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ACTIVATED CARBON IN THE PREPARATION OF BINDER PITCH

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ABSTRACT OF THE DISCLOSURE

This disclosure relates to a process for producing petroleum pitches by (1) heating, under partial reflux conditions, a petroleum hydrocarbon fraction in the presence of an activated carbon catalyst to form an overhead fraction and a bottoms fraction; (2) separating said catalyst from said bottoms fraction; (3) subjecting said bottoms fraction to a vacuum distillation; and (4) recovering as pitch the residuum of said vacuum distillation.

This invention relates to a process for the manufacture of a pitch binder from hydrocarbons of petroleum origin which is suitable for use in producing molded carbonaceous articles, such as carbon electrodes and to the pitch binders produced thereby. In particular, this invention relates to a process for increasing the yield of pitch binder derived from hydrocarbons of petroleum origin.

In the manufacture of molded carbonaceous materials, such as briquettes, electrodes, brushes, internal linings of electric furnaces and electrolytic cells, and especially in the manufacture of Soderberg or self-baking electrodes which are used in the electrolytic production of aluminum, calcined coke is generally used as the starting material. Crushed, calcined coke is conventionally mixed with a binder, such as coal tar pitch or other bituminous tar or pitch, and then the admixture is molded or extruded to the desired shape and baked in order to carbonize the binder material and impart the necessary physical and electrical properties to the molded carbonaceous material.

In electrode manufacture, it has been found that the nature and the quality of the binder used is extremely critical. It has been the usual practice to utilize, almost exclusively, coal tar pitch, i.e., the dark brown to black amorphous residue left after coal tar is redistilled, as the thermoplastic binder in the manufacture of such shaped carbon articles, especially carbon electrodes. More recently, it has been discovered that pitches, suitable as binders, can be prepared from petroleum hydrocarbons. See, for example, co-assigned U.S. Patent 3,173,851.

The yield of petroleum-derived pitch by the use of vacuum reduction is in the range of between about 20 and about 25 volume percent. That portion of the petroleum feed stock which is not converted to pitch is conventionally looked upon as a waste product. It would, therefore, be exceedingly advantageous if the yield of petroleum-derived pitch could be substantially increased at minimum cost. It has now been found that the yield of pitch can be as much as doubled by preheating the petroleum hydrocarbon feed in the presence of an activated carbon catalyst.

It is, therefore, an object of the present invention to provide the art with a process for producing a petroleum-derived pitch suitable for use as a binder in the manufacture of molded carbonaceous materials. It is a further object to provide a process wherein the yield of pitch obtained by vacuum reduction is substantially increased. These and other objects as well as the exact nature of the instant invention will be more clearly perceived and more fully understood by referring to the following description and claims.

In accordance with the present invention, a petroleum hydrocarbon feed having an initial boiling point of about 400° F. and an end boiling point of above about 1100° F. is heated, under partial reflux conditions, with between about 1 and about 10 wt. percent of an activated carbon catalyst at a temperature of between about 650° F. and about 800° F. for between about 10 and about 20 hours. The bottoms fraction obtained from this heat treatment is then subjected to a vacuum distillation wherein the pressure is gradually reduced in order to hold the pot temperature below about 625° F. The residuum of said vacuum distillation is recovered as the pitch product desired and is obtained in substantially increased yield over that obtained by a simple vacuum reduction of the hydrocarbon feed.

The hydrocarbon feed stock utilized to prepare the pitch of the instant invention is, in general, a petroleum hydrocarbon fraction having an initial boiling point of about 400° F. and an end boiling point of above about 1100° F. and is composed of between about 30 and about 70 wt. percent of heavy aromatics and between about 70 and about 30 wt. percent of naphthenes, paraffins, olefins and diolefins. A specific example of a suitable petroleum hydrocarbon feed stock is vacuum reduced catalytic cracker fractionator bottoms.

