

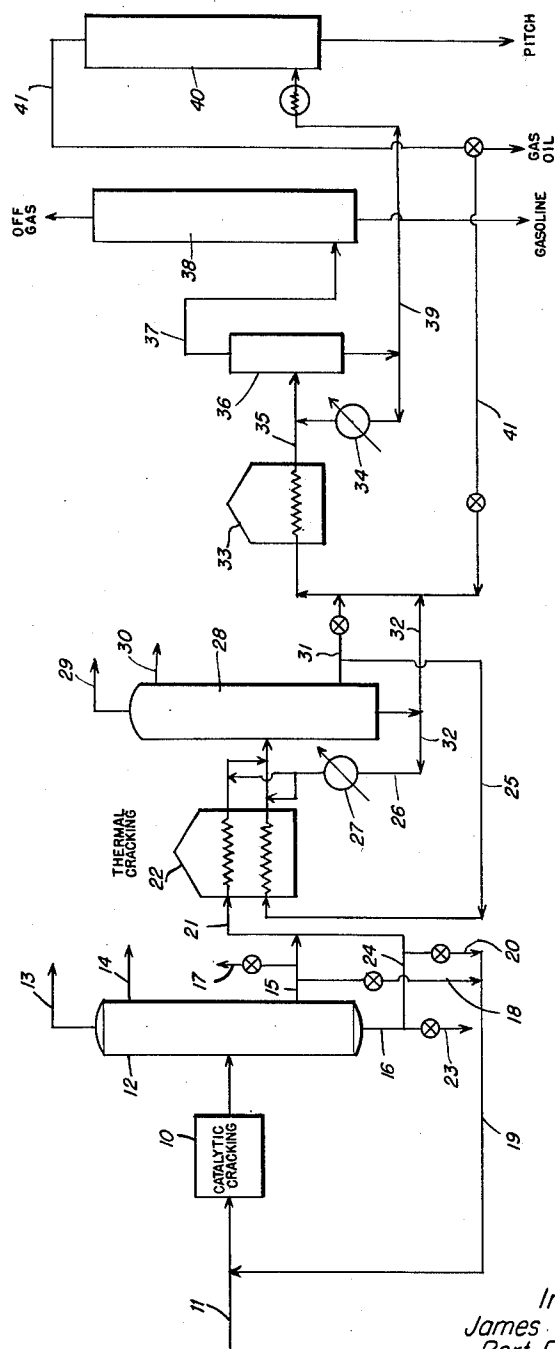
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PROCESS FOR PREPARING BINDER PITCHES

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PROCESS FOR PREPARING BINDER PITCHES

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9 Claims. (Cl. 208—40)

The invention relates to a process for the manufacture of a pitch binder from hydrocarbons of petroleum origin suitable for use in producing molded carbonaceous articles such as carbon electrodes. More particularly, this invention provides a continuous process for the manufacture of petroleum-derived pitch binder wherein a hydrocarbon fraction is catalytically cracked and a specific heavy bottom fraction obtained from the cracking operation is thermally cracked to produce a thermal asphalt which in turn is subjected to a continuous soaking zone under specific soaking conditions to provide a pitch substantially free of undesirable contaminants and suitable for use as a binder in the manufacture of molded carbonaceous articles.

In the manufacture of molded carbonaceous materials, such as carbon electrodes, calcined coke is generally used as the starting material. Since the coke has no natural adhesiveness, it must be bound together in suitable shapes with a compatible material. In producing carbon electrodes, the coke is ground, mixed with a binder, molded and baked to carbonize the binder. A binder used for these purposes must be sufficiently fluid at the temperatures at which it is mixed with solid coke to completely wet and penetrate the coke. In addition to these properties, the binder should have a relatively stable viscosity when held at temperatures of about 200° C. Because of the stringent requirements, commercial pitch binders have been almost exclusively made from selected coal tar products.

The binder which is used in the production of molded carbonaceous articles, especially carbon electrodes, should generally be a stable hydrocarbon mixture of uniform consistency and quality and substantially free of contaminant contents. One of the contaminant contents which has in the past prevented the use of petroleum-derived pitch in carbonaceous articles is a coke-like material. The term "coke" or "coke-like material," as used herein, is an undesirable hydrocarbon having a carbon to hydrogen atomic ratio of about 2.0 or higher and is generally produced as a result of excessive polymerization and condensation reactions which are necessary to produce a pitch binder with desirable properties. A satisfactory pitch binder for carbon electrodes can hold in stable suspension only about 2.5 weight percent coke-like material. At coke concentrations greater than about 2.5 weight percent, the excess coke-like material tends to agglomerate and separate from the pitch producing a non-uniform product and providing a non-uniform binder. The coke-like material has been found to have poor binding properties and does not contribute to the desired characteristics of the finished products. The presence of excess coke in petroleum derived pitch, therefore, is one of the main factors in decreasing bonding characteristics of the pitch binder which results in migration during baking of a carbon electrode and leaves areas of unbonded carbon in the finished article. In this condition, a carbon electrode using a petroleum pitch binder is produced having uneven mechanical strength and is variable in conductivity for these reasons, petroleum pitches were, heretofore, not generally considered satisfactory binders since they failed to meet the stringent requirements of a good

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pitch binder and commercial pitch binders have been almost exclusively produced from coal tar.

