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PRODUCTION OF COKE FROM PETROLEUM HYDROCARBONS

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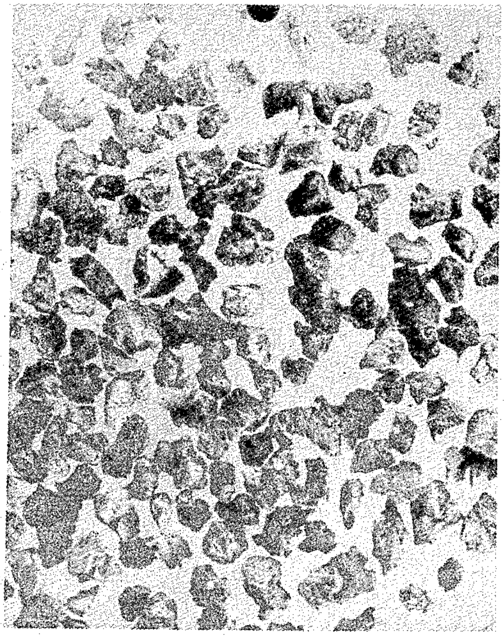
Fig. 2.



NON-NEEDLE COKE

Fig. 1.

NEEDLE COKE

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PRODUCTION OF COKE FROM PETROLEUM HYDROCARBONS

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This invention relates to a process for manufacturing coke from petroleum residues. More particularly, it relates to a method of producing coke having a needle-like structure.

Petroleum hydrocarbons having high boiling ranges undergo thermal decomposition at temperatures in the range of about 350° to 600° C. to produce solid infusible materials referred to as coke.

Coking is conventionally carried out in vessels into which a batch of heavy oil is charged and coked by external heating, or in coking drums into which hot residuum is charged continuously with or without added heat until the coke layer builds up and the drum is full. The latter is probably the most widely used method.

The principal charging stocks for coking operations are high boiling virgin or cracked petroleum residues which may or may not be suitable as heavy fuel oils. The operation is carried out in conjunction with the cracking operation and the principal consideration is a balancing of the operations so that the residue is coked at the same rate as produced. An important use of coke is as domestic or industrial fuel although a substantial tonnage is processed and used in making carbon or graphite electrodes for use in the metals industries. It is with coke for the latter purposes that this invention is concerned.

Not all petroleum cokes are useful in electrode manufacture, especially for the production of graphite electrodes. Cokes having properties particularly suitable in graphite electrodes command premium prices and are widely sought, but the demand far exceeds the supply. Extensive research has been conducted to determine why some cokes are superior to others, and to devise methods for increasing the supply. The quality of such cokes has heretofore been regarded as inherent in the crude oil source.

I have found that cokes most desirable for graphite electrodes have a striated appearance throughout the particles. When crushed to a fine size, they have a high metallic luster and needle-like structure. The needle produces an X-ray diffraction pattern showing crystal orientation that is not present in the structure of ordinary coke.

So far as I am aware, no method has been described for producing coke of this needle-like structure from petroleum residues. Coking any residue by any conventional means in the main produces non-needle coke.

I have discovered methods for producing needle coke from certain petroleum residues by converting the same to a thermally stable product by one or more treatments hereinafter described, followed by coking the resulting product under carefully controlled conditions. The combination treatment makes available high-grade needle coke from stocks from which it otherwise cannot be produced.

Under the conditions employed in conventional coking operations most petroleum residues produce a massive, relatively porous type of coke which has a dull gray-black sheen. When crushed this coke breaks into lumps of irregular shape. It generally has no regular structure as in most instances the dimensions of the particles are about the same in all directions.

It is an object of the present invention to produce a coke having a needle-like or splintery structure which is less porous than the usual type of coke and which has a high metallic sheen or luster, from charging stocks not suitable for this purpose when coked by known processes.

The needle-like coke produced by this invention is particularly useful in the production of graphite electrodes for electric furnaces. The graphite electrodes produced from this coke are characterized by lower resistivity and lower coefficient of thermal expansion (300–800° C.) than any other graphite electrodes known to me.

Figure 1 is a photomicrograph of needle coke. Figure 2 is a photomicrograph of a conventional non-needle coke. The photomicrographs were taken of coke particles of 20 to 40 mesh size, and are magnified 10 times.