Catalytic cracker fractionator bottoms (CFB) comprises materials boiling in the range of between about 475° F. and about 1100° F., with generally not more than 10–15% distilling below 700° F. This bottoms material, as indicated, is obtained by high-severity catalytic cracking of gas oil. The inspections of typical gas oil feeds, reactor conditions for high-severity catalytic cracking and inspections of typical high-severity catalytic cracking fractionator bottoms are summarized in Table I.

TABLE I

	Broad Range	Preferred
Catalytic Cracking Operation:		
Feed Gas Oil Gravity		
AR (Percent Carbon in Aromatic Rings)	21–25	23.5–24
NR (Percent Carbon in Naphthenic Rings)	11–15	(1)
Cat. Cracker Reactor Conditions:	35–39	(1)
Temperature, °F.		
Recycle, Percent Fresh Feed	935–955	950
Total Conversion, Percent Corr. 430° F.	38–55	45–50
Inspection of Bottoms:	58–65	62
Gravity, °API		
Viscosity, 210° F., SUS	−1.0–5.0	(2)
Asphaltenes	60–80	~70
ASTM Distillation, °F.:	Trace	
IBP	490–510	500
5%	660–700	680
10%	720–750	730
20%	750–790	775
30%	790–825	810
40%	815–855	840
50%	840–880	860
60%	860–890	875
70%	890–915	905
BMCI	90–125	(1)

[1] As high as possible. [2] As low as possible.

The high severity catalytic cracker fractionator bottoms are vacuum reduced at a maximum still temperature of about 625° F. and at pressures below 100 mm. mercury, preferably at 10–1.7 mm. mercury absolute pressure to a final vapor temperature of about 925° F. atmospheric equivalent to produce petroleum pitches having a softening point of between about 175° F. and about 250° F. Pitch binders for Soderberg electrode manufacture should have a softening point of between about 190° F. and about 205° F., while for prebaked electrodes, softening points of up to about 230° F. or higher are preferred. In the case of catalytic fractionator bottoms, it is essential to remove catalyst fines as by hot settling or the use of a hydrocyclone apparatus or the like in order that the

ash content of the pitch binder be held below about 0.3 wt. percent.

In accordance with the present process, a hydrocarbon feed stock, e.g., vacuum-reduced catalytic cracker fractionator bottoms is heat treated at between about 650° F. and about 800° F., preferably between about 700° F. and about 750° F., more preferably about 700° F., in the presence of an activated carbon catalyst for between about 10 and about 20 hours, e.g., about 16 hours, under partial reflux conditions. By partial reflux conditions is meant that nominal total reflux conditions are imposed during the activated carbon heat treatment; however, some very light products, e.g., gases, are formed which are not condensible by ordinary water-cooling systems and, therefore, pass overhead without recovery. The heavier products are condensed and totally refluxed. The heat treatment, under partial reflux, yields a volatile material, which is taken overhead and condensed, and a high boiling polymeric component which remains behind as a residuum or bottoms product.

The activated carbon catalyst utilized in the present process can be any of those generally known in the art. The carbon itself is conventionally produced by the destructive distillation of wood, peat, lignite, nut shells, bones, vegetable or other carbonaceous matter. Activation is usually achieved by heating to high temperatures (800–900° C.) with steam or carbon dioxide, which brings about a porous particle structure. The internal surface area is estimated to be about 3600 square feet per gram and densities range from 0.08 to nearly 0.5. Although not critical to the instant invention, the activated carbon catalyst will generally have a particle size of between about 12 and about 40 mesh. In general, between about 1 and about 10 wt. percent, based on petroleum hydrocarbon feed, of the activated carbon catalyst is employed. Preferably, about 5% by weight of the activated carbon catalyst, based on hydrocarbon feed, is employed; however, the exact amount of catalyst employed is not critical to the present novel process.