In the prior art, a method is described to prepare a pitch binder from a petroleum-derived hydrocarbon. This process thermally cracks a high boiling petroleum hydrocarbon fraction and passes the hot cycle residue into a soaking tank of substantial capacity maintained under superatmospheric pressure. The flow of the cycle residue is regulated through the soaking tank so that the residence time for any given increment of feed stock ranges between about 3 to 5 hours. The initial pitch produced therein is not considered of satisfactory quality and recycled into the soaking tank to improve the quality. However, over the extended soaking time, an excessive amount of coke-like material is produced in the upgrading of the pitch product while some of the excessive coke separates and tends to accumulate at the bottom of the soaking tank. This requires an extensive cleaning operation to remove the undesirable coke which accumulates in the soaking tank. Furthermore, the excess coke produced contaminates the pitch product and provides the undesirable characteristics of a non-uniform pitch binder, heretofore described. In addition to these problems, the extended soaking operation of the prior art process, if used on a commercial basis, is a time-consuming and expensive operation required to improve the quality of the pitch binder.

It is the principal object of this invention to provide an improved process for the manufacture of a satisfactory pitch binder derived from a petroleum-derived hydrocarbon. A further object of the invention is to provide a commercially feasible process wherein satisfactory petroleum-derived pitch binders, which are devoid of excessive coke content, can be produced in a continuous operation. These and other objects will become apparent to those skilled in the art upon the consideration of the following disclosure and appended claims.

In accordance with the present invention, a continuous and improved process for the manufacture of satisfactory petroleum-derived pitch binders is provided which utilizes a combination of cracking various hydrocarbon fractions, thermal cracking of specific hydrocarbon products obtained from the cracking operation and a soaking operation of the thermal asphalt obtained from the thermal cracking operation for a limited period of time and under specific reaction conditions. By this invention, a pitch binder suitable for use in the manufacture of molded carbonaceous articles is produced by contacting a petroleum hydrocarbon fraction which boils predominately above about 400° F. and has an end boiling point as high as 1200° F., with a preferred range of about 400° F. to about 1050° F. with a cracking catalyst under cracking conditions. From the product of the cracking operation, a hydrocarbon fraction boiling predominately above about 500° F. and having an atomic carbon to hydrogen ratio in the range from about 0.6 to about 0.91 is then subjected to a thermal cracking operation under conditions that include a temperature not in excess of 1050° F. and can range from about 850° F. to about 1050° F., for a period of time sufficient to produce a thermal asphalt having a specific gravity in the range from about 1.10 to about 1.20, preferably in the range from about 1.15 to 1.19, at softening points ranging from about 130 to about 180° F. The thermal asphalt obtained from the thermal cracking operation with or without added thermal or soaker gas oils is then subjected to a soaking zone maintained under specific reaction conditions including temperatures ranging from about 900° F. to about 1100° F., a cold liquid residence time ranging from about 4 to about 20 minutes and at pressures ranging from about 30 to about 400 pounds per square inch. The unique

feature of the process of the invention relates to the fact that in utilizing short residence times and high lineal velocities in the soaking step, a continuous process in the preparation of a pitch binder is provided and the pitch binder product of the process is devoid of excessive coke which can be significantly detrimental to the preparation of uniform molded carbonaceous articles.

The hydrocarbon fractions to be catalytically cracked which are utilized herein can be any petroleum-derived hydrocarbon fraction boiling predominately above about 450° F. and not boiling in excess of 1200° F. These hydrocarbon fractions can be obtained by vacuum distillation or like distillation of crude oils such as Mid-Continent, Tia Juana, California Coastal, West Texas, and the like. A preferred hydrocarbon charge is one wherein approximately 10 volume percent of the charge boils in the range from about 500° F. to about 622° F., 50 volume percent of the charge boils from about 600° F. to about 781° F. and 90 volume percent of the charge boils in the range from about 775° F. to about 990° F.