In a broad embodiment the present invention comprises removing the major portion of the material contained in heavy petroleum hydrocarbon residues which tends to readily form an insoluble phase on heating in the range of about 350°–550° C., and thereafter subjecting the remaining liquid hydrocarbons to thermal coking under conditions such that the liquid hydrocarbons are in a state of substantial quiescence or thermal homogeneity during the solidification thereof and such that the temperature gradient through the body of liquid hydrocarbon is small.

One embodiment of the invention comprises heating a heavy petroleum residue at a temperature of 325°–500° C. for a time sufficient to form a precipitate, separating the liquid oil from the insoluble material formed, and subjecting the liquid oil to homogeneous coking conditions in a quiescent pool maintained without agitation except for the natural movement of vapors evolved during coking, and recovering the coke thus formed.

The residues with which this invention is particularly concerned are produced either by the thermal cracking of petroleum crude oils or as a residue remaining after the distillation of gasoline, kerosene or higher boiling fractions from crude oils. The oils are those which, in the condition they are produced, cannot be converted into coke of the needle-like structure. These include particularly the so-called asphalt base and naphthenic base oils. In general, such oils are characterized by containing a substantial proportion of the order of about 1 to 10% or more of components which are rendered insoluble by heating at a temperature of 325°–400° C., for example 375° C. for six hours, and which tend to coke before the main body of the oil. These components are insoluble in low boiling paraffinic hydrocarbons such as liquid propane, liquid butane, liquid pentane and the like and can be precipitated from the oil by adding such hydrocarbons to the residue. The residue oils are characterized by an asphaltene content of about 1–10% or more by weight as determined by A. S. T. M. procedure D893–46T. Cracked or straight run residuums produced from Mid-Continent, East Texas, West Texas, Arabian and similar crude oils are examples of those which require treatment according to the present invention in order to produce needle-type coke.

In order to be suitable for the production of needle coke which is to be used in the manufacture of graphite electrodes the residue should have a comparatively low sulfur content, namely, below about 1.5% and preferably below about 1%.

The residue should preferably have a high initial boiling point and in general should not contain more than about 25 to 30% distilling below 360° C. and should preferably have an initial boiling point above about 250° C. Such residuums upon distillation to dryness in the Engler distillation test will leave about 5% or more of bottoms and coke in the flask. The residues as produced by cracking or topping contain very little insoluble material removable directly by filtration or centrifuging, say less than 1% and generally of the order of 0.3% or less. The undesirable constituents are substantially completely dissolved in the oil as received from the still or cracking unit.

One method of preparing a suitable charging stock for the needle coking operation is by flash distilling about 80 to 95% of the hydrocarbon from a residuum of the type described above, leaving a substantially solid pitch or coke amounting to 5 to 20% of the oil charged. This operation may be carried out in one of several ways. A batch distillation may be conducted in which a body of the oil in an appropriate still is heated to the boiling point and the evolved vapors are removed overhead, either being passed directly to a coking unit or through a cooler and collected ready for coking. The coke or pitch-like residue remaining in the still may be removed and used for other purposes, but is not suitable for use in manufacture of graphite electrodes. During the distillation, care should be taken that there is little or no entrainment of the charge by the vapors. This may be done, e. g., by passing the vapors through a knock-out drum or a column containing baffles, packing, bubble caps, or the like.

It is within the scope of the invention that the vapors from the still may be passed directly into a coking drum.

Another method for carrying out the preparation of suitable charging stock is to preheat the residuum in a conventional pipe coil to a temperature in the range of about 400° to 600° C. and continuously pass the oil into a flash distillation zone from which vapors are taken overhead and the nonvolatile residue contained in the charging stock accumulates in the flash drum. The vapors from the flash drum may then be coked as hereinafter described. The oil passing through the pipe still may be maintained under a superatmospheric pressure sufficient to prevent vaporization of the residuum and the flash drum may be held at a lower pressure including subatmospheric. Care should be taken that the residence time and temperature in the coil and flash drum is not sufficient to cause the major portion of the hydrocarbons to be converted to coke at that stage.