Following the heat treatment the residuum of bottoms product is preferably cooled down to a temperature of between about 300° F. and about 400° F. in order to achieve an atmospheric transfer to a fractionation tower. Alternatively, the residuum can be transferred at the temperature of the heat treatment by the use of superatmospheric pressure. In a batch operation, the lighter boiling components can be flashed off from the reaction vessel and the activated carbon catalyst screened out before proceeding to fractionation. The fractionation tower essentially performs a flashing operation or perhaps a distillation with one theoretical plate efficiency. Fractionation is carried out under a vacuum of between about 100 mm. of mercury and about 10 mm. of mercury or less. The pot temperature of the fractionation tower is kept below about 625° F. in order to prevent cracking of the residuum. Pot temperature is regulated by gradually reducing the pressure, i.e., going to a higher vacuum, as the light ends are distilled overhead and collected as condensate.

The residuum of the vacuum distillation stage is recovered as the product of the instant process and comprises a pitchlike product which is suitable for use as a binder in the manufacture of molded carbonaceous materials. When the binder is to be employed in the manufacture of electrodes, it is desired that the pitch have a softening point of between about 175° F. and about 250° F., preferably about 200° F. Pitches having a specific softening point can be obtained by stopping the vacuum distillation at a point when the residuum reaches the softening point desired. Thus, the residuum feed from the heat treatment step which is charged into the vacuum fractionation tower has a particular softening point value, which may be quite low. During vacuum distillation and with the loss of light ends, the softening point of the residuum rises. Therefore, it is possible to obtain a pitch with a specific softening point by regulating the vacuum distillation so that said distillation is terminated when the desired product is obtained.

The only really satisfactory test for determining the effectiveness of a binder pitch prepared from petroleum hydrocarbons is to manufacture the article desired, such as a carbon electrode or a test electrode compression block, with the pitch and then test the resultant article. For example, in the case of a Soderberg electrode, the binder and coke aggregate are usually mixed at a temperature of about 300–325° F. in a sigma bladed mixer. The resulting mixture is then molded in the form of test cylinders, 1.25 inches in diameter and 4 inches long, in graphite molds and baked in an inert atmosphere at temperatures up to a maximum of about 1000° C. (1832° F.) for about 23.5 hours under applied pressure to simulate the weight of the green mix above a Soderberg electrode in an actual furnace. The test cylinders are then tested for compressive strength by means of a hydraulic press which is suitable for evaluating asphalt aggregates. This press measures the crushing strength of the cylinder in kilograms per square centimeter. Satisfactory electrodes have a crushing strength of at least 300 kg./sq. cm. and, in general, range between about 300 and about 450 kg./sq. cm., preferably at least about 385 kg./sq. cm.

In the manufacture of Soderberg electrodes, about 28 to 35 wt. percent of binder, based on the green mix, is used; while in the manufacture of prebaked electrodes, about 15 to 25 wt. percent of binder will suffice.

The process of the present invention can be carried out by either batch or continuous means. Space velocities for the continuous process will vary with the unit employed; however, in general, space velocities can vary between about 0.5 and about 1.0 volume of feed/volume of catalyst/hour (v./v./hr.). In a batchwise process, the ratio of feed to catalyst volume and residence time are arranged to give an equivalent v./v./hr. of between about 0.5 and about 1.0. The petroleum hydrocarbon-based pitches produced in accordance with the present process can be further modified by incorporating therein up to about 10 wt. percent, based on pitch, of a "reinforcing" or "semireinforcing" carbon black in accordance with the disclosures of coassigned U.S. Serial No. 329,994, now U.S. Patent No. 3,316,183. This procedure eliminates the tendency of the petroluem pitch to bleed from the green mix or coke particle-pitch binder compositions during baking.

The inventive process is more particularly described in the following examples which are intended as illustrative only since numerous modifications and variations therein will be apparent to those skilled in the art.

Example 1

A suitable gas oil was subjected to high-severity catalytic cracking and the bottoms from this operation were used as the petroluem hydrocarbon feed stock for the production of a petroleum pitch. Average inspections of the feed gas oil and bottoms, as well as the catalytic cracker reactor conditions are tabulated in Table II.