The catalysts which can be used in the cracking operation can be any catalyst which under cracking conditions provides not only satisfactory yields of gasoline but a higher boiling product which boils predominately above about 500° F. and having an atomic carbon to hydrogen ratio in the range from about 0.6 to about 0.91. Among the typical catalysts which can be used are included activated clays, aluminosilicates, silica-alumina, and silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania, as well as ternary combinations such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia, silica-magnesia-zirconia and mixtures thereof. Preferred cracking catalysts used in the process of the invention are a crystalline aluminosilicate, more preferably a crystalline rare earth aluminosilicate having an alkali metal content of less than three weight percent or an admixture of said crystalline aluminosilicate suspended and distributed throughout an inorganic oxide gel matrix such as silica-alumina, and the like, which have cracking properties themselves.

To prepare a crystalline aluminosilicate, a crystalline alkaline metal aluminosilicate, such as described in U.S. 2,882,244, is base exchanged with a solution containing at least one ion capable of substantially replacing the available alkali metal. The base-exchange material is washed free of water soluble matter, dried and if desired subjected to a conventional thermal activating treatment. The resulting crystalline aluminosilicate will have a rigid three-dimensional networks characterized by a uniform effective pore diameter between 6 and 15 Angstrom units.

If the admixture of crystalline aluminosilicate and an inorganic gel is to be used as the cracking catalyst, the procedure of base exchanging the resulting composite substantially free of alkali metal by treating with a solution containing at least one ion capable of replacing the alkali metal, washing the resulting base-exchange material free of water-soluble matter, drying the washed composite and subjecting the same to a thermal activating treatment can be used. Alternatively, the crystalline aluminosilicate may undergo base exchange, as above, prior to intimate admixture thereof with the inorganic oxide hydrogel. In accordance with such manner of operation, the resulting mixture of finely divided previously base-exchanged aluminosilicate distributed throughout and held suspended in a matrix of the inorganic oxide hydrogel, is washed free of soluble matter, dried and thermally activated. The relative proportions of finely divided crystalline aluminosilicate and inorganic oxide gel matrix may vary widely with the crystalline aluminosilicate content ranging from about 2 to about 90 percent by weight and more usually, particularly where the composite is prepared in the form of beads, in the range of about 5 to about 50 percent by weight of the composite.

Base exchange required for introducing the necessary replacing ions is carried out for a sufficient period of

time and under appropriate temperature conditions to replace at least about 90 percent of the alkali metal originally contained in the aluminosilicate and to effectively reduce the alkali metal content of the resulting composite to below about 3 weight percent. It is contemplated that any ionizable compound of a metal capable of replacing the alkali metal may be employed for base exchange either alone or in combination with other ions. Compounds will be used wherein the replacing ion is in the cationic state. Inorganic salts will usually be employed. Suitable materials include soluble compounds of calcium, magnesium, manganese, vanadium, chromium, cerium, aluminum, lanthanum, praseodymium, neodymium, samarium and other rare earths, as well as solutions containing mixtures of these ions and mixtures of the same with other ions, such as ammonium. Organic salts of the foregoing metals, such as acetate and formate may also be used, as well as very dilute or weak acids.

Cracking, utilizing the catalyst described herein, may be carried out at catalytic cracking conditions employing a temperature within the approximate range of about 600° F. to about 1200° F., preferably, in the range from about 800° F. to about 1000° F. and under a pressure ranging from subatmospheric pressure up to several hundred atmospheres, preferably in the range from about 5 to about 30 pounds per square inch gauge. The contact time of the oil within the catalyst is adjusted in any case according to the conditions, the particular oil feed and the particular results desired to give a substantial amount of cracking to lower boiling products. In the process of this invention, the liquid hourly space velocity can range from about 0.5 to about 5.0, preferably in the range from about 0.8 to about 2.5. The volume of catalyst to the volume of oil ratio can range from about 0.8 to about 20, preferably in the range from about 1.5 to about 4.0. Cracking may be effected in the presence of the instant catalyst utilizing well-known techniques including, for example, those wherein the catalyst is employed as a fluidized mass or as a compact particle-form moving bed. The hydrocarbon product of the above-described catalytic cracking operation is then distilled to remove the gasoline, gas oil products and the like to recover a hydrocarbon fraction which boils predominately above about 500° F. and having an atomic carbon to hydrogen ratio in the range from about 0.6 to about 0.91 which is to be thermally cracked.

The thermal cracking of the catalytically cracked hydrocarbon boiling predominately above about 500° F. and having an atomic carbon to hydrogen ratio between about 0.6 and about 0.91 is conducted at temperatures within the range of about 850° F. to about 1050° F., preferably in the range from about 940° F. to about 1040° F. and at pressures in the range from about 250 to about 900 pounds per square inch gauge, preferably in the range from about 300 to about 700 pounds per square inch gauge. The severity of the thermal cracking operation is controlled so as to provide a thermal asphalt having a soft point in the range from about 130° F. to about 180° F., preferably in the range from about 140 to about 170° F. and a specific gravity in the range from about 1.00 to about 1.20, preferably in the range from 1.15 to 1.19. The product of the thermal cracking operation can be distilled to remove the gas, gasoline and part of the gas oil products from the thermal asphalt product. Part of the gas oil product can be recycled through the cracking step preferably through a separate cracking coil.