Another method for preparing the charging stock for the needle coking operation is to charge a batch still with the residuum and to raise the temperature of the charge to about 325° to 400° C. although with certain stocks and under some conditions higher temperatures may be reached. The pressure may be atmospheric or above. The time required in this temperature range is in excess of about five hours, and is generally about 10 to 30 hours. In any event, the temperature and time should be correlated to polymerize the most reactive constituents of the residuum, thereby forming a precipitate of granular, coke-like material amounting to about 1–10% or more of the charge and usually of the order of about 2% to about 6%. This constitutes to a large extent material which tends to coke under milder conditions of temperature and time than should be used for coking the main body of the oil. During the course of this heat soaking operation the heating is regulated to give time for the reactive constituents to undergo polymerization and to form insoluble coke-like bodies. Generally, the temperature is gradually raised as the soaking treatment progresses from say 325° to about 400°–425° C.

If the residue contains fraction boiling in or below this range, a distillate fraction may be taken overhead. During the course of the distillation and heat treatment just described, additional quantities of residuum may be added to the still from time to time. The residue left in the still is coke from the more reactive components of the feed, plus a heavy, high boiling hydrocarbon liquid concentrate capable of making excellent needle coke. The liquid is separated from the coke by filtration or other means before being used to make needle coke. The total liquid concentrate recovered from the still in this way amounts to about 10–60% of the original residuum and in most instances represents a minor proportion of the starting oil. The concentrate is convertible to coke in yields of about 30–65%.

In the heat treating step only so much of the oil should be taken overhead as will leave a product of sufficiently low viscosity, at least in the heated stage, which is readily centrifuged or filtered to remove suspended materials formed during the heat treatment.

The insoluble material is amorphous, has no well-defined structure, does not have the needle-like appearance of the coke produced as hereinafter described and is a relatively porous, dull, massive coke devoid of needle structure.

The filtered oil is then ready for the coking step and may be passed to the coke drum with or without cooling between the stages.

Another method for producing needle coke feed stock comprises heating the residuum under pressure at a temperature of about 400 to 600° C. until 5 to 10% or more of the residuum has precipitated. This may be done by heating in a pipe still and then passing the oil into an insulated pre-coking drum wherein the principal thermal polymerization of the residue occurs. Conditions prevailing in the heat treating vessel and subsequent treatment may be as described above.

It is also possible to add a polymerization catalyst such as activated clay, silica alumina catalyst, activated alumina and the like to increase the rate or reduce the temperature at which the insoluble phase forms in either of the last two methods.

According to another embodiment, liquid residuum is mixed with a low boiling liquid paraffinic hydrocarbon such as liquid propane, liquid butane, pentane, hexane and the like. The proportion of paraffin to residue is suitably about 1:1 to 10:1 or more. The major portion of the hydrocarbon residuum dissolves and a mass of heavy, viscous or normally solid substances ordinarily referred to as asphaltenes precipitates. The mixture may be filtered, if necessary, or allowed to settle and the clean solution of oil in low boiling paraffin is recovered. The solvent is removed from the heavy residuum by distillation. The purified residual oil thus obtained may then be subjected to the hereinafter described coking step.

An alternative method for producing needle coke feed stock involves an initial distillation of high boiling virgin or cracked petroleum residuums followed by a selective solvent extraction. The distillation may be carried out at sub-atmospheric pressure, or according to one of the methods described above. For example, topped or reduced crude oil may be vacuum distilled to produce an overhead which may have lubricating qualities. The overhead fraction may then be extracted using a solvent such as furfural, phenol, liquid sulfur dioxide, and the like, which are selective for aromatic hydrocarbons. The extract phase may be separated from the raffinate, the solvent removed and the hydrocarbon extract thus recovered may be subjected to the needle coking operation. The extract is capable of yielding relatively high proportions of coke.

According to another method, a needle coking stock may be made in the following manner: a charging stock for catalytic cracking is prepared from petroleum oils by one of the known processes. These generally embody removal of a gas oil fraction from crude oil by distillation; recovery of coke still overhead; or by the propane or butane treatment of virgin petroleum residues to remove asphaltenes, etc. These charging stocks may be passed to a catalytic cracking process involving fixed bed, moving bed or the so-called fluidized catalyst processes. The oil is cracked at a temperature of the order of 400°–500° C., the cracked vapors being fractionated to separate gas, gasoline, a distillate or side stream recycle stock and a heavy, highly aromatic residue. The highly aromatic residue which may have an A. P. I. gravity of about 15, is subjected to the needle coking operation hereafter described. The coke still overhead may be returned to the catalytic cracking step.