TABLE II

Feed gas oil:	
Gravity, ° API	24.6
Aromatic rings	15.0
Naphthene rings	39.0
Crackability	0.55
Reactor conditions:	
Temperature, ° F.	940
Recycle, vol. percent fresh feed	44.3
Conversion, percent corr. 430° F.	65.6
Inspection of bottoms:	
Gravity, ° API	1.0
Viscosity, 210° F., SUS	69
ASTM distillation:	
IBP, ° F.	531
5%	681
10%	734

TABLE II—Continued

20%	764
30%	823
40%	852
50%	878
60%	908
Bureau of Mines correlation index (BMCI)	115
Water, vol. percent	0.05
Ash, wt. percent	[1] 0.005

[1] After settling in a tank at 180° F. for 90 days.

A portion (1434 grams) of the catalytic fractionator bottoms described in Table II was subjected to vacuum reduction in a "Hivac" still at pressures below 100 mm. of mercury. Most of the overhead product was collected at between about 10 mm. of mercury and about 1.7 mm. of mercury. The amount of the overhead fraction was 1075 grams. Three hundred fifty-nine grams of bottoms having a softening point of about 189° F. and a boiling point of 930+ ° F. were also recovered. The bottoms fraction amounted to about 25 wt. percent (22 vol. percent) based on the feed to the "Hivac" still. Analytical inspections of the bottoms product appear in Table IV.

Example 2

A quantity (1434 grams) of the catalytic fractionator bottoms described in Table II of Example 1 was heat-soaked for 18 hours with stirring in a two-liter stainless steel reaction flask under partial reflux at 700° F. Any water liberated, plus cracked products, were taken overhead during the course of the reaction. The amount of overhead product, including gas, was about 3 wt. percent of the feed. The product left in the reaction vessel was then reduced in a "Hivac" still at pressures below 100 mm. of mercury to an atmospheric equivalent overhead temperature of about 900° F. Most of the overhead product was collected at between about 10 mm. of mercury and about 1.7 mm. of mercury. The resultant yield of bottoms was 36.5 wt. percent, or 32 vol. percent, of the charge to the heat-soaking vessel. The softening point of the bottoms was 198° F. (cube-in-air method).

Example 3

In accordance with the process of the instant invention, 1434 grams (1432 cc.) of the same bottoms feed stock employed in Examples 1 and 2 were heated batchwise for 20 hours with stirring in the presence of 71.5 cc. of an activated carbon catalyst in a stainless steel vessel under partial reflux at 700° F. and atmospheric pressure. The activated carbon catalyst was type CAL (Pittsburgh Coal and Chemical Co.) and had a particle distribution of 12–40 mesh. All of the water liberated and most of the cracked products from the heat treatment were taken overhead during the course of the reaction. Considerable quantities of hydrogen sulfide were evolved. Yield data and product inspections are summarized and tabulated in Table III.

About 12 wt. percent of light (170–520° F. ASTM boiling point) product, consisting of about ⅓ aromatics and the remainder saturates, was recovered as the overhead fraction. This fraction was cracked material, all boiling below the initial boiling point of the feed. The bottoms fraction, about 88 wt. percent of the feed, had a boiling range similar to that of the original feed but, was lower in gravity and higher in Bureau of Mines correlation index (132 vs. 115) than the original feed, indicating higher aromaticity by condensation, cyclization and polymerization reactions during contact with the activated carbon.

Most of the bottoms fraction recovered from the heat treatment of the initial feed stock (1175 grams, 1060 cc.) was then further reduced by "Hivac" vacuum distillation. The pressure during vacuum distillation was reduced gradually from 50 to 20 to 1.6 mm. of mercury in order to hold the pot temperature below 625° F. No cracking was evident during the vacuum distillation. The residue obtained from the vacuum distillation weighed 573 grams

(48.8 wt. percent of the still charge; 42.5 wt. percent of the original feed stock) and had a softening point of 188° F. Thus, it can be seen that the quantity of pitch (42.5 wt. percent, 37.5 vol. percent) was almost double that obtained (25 wt. percent, 22 vol. percent) by direct vacuum distillation of the same feed stock and about 20% higher than the heat-soaked feed. Other inspections of the bottoms product obtained are found in Table IV and are compared to the bottoms product of Example 1.