The thermal asphalt produced in the thermal cracking operation with or without added recycle gas oil is then passed through a continuous soaking zone. The soaking zone is maintained at temperatures in the range from about 900° F. to about 1100° F., preferably in the range from about 940 to about 1020° F. and pressures in the range from about 30 to about 400 pounds per square inch, preferably in the range from about 100 to 200

pounds per square inch gauge. The thermal asphalt is passed through the soaking zone at such a rate so as to obtain a liquid residence time of the pitch of at least about 4 minutes to no greater than 20 minutes, preferably in the range from about 7 to about 15 minutes. Liquid residence times of the thermal asphalt must not exceed 20 minutes and the recycle of the pitch product in the soaking zone cannot be tolerated in preparing a pitch substantially devoid of excess coke. If desired although not critical, the gas oil which may be produced in the soaking zone or gas oil produced in the thermal cracking operation up to 35 percent of the thermal asphalt feed can be recycled or cycled into the soaking zone to help maintain the liquid level and also aid in maintaining uniform temperatures in the soaking step.

The use of pressures and specific residence times are essential in the soaking zones to avoid the formation of excess coke in the pitch binder product. At temperatures in excess of 900° F. and pressures below 30 pounds per square inch gauge, the thermal asphalt being soaked would tend to lose its volatile components and establish a condition where large amounts of coke would be formed. At liquid residence times in excess of 20 minutes, it will be shown, hereinafter, that the amount of coke produced in the pitch binder product is in excess of 2.5 weight percent and, as has been heretofore described, this high quantity of coke is undesirable from the standpoint of a practicable unit operation for a pitch binder to be used in the preparation of carbon electrodes.

The following specifications have been suggested as indicative of a satisfactory binder for carbon electrodes:

Softening point ¹° F.	190-250
Minimum atomic carbon to hydrogen ratio ² ...	1.4
Specific gravity, 77/77° F.....	1.24-1.32
Minimum benzene insolubles, ³	
weight percent.....	15
Minimum beta resins, ⁴ weight percent.....	14
Coking value ⁵	50-55
Maximum sulfur, weight percent.....	1.25
Maximum ash, weight percent.....	0.15

¹ The term "soft point" as used herein, is the soft point determined by Method D-7 in "Methods of Testing Coal Tar Products" (1950), published and copyrighted by the Barrett Division of Allied Chemical and Dye Corp., New York, New York.

² The term "atomic carbon to hydrogen ratio," as used herein, refers to the atomic carbon to hydrogen ratio determined in accordance with the method described on page 80 of "Organic Quantitative Microanalysis" (John Wiley and Sons, 2nd Edition, 1942).

³ The term "benzene insolubles" refers to the benzene insolubles determined by Method B-7 in "Methods of Testing Coal Tar Products" (1950), published and copyrighted by the Barrett Division of Allied Chemical and Dye Corporation, New York, New York.

⁴ The term "beta resins" is the benzene insolubles minus the quinoline insolubles which are determined by Method B-21 of the aforementioned "Methods of Testing Coal Tar Products."

⁵ Coking value determined as "Conradson Carbon residue" which is determined by test designation D189-52 of the American Society of Testing Materials.

Pitches which are satisfactory as binders have, however, been made which did not meet one or more of these specifications. The only really satisfactory test is to manufacture an article, such as a carbon electrode or a test electrode compression block, with the pitch and test that article. Pitches prepared in accordance with the process of this invention when so treated are found to be satisfactory.

The invention is illustrated in the attached drawing, which is a highly diagrammatic flow sheet of a process operated in accordance with this invention.

The drawing illustrates an embodiment of this invention. A petroleum hydrocarbon fraction having an initial boiling point above about 400° F. and an end boiling point as high as 1200° F. is supplied to a catalytic cracker 10 by means of passage 11. The catalytic cracker may be of any conventional design. The most commonly used are Fluid Catalytic Cracking and Thermo-

cracking. The thermal asphalt is continuously moved between a reaction zone and a regeneration zone and the cracking reaction is normally conducted at a temperature within the range 850° F. to 925° F.