According to another method, needle coke stock may be prepared in the following manner: a Mid-Continent virgin crude oil is subjected to a straight thermal distillation. The gas oil fraction from this operation is conducted to a catalytic cracking zone maintained at a temperature between 400–500° C. to produce gas, gasoline and a catalytically cracked gas-oil or cycle oil. The latter product is subjected to an additional cracking operation in a catalytic zone within the aforementioned temperature range to produce gas, gasoline and a recycle oil. The later product is passed to a thermal cracking unit after being heated to a temperature of about 525° C. The thermal cracking operation may be conducted at pressure slightly above atmospheric up to 400 p. s. i. This operation produces gas, gasoline and a heavy, high-boiling refractory hydrocarbon material which is commonly referred to as "pressure tar." This material has an A. P. I. gravity between —3.0 to about 5.0. This "pressure tar" is subjected to the needle coking operation hereinafter described. Alternatively, a mixture of catalytically cracked cycle oil and virgin gas-oil from the first thermal distillation may be fed to the thermal cracking unit to produce the "pressure tar." Under normal operations the virgin gas-oil produced in the initial straight distillation has a sufficient amount of asphaltenes or other ready coke producers removed during that operation so that they will not contaminate the "pressure tar" and inhibit or prevent formation of needle coke in the coking operation.

The needle coking step is carried out by passing the treated oil at a temperature above about 350° C. and preferably between about 375° to 500° C. into a coking drum usually of the vertical type.

As the oil accumulates and heat-soaks in the coking vessel under uniform conditions which preclude large thermal gradients, it gradually undergoes polymerization and cracking with evolution of gas and vapors which are removed from the still. The oil gradually becomes more viscous until it eventually solidifies. The specific gravity increases as coking proceeds so that incoming oil tends to float on top. If the viscous oil is maintained in a state of thermal homogeneity, especially during the critical stage just before solidification of the charge occurs, the coke produced has a striated appearance and is metallic in sheen. The striations extend throughout the body of the coke.

If the pool of oil is disturbed by maintaining a high heat gradient setting up a high degree of thermal circulation or turbulence, needle coke formation is impaired and may be prevented.

The formation of needle coke is primarily dependent on two factors (1) a clean charging stock and (2) coking in such a manner that a minimum of thermal gradient obtains, especially during the period that the oil is changing from the liquid to the solid phase. I have also found that the presence of the aforementioned granular precipitate in the oil during coking markedly accelerates the rate of coking, thus preventing formation of needle-like coke.

If a charging stock is used which contains asphaltenes and other constituents which are readily converted to solids at low temperatures, it cannot be coked directly to needle coke by use of the coking process just described. Conversely, even clean stocks cannot be converted to needle coke unless the coking procedure described is used. Both factors are necessary.

Without being bound by the theory, the following explanation is offered. If a "dirty" stock, i. e., containing insoluble or suspended matter, or having constituents such as asphaltenes which are readily polymerized to solids at relatively low temperatures is coked as described above, a suspension of solid particles in oil results in the early stages of coking. These solids are dispersed in the main body of the oil at the critical period when it is passing through the highly viscous state immediately preceding conversion to the solid state. For some reason the solids interefere with the orientation that is needed to form the needles. This is borne out by the fact that the formation of needles can be prevented by adding carbon black to a clean oil and then coking it as above explained.

The temperature gradient through the body of the oil in the coking vessel should be kept low. Localized hot spots should be avoided because a solid phase of coke or high-carbon matter may be formed prematurely which would interfere with needle coke formation. Two types of coking can be used for illustrative purposes. In the first, a thermally stable refractory oil is placed in a batch still heated externally or by means of a heating coil immersed in the oil. Agitation of the charge is usually dependent solely upon thermal currents set up during the heating operation and care must be taken that this is not accompanied by sharp thermal gradient which would cause premature deposition of undesirable carbonaceus material. The charge must be heated up very slowly in this operation. On the other hand, the charge to be coked in a delayed-type coking vessel is normally passed through a metal tube heat exchanger. While the temperature outside of the tubes through which the oil passes is considerably higher than that of the oil within the tubes, the rate of flow of the oil through the tubes and the turbulence incident thereto is maintained such that sharp thermal gradients through the oil are precluded or minimized. It is essential to the formation of needle coke in the coking vessel, according to my invention, that this turbulence or rate of flow in the heat exchanger be maintained to avoid premature deposition or formation of carbonaceous matter in the oil passing through the tubes which would contaminate the charge in the coking vessel. The temperature external to the tubes must be balanced against that of the oil passing through them to avoid this harmful effect.