TABLE III

Operating Conditions (batchwise):

Temperature, ° F.	700.
Pressure	Atmospheric.
Feed	1432 g. (1430 cc.) cat. fractionator bottoms (CFB).
Catalyst	71.5 cc. activated carbon, type CAL, 12–40 mesh.
Duration	20 hours.
Equivalent space velocity, v./v./hr.	1.0.

	Feed	Overhead Fraction	Bottoms Fraction [1]
Material Balance:			
G.	1,434	[2] 180	1,245
Wt. percent	100	[2] 12.5	87.5
Product Inspections:			
Gr. °API		47.7	−3.3
Sp. Gr.		0.790	1.104
FIA Aromatics, percent		34	
Olefins, percent		Nil	
Saturates, percent		66	
Sulfur, wt. percent		0.13	
		D–86	D–1160 (Vacuum)
ASTM Distillation, ° F.:			
IBP		170	530
5%		220	670
10%		245	700
20%		290	730
50%		373	860
90%		472	
95%		514	
FBP		520	
Visc. at 210° F., SUS			123
Ash, wt. percent [3]			0.01
Bureau of Mines Correlation Index		[4]	132

[1] Approx. 700+ ° F., B.P.
[2] Some loss due to spillage (approx.).
[3] Clarified by hot settling.
[4] Too light.

TABLE IV.—INSPECTION OF PETROLEUM PITCH

Inspection	Example 1	Example 3
Softening Point:		
Ring and Ball, ° F.	197	188
Cube-in-air, ° F.	[1] 196	
Gravity, °API		−15.0
Sp. Gravity 60/60° F.	1.218	1.215
Coking Value, Percent	47	47
Benzene Insoluble Percent	1.1	6.2
Quinoline Insoluble Percent	Nil	Nil
Sulfur, Percent	1.4	1.8
Asphaltenes, Percent		38.4
Viscosity,[1]:		
EVT_{15} ° C.	143	143.5
EVT_{1015} ° C.	107.5	107
T_c, poises/° C.	28	28.5

[1] After addition of 5% Regal SRF carbon black.

Example 4

The petroleum pitches produced in Examples 1 and 3 were each admixed with 5% SRF carbon black and the respective admixtures used to prepare test electrodes by mixing 31 wt. percent of the resultant pitch with ground delayed petroleum coke that had been calcined at about 2000° F. The ground coke particles (coke aggregate) used for the preparation of the test electrodes were such that 100% passed through a 4-mesh screen and about 30 wt. percent was fine enough to pass through a 200-mesh screen. The binder and coke aggregate were mixed at about 300–325° F. in a sigma bladed mixer. The resulting mixture was then molded in the form of test cylinders, 1.25 inches in diameter and 4 inches long, in graphite molds and baked in an inert atmosphere at temperatures

up to a maximum of about 1000° C. (1832° F.) for about 23.5 hours under applied pressure to simulate the weight of the green mix above a Soderberg electrode in an actual furnace. Preliminary electrode performance data, as obtained in the laboratory, are given in Table V along with comparable values for a typical coal tar binder.

TABLE V.—ELECTRODE BINDER PERFORMANCE DATA

	Binder, wt. percent	Before Aging			After aging paste 24 hrs. at 225° C.		
		Green Mix Elongation, Percent	Baked Electrode		Green Mix Elongation, Percent	Baked Electrode	
			Apparent Density, g./cc.	Compressive Strength, kg./cm.²		Apparent Density, g./cc.	Compressive Strength, kg./cm.²
Example 1	31	52	1.37	325	58	1.46	369
Example 1 [a]	31	67	1.37	325	66	1.44	404
Example 3 [b]	31	52	1.41	359	27	1.45	376 / 306
Coal Tar (typical)	32 (approx.)	60	1.40–1.45	320+	30–40		375 (approx.)