The catalytically cracked product is supplied to a distillation column 12 from which there may be taken as products a gas stream through line 13, gasoline through line 14, a catalytic fuel oil or light gas oil through line 15 and heavy gas oil or bottoms product through line 16. A part or all of the catalytic fuel oil which might typically boil within the range about 400° F. to 650° F. may be taken as product through line 17. A part or all of this material may also be recycled to catalytic cracker 10 through lines 18 and 19. Still another option is to pass a part or all of this material to thermal cracking unit 22 through line 21.

Similarly, with the bottoms material withdrawn as product through line 23, it may also be recycled to catalytic cracker 10 through lines 20 and 19 or passed to thermal cracker 22 through lines 24 and 21. The material which passes to thermal cracking unit 22 will therefore be a catalytic gas oil boiling, for example, within the range from about 400° F. to about 1000° F., having an atomic carbon to hydrogen ratio in the range from about 0.6 to about 0.91.

This catalytic gas oil is then thermally cracked in zone 22 which operates in a manner conventional to thermal cracking operations in oil refineries. Generally, the temperature of cracking should be within the range 900 to 1050° F. and preferably within the range 940 to 1040° F. Pressures within the range 250 to 900 pounds per square inch gauge and preferably 300 to 700 pounds per square inch gauge are employed. The thermal cracking operation should employ recycle of thermal gas oil boiling somewhere above gasoline and below the asphalt specified below. Typically, this gas oil might boil from about 400° F. to 1000° F. The recycle is injected through line 25 to a separate cracking coil. Recycle ratios within the range 2 to 8, and preferably 3 to 5 volumes of total feed per volume of fresh feed through line 15 to the thermal cracking operation can be used.

The product of the thermal operation is quenched, for example, by injection of cooled bottoms of fractionator 23 through line 26 and by application of outside cooling in cooler 27. The thermally cracked product is then fractionated in fractionator 28 to produce gas through line 29, thermal gasoline through line 30, gas oil through line 31 and thermal asphalt through line 32.

The thermal asphalt obtained from line 32 must have a soft point within the temperature range from about 130° F. to about 180° F. and a specific gravity in the range from about 1.15 to 1.19. This may then be combined with recycle gas oil either from the thermal cracking step or the soaking step. It is essential to this invention that the thermal asphalt charged to soaking coil have a soft point no higher than about 180° F. With a thermal asphalt having soft points higher than this range, it is not possible to produce satisfactory pitches without excessive coke production in the continuous soaking step described below.

The thermal asphalt is passed via line 32 to the soaking coil 33 in a suitable furnace. The flow of the thermal asphalt is controlled in the soaking coil to provide liquid residence times of said asphalt for at least about 4 minutes and no greater than about 20 minutes. The resulting product of the soaking coil 33 is then passed via line 35 to a flash tower 36 which flashes the off gases and gasoline through line 37 to a bubble tower 38 separating the off gas and gasoline. Bottoms from the flash tower after cooling in cooler 34 are used to quench the product from the soaking coil. The gas oil and pitch binder product is passed via line 39 to a vacuum tower 40 where the pitch binder and gas oil are separated. If desired, a portion of the gas oil obtained in the soaking operation can be recycled through line 41 to combine with thermal

asphalt and passes to the continuous soaking coil. It should be understood that other modifications within the scope of this disclosure can be made to the accompanying drawing.

The following examples will further illustrate the process of the invention without limiting the same:

EXAMPLE 1

The petroleum charge stock used in the catalytic cracking operation had the following properties:

Gravity, ° API	24.9
Distillation boiling point (vacuum assay), ° F.:	
10 volume percent	445
50 volume percent	510
90 volume percent	690
End point	825
Sulfur, weight percent	0.95

This charge stock was subjected to a conventional cracking operation using an acid treated clay cracking catalyst having the following properties:

Surface area, m. ² /gram	145
Activity (A.I.)	30
Loose density, g./cc	0.70
Packed density, g./cc	0.79
Average particle diameter, inch	0.16
Diffusivity, (c. ² /sec.) × 10 ³	50

The cracking conditions are listed as follows:

Temperatures, ° F.:	
Vapor inlet	890
Catalyst inlet	1014
Vapor outlet	895
Catalyst to oil volume ratio	1.7
Recycle ratio of 425° F. to 630° F. boiling range material per volume of fresh feed, volume	0.8

The amount of conversion of fresh feed charge stock to products boiling below a gasoline of 369° F. @ 90 percent point was 44.5 volume percent. From the catalytic cracked products, 12.4 volume percent of syntower bottoms were obtained having the following properties:

Gravity, ° API	11.4
Distillation boiling points, ° F. (vacuum assay):	
10 volume percent	648
50 volume percent	747
90 volume percent	835
End point	902
Sulfur, weight percent	0.7
Aniline point, ° F.	120
Atomic carbon to hydrogen ratio	0.767