When the hot oil is passed continuously into the coking drum, the coke builds up gradually until the drum is full. It is also within the scope of the invention to heat the oil to a coking temperature and substantially fill the drum allowing the oil to soak until it eventually is converted to coke. It may be necessary under these conditions to heat the vessel but this should be done in such a way that no high thermal gradients are set up: that is, keeping a low temperature differential outside and inside the still. Overheating at the shell of the still should be avoided since there is likely to be an overheated area at that point with the resulting formation of non-needle coke.

If additional heat is required during the coking operation, this can be supplied by introducing a superheated stream of relatively light hydrocarbon or steam into the coke still.

After the coke drum is full, coke may be removed by known methods, broken into lumps and then calcined, generally at a temperature of 1000° to 1500° C. to prepare the material for use in the manufacture of graphite electrodes. The lumps of the coke contain bubbles of various sizes. An examination of the coke shows strongly defined lines or striations. The coke has a metallic appearance throughout. Examination of even the finest particles shows that this is true. Particles of the ground coke examined under a microscope continue to have the metallic luster and striated appearance. When subjected to X-ray diffraction, the individual needle exhibits a characteristic orientation of crystals not exhibited by the non-needle coke which would be produced from the same residuum by other processes. These coke needles are substantially less porous than the coke of the prior art and the needles can be separated from prior art coke by sink-float methods. The needles tend to sink to the bottom and the dull gray particles of prior art coke tend to rise to the top when the mixture is placed in a liquid medium of a suitable specific gravity.

This needle-type of coke is particularly advantageous when used in the manufacture of graphite electrodes. When the calcined needles are mixed with a binder such as coal tar pitch and with coke flour and then extruded or molded, the needles apparently tend to orient themselves with the direction of flow of the mixture. The green electrode thus produced can be baked and then graphitized, the baking step occurring at a temperature of about 500° to 1300° C. and the graphitizing step at about 2500° to 3000° C. The graphitized electrodes have a lower resistivity and a lower coefficient of thermal expansion (300–800° C.) than electrodes similarly produced from non-needle coke. Heretofore, it has been impossible to utilize the hydrocarbon residues containing components which are readily coked within the range of about 325° to 500° C., to produce needle coke.

The following examples are illustrative of specific methods which can be used in the preparation of needle coke from various petroleum residuums. The resistivity values are longitudinal specific resistivities in ohms per in.^{3} at room temperature. The C. T. E. values are longitudinal coefficients per ° C. for the temperature range of 300° to 800° C.

Example I

A cracked residuum from an East Texas crude oil was used for this run. By the A. S. T. M. Engler distillation 25% boiled below 360° C. and the A. P. I. gravity at 20° C. was 3–4. It was charged to a still and heated at atmospheric pressure for six hours at 380°–400° C. and 9½ hours at 400°–410° C., the temperature being gradually raised over this period. It was then passed hot through a filter cloth having a precoat of diatomaceous earth and charged to a coking still where it was held under conditions of quiescence as described. It was raised to 400°–410° C. and held there for seventeen hours. During the next six hours the temperature was increased to 480° C. at which it was held for forty-one hours and the temperature was again increased in two hours to 570° C. The coke was calcined at 1000° C. and crushed to make an electrode aggregate.

The precipitate from the first step amounted to 0.9% by weight. The coke yield was 13.1% of the charge.

When crushed, the particles had a needle-like appearance and a high metallic luster.

A graphitized electrode made up of 100 parts of calcined needle coke flour and 48 parts coal tar pitch binder in the usual manner had a resistivity in ohms per inch^3 of 23×10^{-5}. The coefficient of thermal expansion (300°–800° C.) was 19×10^{-7}.

A graphite electrode made from 100 parts by amorphous coke flour formed from the above residuum by the conventional process had a specific resistivity of 35×10^{-5} and the coefficient of thermal expansion was 64×10^{-7}/per ° C. (300°–800° C.)

Example II

A West Texas cracked residuum had 34% boiling below 360° C. and an A. P. I. gravity of 12°. Its temperature was raised to 400° C., and then to 410° C. in ten hours. The distillate and gas amounted to 81.6%, liquid bottoms 15.7%, and 2.7% was filtered off as granular coke-like material.

