below of a particularly useful thermal soak method.

In carrying out the thermal soak as a batch operation, temperature 650 to 800° F. and residence times within the soaking drum of 3 to 90 minutes are most often employed. Pressures ranging from atmospheric to 30 p.s.i.g. are also used in the batch thermal soak. In the batch thermal soak, it is necessary that there be an even heating of the cracked residue and that overheating around the periphery be avoided. Overheating often results in the formation of coke or carbon particles in the residue which materials are generally undesirable in binder pitches. A particularly useful means of maintaining constant agitation of the soaking mass and insuring relatively uniform heating is that of continuously circulating a portion of the soaking residue through a pump which continuously recirculates the residue back into the soaking drum. Throughout the soaking operation, an aromatic oil is continuously taken overhead until the thermal soak is completed. The thermal residue is then recovered for use as a binder composition.

The batch process described above may be readily converted to a continuous or semi-continuous process by continuously or semicontinuously removing a portion of the soaking mass from the soak drum while at the same time adding fresh cracked residue to the soak drum.

Another very useful means of carrying out the thermal soaking step comprises passing the cracked residue through a tube of relatively narrow diameter in which the residue is rapidly heated to a temperature of 800 to 1000° F. The residence time of the cracked residue in the heating zone is relatively short by comparison with the batch method, usually ranging from 2 to 30 minutes. In this method pressure is advantageously used, pressures ranging from 50 to 350 p.s.i.g., preferably about 150 to 275 p.s.i.g. On exiting the heating zone, the high temperature product is passed into a flash distillation column in which the pressure is instantly reduced to approximately 5 to 100 p.s.i.g. On reduction of the pressure, aromatic oils produced in the thermal soaking zone are flashed overhead. The remaining thermal residue is then recovered for use as a binder.

The aromatic oils which are produced in the thermal soak step represents an additional recovery of valuable products from the process of the present invention. These aromatic oils which usually boil substantially within the temperature range of approximately 175 to 800° F., are useful as plasticizers, both primary and secondary, as extender oil and as feeds for carbon black production. Further, removal of this aromatic oil greatly stabilizes the resulting thermal residue and results in an improved material for electrode binder use.

The thermal residue produced by the thermal soak and which is the binder pitch of the present invention generally has the following properties:

Softening point, R&B, ° F.	185–215
Specific gravity	1.235–1.255
Benzene insolubles, wt. percent	20–40
Quinoline insolubles, wt. percent	<5
Sulfur, wt. percent	<0.5
Carbon to hydrogen atomic ratio	>1.5
Distillation, ASTM D–20:	
Wt. percent boiling 455 to 518° F.	0
Carbon to hydrogen atomic ratio	>1.5

While the compositions disclosed and claimed herein are useful as binders for carbon electrodes, they are useful on other applications also. They may be used as primary or secondary plasticizers, as impregnants for various materials as well as coating materials.

What is claimed is:

1. A process for the production of a petroleum-derived electrode binder pitch which comprises non-catalytically thermally cracking at a temperature of 1350 to 1550 ° F. a wide boiling range naturally-occuring petroleum condensate having an initial boiling point within the range of 20 to 150° F., at least 30% by weight boiling below 400° F. and a final boiling point in excess of 700° F., said condensate having an A.P.I. gravity of no less than 40 to 45 and containing 55 to 70% by weight paraffins, 20 to 30% by weight naphthenic hydrocarbons and 4 to 15% by weight aromatic hydrocarbons, under conditions such that the conversion of the petroleum condensate to C_3 and lighter hydrocarbons is greater than 45%, separating from the cracked products of said thermal cracking substantially all materials boiling below 500 to 575° F. to thereby produce a high-boiling cracked residue, subjecting said high-boiling cracked residue to a thermal soak at a temperature of 600 to 1000° F. and recovering a heavy aromatic oil as an overhead fraction from said thermal soak and a thermal residue as a bottoms fraction from said thermal soak, said thermal residue having a softening point of 185 to 215° F., a carbon to hydrogen atomic ratio of greater than 1.5 and a sulfur content of less than 0.5% by weight and possessing the properties of an electrode binder pitch.

2. The process of claim 1 wherein the thermal cracking is carried out in the presence of a diluent.

3. The process of claim 2 wherein the diluent is steam.

4. The process of claim 2 wherein the amount of diluent present is such as to cause a diluent to petroleum condensate weight ratio of 0.15 to 0.40.

5. The process of claim 1 wherein the naturally-occurring petroleum condensate has an A.P.I. gravity within the range of 50 to 60, an initial boiling point within the range of 90 to 110° F., a final boiling point within

the range of 700 to 750° F., and is one at least 40% of which boils below 400° F., said condensate containing 65 to 70% by weight paraffins, 25 to 30% by weight naphthenic hydrocarbons and 5 to 10% by weight aromatic hydrocarbons.

6. The process of claim 1 wherein the thermal soak is carried out by continuously passing said cracked residue into a soaking drum which is maintained at a temperature to 650 to 800° F. and a pressure of from atmospheric to 50 p.s.i.g. and continuously taking overhead an aromatic oil fraction while continuously withdrawing a thermal residue, the residence time of said cracked residue in said soaking drum being within the range of 3 to 90 minutes.

7. The process of claim 1 wherein the thermal soak is carried out by passing said cracked residue into a tube of relatively narrow diameter wherein it is heated to a temperature within the range of 800 to 1000° F. and a pressure of 50 to 350 p.s.i.g., said cracked residue remaining in said soaking tube of 2 to 30 minutes, passing the thermally soaked cracked residue at elevated temperature into a flash distillation zone wherein the pressure is instantly reduced to a new pressure within the range of 5 to 100 p.s.i.g., thereby flashing overhead an aromatic oil and recovering a thermal residue as bottoms.

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