The syntower bottoms above were thermally cracked at a temperature of 940° F., an outlet pressure of 400 pounds per square inch gauge and a recycle ratio of gas oil to fresh feed of 3.0. The recycle oil was thermally cracked at a maximum temperature of 1040° F. and 400 pounds per square inch gauge outlet pressure. The yields of the major products of the thermal cracker based on the syntower bottoms charged are listed as follows:

Dry gas, weight percent	11.2
Butanes, weight percent	3.6
Pentanes, weight percent	2.8
Gasoline, weight percent	15.3
Gas oil, weight percent	6.1
Thermal asphalt, weight percent	61.0

The thermal asphalt obtained above has a soft point of 160° F. and a specific gravity of 1.187. This thermal asphalt is combined with 10 weight percent soaker gas oil obtained from the soaking operation to provide a thermal tar having a specific gravity of 1.165 and a soft point of about 110° F. The resulting thermal tar is passed through

the continuous soaking zone at various residence times. The conditions and results are listed in Table I below:

Table I

Conditions:	4.2	9.7	9.8	18.5	30.3
Residence time, minutes	4.2	9.7	9.8	18.5	30.3
Temperature, Reactor Outlet, ° F.	1,005	960	970	945	920
Pressure, pounds per square inch gauge	60	120	120	120	120
Yields, weight percent (Based on thermal asphalt charged):					
Pitch Binder	79.6	73.6	74.3	75.4	74.5
Liquid products (including gas oil)	18.5	23.3	22.0	19.3	17.9
Gas	1.9	3.0	3.0	3.0	3.2
Coke (in pitch binder)	<0.5	0.1	0.7	2.3	4.4
Pitch Binder Properties:					
Soft Point, ° F.	230	230	230	230	-----
Specific Gravity, 77/77° F.	1.252	1.252	1.248	1.256	-----
Coking Value, weight percent	51.8	50.9	52.4	52.3	-----
Benzene Insoluble, weight percent	25.0	24.8	25.9	30.0	-----
Quinoline Insoluble, weight percent	2.8	1.9	1.6	3.5	-----
Beta Resins, weight percent	22.3	22.9	24.3	26.5	-----

The pitch binders produced on continuous soaking of the thermal asphalt at residence times below about 20 minutes all produced satisfactory binders for carbon electrodes. Continuous soaking at a residence time of 30.3 minutes does not provide a suitable operation in view of its high coke yield and consequent short on-stream time.

EXAMPLE 2

A portion of thermal asphalt used in the continuous soaking zone in Example 1 is subjected to a batch soaking procedure having a total residence time of 5 hours. The soaking operation is conducted at a maximum temperature of 820° F. and a pressure of 30 pounds per square inch under the following conditions.

Residence time:

- 1 hour at temperatures from 700° F. to 760° F.
- 1 hour at temperatures from 760° F. to 780° F.
- 1 hour at temperatures from 780° F. to 800° F.
- 1 hour at temperatures from 800° F. to 820° F.
- 1 hour at a temperature of 820° F.

Total residence time, 5 hours.

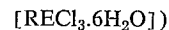
Yield:

Pitch binder, weight percent (based on thermal asphalt charged)	71
Liquid products	20
Gas	3
Coke (in binder)	6

This pitch binder produced here is not considered practicable for commercial operation because of its high coke yield and because the pitch produced is not uniform in consistency and quality.

EXAMPLE 3

A crystalline sodium aluminosilicate, as described in U.S. Patent 2,882,244 identified as 13-X molecular sieve, was base exchanged with a rare earth chloride solution (containing 4 percent of rare earth chloride



at 180–200° F. to remove the sodium ions from the aluminosilicate and replace them with the chemical equivalent of rare earth ions. The rare earth chlorides used had the following analysis determined as oxides.

Compound:	Weight Percent
La ₂ O ₃	24
Ce ₂ O ₃	48
Pr ₆ O ₁₁	5
Nd ₂ O ₃	17
Sm ₂ O ₃	3
Gd ₂ O ₃	2
Y ₂ O ₃	0.2
Other RE oxides	0.8

After the base exchange, the aluminosilicate was then washed free of soluble salts, the rare earth aluminosilicate produced contained 1.0–1.5 weight percent sodium and about 23 weight percent rare earth ions calculated as R_2O_3 .

A total of 1562 pounds of finished bead catalyst was made by adding finely ground rare earth aluminosilicate, prepared above, and alumina fines to a sodium silicate solution in the weight proportions of 1.0 rare earth aluminosilicate; 5.3 inert alumina fines (Alcoa A-2); $8.3SiO_2$ from sodium silicate solution. A stream of this slurry was then mixed with a stream of acid alum solution (Al_2O_3 from acid alum solution is 0.65 to 1.0 rare earth aluminosilicate in above proportion scheme) and then passed over a cone, wherein droplets were formed. These droplets form into bead hydrogel during the falling period through a tower containing an immiscible oil. This bead forming method is conventional for manufacture of bead cracking catalyst.