The filtered concentrate was heated in a quiescent, homogeneous condition, as follows:

12 hours at 400–410° C.
3 hours at 410–438° C.
15 hours at 430–475° C.
7 hours at 475–588° C.

The coke yield was 6.7% of the original charge. It was of the needle structure. After calcination it was made into an electrode using 36 parts binder to 100 parts coke. In the graphitized state the apparent density was 1.59 and specific resistivity 25×10^{-5} ohms per in.^{3}. The coefficient of thermal expansion was 21×10^{-7}.

A graphite electrode prepared from calcined non-needle coke made from the unfiltered residuum had a specific resistivity of 32×10^{-5} and a coefficient of thermal expansion of 38×10^{-7}.

Example III

A residuum from a mixed Mid-Continent West Texas crude oil had 25% boiling below 360° C. and an A. P. I. gravity of 14.

It was flash distilled by charging the oil into a flash chamber at 450°–540° C., the still being held at 450°–500° C. There remained 7.7% of coke in the still. The overhead had 40% boiling below 360° C. This overhead was coked as follows:

11 hours at 400°–450° C.
4 hours at 450° C.
5 hours at 450°–500° C.

The yield of needle coke based on the charge was 6%. A graphite electrode made from the calcined needle coke particles had a specific resistivity of 25×10^{-5} ohms per in.^{3} and a coefficient of thermal expansion of 21×10^{-7}.

The original oil after coking without refining yielded graphite electrodes having a specific resistivity of 30×10^{-5} and a coefficient of thermal expansion of 31×10^{-7}.

Example IV

The charging stock of Example III was heat treated at 500–600 p. s. i., the temperature being raised in 1.1 hours to 430° C. and to 455° C. in an additional half hour; distillate and loss was 34.7%. It was filtered to remove 4.3% solids. The 61% of filtered concentrate was coked at atmospheric pressure as follows:

8 hours at 400°–450° C.
13 hours at 450°–500° C.
0.5 hour at 500°–550° C.

The needle coke yield was 19.4% of the original residuum or 31.3% of the concentrate charged to the coking zone.

A graphitized electrode prepared from this calcined needle coke had a resistivity of 27×10^{-5} ohms per in.^{3} and a coefficient of thermal expansion of $19–20\times10^{-7}$. The coke obtained by coking the original residuum without refining yielded comparable graphite electrodes which had resistivities of 30×10^{-5} ohms per in.^{3} and C. T. E.'s of 31×10^{-7}.

Example V

A Texas cracked residuum had 30.5% overhead at 360° C. and an A. P. I. gravity of 12.

The residuum was heated at atmospheric pressure for 22 hours at 360°–400° C., 2.3% of solid was filtered off. The filtered concentrate was 12.9% of the charge and was coked by the present method at 450°–470° C. The needle coke yield was 63% of the concentrate or 8.1% of the charge.

A graphitized electrode prepared from the needle coke obtained had a specific resistivity of 24×10^{-5} and a coefficient of thermal expansion of 23×10^{-7}.

A comparable electrode prepared from non-needle coke of the same source had a specific resistivity of 27×10^{-5} and a coefficient of thermal expansion of 32×10^{-7}.

Example VI

The residuum from Example V was mixed with 10 volumes of pentane, filtered to remove asphaltenes and the clean residue coked as in Example III. The needle coke yield was 6.7% of the charge. The graphitized electrode made from this coke had a resistivity of 22×10^{-5} and a coefficient of thermal expansion of 21×10^{-7}.

Example VII

A Mid-Continent topped crude oil was subjected to vacuum distillation to recover an overhead fraction and to leave a pitch residue. The overhead fraction was subjected to extraction with furfural in the manner used for the solvent refining of lubricating oils. The extract phase was separated and the solvent recovered therefrom. Forty-six percent of the extracted hydrocarbons boiled below 360° C. was coked. The temperature was maintained at about 400–445° C. for a period of seventeen hours, the temperature then being raised to 500° C. over a period of 5 hours and finally raised to 570° C. over a period of 12.5 hours. The yield of needle coke amounted to 24.8% of the extract charged to the coking unit. The needle coke was calcined and made into a 100% flour electrode. The green electrode was baked and graphitized in the usual manner. It had a specific resistivity of 25×10^{-5} ohms per in.^{3} and a coefficient of thermal expansion of 22×10^{-7}. These values are considerably better (i. e. lower) than those obtainable with the usual electrode grade of petroleum coke.