[a] Vacuum-reduced product containing 5% Regal SRF carbon black.
[b] Batchwise reaction of cat fractionator bottoms over activated carbon at 700° F. followed by vacuum flashing and incorporation of 5% Regal SRF carbon black.

The data of Table V show that at the same binder content, initial flow properties of the green mix were the same as before, but density and compressive strength were higher. After the Soderberg paste was held at 225° C. for 24 hours, density increased and viscous flow decreased in much the same way as with coal tar binder. Compressive strength was increased on aging of the paste, which is not an unusual occurrence. Soderberg paste made with most petroleum residua as binders tend to turn fluid in the aging test (24 hours at 225° C.) and in actual practice. This is dangerous since it causes leakage from the cell casing. When sufficient carbon black of the right particle size is present in the binder initially, this thinning out of the paste does not occur.

The pitch binder made in accordance to the present invention is useful in the production of prebaked or Soderberg electrodes and is especially useful in the production of electrodes for use in aluminum manufacture, but is not restricted thereto.

While there are above-described a number of specific embodiments of the present invention, it is obviously possible to produce other embodiments of various equivalent modifications and variations thereof without departing from the spirit of the invention.

Having now set forth the general nature and specific embodiments of the present invention, the true scope is now particularly pointed out in the appended claims.

What is claimed is:

1. A process for producing a petroleum-derived pitch which comprises (a) heating, under partial reflux conditions, a petroleum hydrocarbon fraction having an initial boiling point of about 400° F. and an end boiling point of about 1100° F. in the presence of an activated carbon catalyst to form an overhead fraction and a bottoms fraction; (b) separating said catalyst from said bottoms fraction; (c) subjecting said bottoms fraction to a vacuum distillation; and (d) recovering, as the pitch product, the residuum of said vacuum distillation.

2. A process according to claim **1** wherein between about 1 and about 10 wt. percent of said activated carbon catalyst is employed.

3. A process according to claim **1** wherein said petroleum hydrocarbon fraction is heated, under partial reflux conditions and in the presence of said activated carbon catalyst, at a temperature of between about 650° F. and about 800° F. for between about 10 and about 20 hours.

4. A process according to claim **1** wherein the pot temperature of said bottoms fraction vacuum distillation is kept below about 625° F.

5. A process according to claim **1** wherein said petroleum hydrocarbon fraction is vacuum-reduced catalytic cracker fractionator bottoms.

6. A process according to claim **1** wherein said petroleum hydrocarbon fraction comprises between about 30 and about 70 wt. percent of heavy aromatics and between about 70 and about 30 wt. percent of a mixture selected from the group consisting of naphthenes, paraffins, olefins and diolefins.

7. A process according to claim **1** wherein said activated carbon catalyst has a particle size distribution which varies between about 12 and about 40 mesh.

8. A process for producing a petroleum-derived pitch which comprises (a) heating, under partial reflux conditions, a petroleum hydrocarbon fraction having an initial boiling point of about 400° F. and an end boiling point of above about 1100° F. with between about 1 and about 10 wt. percent of an activated carbon catalyst at a temperature of between about 650° F. and about 800° F. for between about 10 and about 20 hours to form an overhead fraction and a bottoms fraction; (b) separating said catalyst from said bottoms fraction; (c) subjecting said bottoms fraction to a vacuum distillation wherein the pot temperature is kept below about 625° F.; and (d) recovering, as the pitch product, the residuum of said vacuum distillation.

9. A process for producing a petroleum-derived pitch which comprises (a) heating, under partial reflux conditions, vacuum-reduced catalytic cracker fractionator bottoms with between about 1 and about 10 wt. percent of an activated carbon catalyst at a temperature of about 700° F. for about 20 hours to form an overhead fraction and a bottoms fraction; (b) separating said catalyst from said bottoms fraction; (c) subjecting said bottoms fraction to a vacuum distillation wherein the pot temperature is kept below about 625° F.; and (d) recovering, as the pitch product, the residuum of said vacuum distillation.

10. The petroleum derived pitch produced according to the process of claim **1**.

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