The resultant gel beads were base exchanged with an aqueous ammonia sulfate solution containing 1.4 weight percent ammonia sulfate to remove sodium from the silica-alumina matrix mixture and the resultant product was washed free of water soluble salts. The silica-alumina matrix mixture was dried at 250–300° F. to remove the water and then calcined for 4.4 hours at 1250° F. and 15 pounds per square inch pressure in 100 percent steam. The finished catalyst contained 7 weight percent of rare earth aluminosilicate, 34 weight percent of alumina fines and the remainder was cogelled silica-alumina. The catalyst had the following properties:

Loose density, g./cc.....	0.71
Packed density, g./cc.....	0.77
Average particle diameter, inches.....	0.14
Surface area, square meters per gram.....	132
Diffusivity ($cm.^2/sec.$) $\times 10^3$	47

The catalyst, above, utilized under the cracking conditions described in Example 1 was used to crack a hydrocarbon gas oil having the same properties as the hydrocarbon gas oil described in Example 1.

The amount of conversion of fresh feed charge stock to products boiling below a gasoline of 369° F. @ 90 percent point was 67.1 volume percent. From the cracked products 6.4 volume percent of syntower bottoms was obtained having the following properties.

Gravity, ° API.....	2.8
Distillation boiling points, ° F. (vacuum assay):	
10 volume percent.....	737
50 volume percent.....	766
90 volume percent.....	936
95 volume percent.....	1013
Sulfur, weight percent.....	0.61
Aniline point, ° F.....	116
Atomic carbon to hydrogen ratio.....	0.895

The syntower bottoms, above, were thermally cracked at a coil outlet temperature of 940° F., an outlet pressure of 400 pounds per square inch gauge and a recycle ratio of gas oil to fresh feed of 3.0. The yields, the major products of the thermal cracker based on the syntower bottoms charged, are listed as follows.

Dry gas, weight percent.....	11.9
Butanes, weight percent.....	3.6
Pentanes, weight percent.....	2.7
Gasoline, weight percent.....	16.0
Gas oil, weight percent.....	3.0
Thermal asphalt, weight percent.....	62.8

The thermal asphalt obtained, above, has a soft point of 158° F. and a specific gravity of 1.1190. The thermal asphalt is combined with 10 weight percent soaker gas oil obtained from the soaking operation to provide a thermal asphalt having a specific gravity of 1.169 and a soft point of 110° F. The resulting thermal asphalt is passed through the continuous soaking zone at a residence time

of 10 minutes, temperature of the reactor outlet of 970° F., and a pressure of 120 pounds per square inch gauge. The following yields based on the thermal asphalt are obtained.

5 Pitch binder, weight percent.....	76.7
Liquid products, weight percent (including gas oil) ..	19.6
Gas, weight percent.....	3.1
Coke (in binder).....	0.6
10 The pitch binder properties obtained are listed as follows.	
Soft point, ° F.....	230
Specific gravity, 77/77° F.....	1.253
Coking value, weight percent.....	53.7
Benzene insolubles, weight percent.....	27.5
15 Quinoline insoluble, weight percent.....	2.5
Beta Resins, weight percent.....	25.0

In using the catalyst above, containing rare earth aluminosilicate, the syntower bottoms are found to contain a product having an appreciably higher aromatic content than the activated clay catalyst of Example 1. The higher aromatic content syntower bottoms results in higher thermal asphalt yields, higher yields of finished binder pitch, improved thermal asphalt qualities and generally lower coke yields. In view of these improvements, the catalyst containing the rare earth aluminosilicate is considered more preferable for use in the catalytic cracking operation of this invention.

EXAMPLE 4

30 The pitch binder product from the continuous soaking of thermal asphalts as prepared in Examples 1 and 3 has excellent binding characteristics for electrodes used in the aluminum industry as shown in the following comparison with standard coal tar pitch:

	Continuous Soaking petroleum pitch	Coal Tar pitch
40 Test Electrode Composition:		
Binder, weight percent.....	28	28
Calcined coke aggregate, weight percent.....	72	72
Calcined Test Electrode Properties:		
Apparent density, grams/cc.....	1.55	1.53
Resistivity, ohms./in./cm. ²	54.9	59.5
45 Crushing strength, pounds per square inch.....	6,575	6,550

It should be noted that in the preparation of carbon electrodes, the use of the pitch binder produced by the process of this invention provides carbon electrodes having the improved properties of a decreased resistivity and increased crushing strength over an electrode produced using a standard coal tar pitch.

What is claimed is:

1. A continuous process for producing a petroleum-derived pitch which is suitable for use as a binder in the manufacture of molded carbonaceous materials which comprises contacting a petroleum hydrocarbon fraction having an initial boiling point above about 400° F. and an end boiling point of about 1200° F. with a cracking catalyst under catalytic cracking conditions; removing from the resulting product a catalytically cracked hydrocarbon fraction boiling predominately above about 500° F. and having an atomic carbon to hydrogen ratio in the range from about 0.6 to about 0.91; subjecting said catalytically cracked hydrocarbon fraction to thermal cracking under conditions that include a temperature in the range from about 850° F. to about 1050° F. producing a thermal asphalt having a soft point in the range from about 130° F. to about 180° F. and a specific gravity in the range from about 1.10 to about 1.20; passing said thermal asphalt through a heat soaking zone at pressures in the range from about 30 to about 400 pounds per square inch gauge and at temperatures in the range from about 900° F. to about 1100° F. at a residence time from about 4 to about 20 minutes.

2. A continuous process for producing a petroleum-derived pitch which is suitable for use as a binder in the manufacture of molded carbonaceous materials which comprises contacting a petroleum hydrocarbon fraction having an initial boiling point above about 400° F. and an end boiling point of about 1050° F. with a cracking catalyst under catalytic cracking conditions; removing from the resulting product a catalytically cracked hydrocarbon fraction boiling predominately above about 500° F. and having an atomic carbon to hydrogen ratio in the range from about 0.6 to about 0.91; subjecting said catalytically cracked hydrocarbon fraction to thermal cracking under conditions that include a temperature in the range from about 850° F. to about 1050° F. producing a thermal asphalt having a soft point in the range from about 140° F. to about 170° F. and a specific gravity in the range from about 1.15 to about 1.19; passing said thermal asphalt through a heat soaking zone at pressures in the range from about 30 to about 400 pounds per square inch gauge and at temperatures in the range from about 940° F. to about 1020° F. at a residence time from about 4 to about 20 minutes.

3. A continuous process for producing a petroleum-derived pitch which is suitable for use as a binder in the manufacture of molded materials which comprises contacting a petroleum hydrocarbon fraction having an initial boiling point above about 400° F. and an end boiling point of about 1050° F. with a cracking catalyst under catalytic cracking conditions; removing from the resulting product a catalytically cracked hydrocarbon fraction boiling predominately above about 500° F. and having an atomic carbon to hydrogen ratio in the range from about 0.6 to about 0.91; subjecting said catalytically cracked hydrocarbon fraction to thermal cracking under conditions that include a temperature in the range from about 850° F. to about 1040° F. producing a thermal asphalt having a soft point in the range from about 140° F. to about 170° F. and a specific gravity in the range from about 1.15 to about 1.19; passing said thermal asphalt through a heat soaking zone at pressures in the range from about 100 to about 200 pounds per square inch gauge and at temperatures in the range from about 940°

F. to about 1020° F. at a residence time from about 7 to about 15 minutes.

4. The process of claim 3 wherein the cracking catalyst is an aluminosilicate having an alkali metal content of less than about three weight percent.

5. The process of claim 3 wherein the cracking catalyst is a rare earth aluminosilicate having an alkali metal content of less than about three weight percent.

6. The process of claim 3 wherein the cracking catalyst consists essentially of about 2 to about 90 weight percent of an aluminosilicate having an alkali metal content of less than about three weight percent and suspended and distributed throughout an inorganic oxide gel matrix.

15 7. The process of claim 3 wherein the cracking catalyst consists essentially of about 2 to about 90 weight percent of rare earth aluminosilicate containing an alkali metal content of less than about three weight percent and suspended and distributed throughout a siliceous-alumina oxide gel matrix.

8. The process of claim 3 wherein the cracking catalyst consists essentially of an acid-treated clay.

9. A continuous process for producing petroleum-derived pitch which is suitable for use as a binder in the manufacture of molded carbonaceous materials which comprises flowing thermal asphalt having a specific gravity in the range of 1.10 to 1.20 and having a softening point in the range of about 130° to about 180° F. through a heat-soaking zone at a pressure in the range of about 30 to about 400 pounds per square inch gauge at a temperature in the range of about 900° F. to about 1100° F., and for a residence time in the range of about four to about twenty minutes and continuously separating gases, gasoline, and gas oil from pitch binder product, said thermal asphalt being derived from catalytically cracked hydrocarbon fraction boiling predominantly above 500° F. having an atomic carbon to hydrogen ratio in the range of about 0.6 to about 0.91.

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