Example VIII

A gas-oil fraction was separated from a Mid-Continent crude oil and subjected to catalytic cracking at about 500° C. The gasoline and gas were separated. A side stream of substantially the same boiling range as the gas-oil charging stock was separated and recycled to the catalytic cracking zone. The high boiling aromatic residue having an A. P. I. gravity of 14 was coked, the temperature in the coking zone being maintained with a temperature gradient of not more than 5° to 10° C. at any time in the range of about 400°–450° C. for 14 hours after which the temperature was raised to 500° C. over a period of about 8 hours and was finally raised to about 600° C. over a period of about 4 hours. The coke formed was of the needle type. It amounted to 28% of the original charge. The coke produced was calcined and incorporated into a 100% flour electrode which after graphitization had a resistivity of 24×10^{-5} omhs per in.^{3} and a coefficient of thermal expansion of 21×10^{-7}. These values may be compared to a resistivity of 27×10^{-5} and a coefficient of thermal expansion of 28×10^{-7} obtained with a common grade of petroleum coke used in the production of graphite electrodes.

Example IX

A gas-oil fraction was separated from the straight thermal distillation of a Mid-Continent crude oil and was catalytically cracked in the presence of a zeolitic catalyst at about 500° C. with separation of gas and gasoline. A side stream of substantially the same boiling range as the gas-oil charging stock was separated and either recycled to the same catalytic cracking zone or was conducted to a second catalytic cracking zone. The side stream of cycle oil from the catalytic cracking zone(s) was heated to a temperature of 525° C. in a thermal cracking unit maintained at a pressure of about 400 p. s. i. The vapors from the thermal cracking unit were stripped to recover gas and gasoline and a high-boiling refractory aromatic material was recovered having an A. P. I. gravity of −2.0 and having the following distillation range:

T° C.:	Cum. vol. percent
0–21°	—
235	—
270	16
315	34
355	44
Residue (wt. percent)	56

Alternatively, from 5 to 30% of virgin gas-oil from the above operation can be blended with the catalytic cracking cycle stock passed through the thermal cracking unit.

The "pressure tar" recovered from the thermal cracking unit in this operation was heated uniformly to a temperature between 485° to 500° C. in a tube heat exchanger and continuously admitted into a Kellogg delayed coking unit. The temperature in this unit was maintained uniformly until the mass set homogeneously into a solid coke having the desired needle structure. The yield of coke was 30% of the material charged to the unit. The coke was calcined and manufactured into a graphite electrode according to the method described in Example VIII, the final electrode having similar properties to those electrodes.

The coking runs previously described were made at atmospheric pressure unless otherwise indicated.

This application is a continuation-in-part of my copending application Ser. No. 99,344, filed June 15, 1949, and now abandoned.

I claim:

1. A process for producing needle-like coke which comprises removing from a high boiling petroleum residuum those components which readily form an insoluble phase upon heating at 350°–550° C., and coking the remaining residuum in a quiescent pool.

2. The process of claim 1 further characterized in that the insoluble phase is removed by a step comprising distilling about 80 to 90% of said residuum and coking the overhead in a quiescent pool.

3. The process of claim 1 further characterized in that the insoluble phase is removed by a step comprising distilling said residuum, recovering a high boiling fraction, subjecting said fraction to solvent extraction with a solvent selective for cyclic hydrocarbons, recovering the extracted hydrocarbons and coking the extract in a quiescent pool.

4. A process for producing needle-like coke which comprises heating a heavy petroleum residuum at a temperature of about 325° to about 550° C. for a time sufficient to precipitate between about 1 and about 10% of the residuum as an insoluble phase, separating said phase, and coking the remaining residuum in a quiescent pool at a temperature of about 375° to about 550° C.

5. The process of claim 4 wherein the insoluble phase is separated by filtration.

6. A process for producing needle-like coke which comprises heating heavy petroleum residuum at a temperature between about 325° to about 550° C. to precipitate a minor part of the residuum as a granular solid, separating the uncoked oil from the solids and coking the separated oil in a quiescent pool to produce needle coke.

7. A process for producing needle-like coke from heavy petroleum residuums which contain from about 1 to about 10% of components which readily form an insoluble phase when heated at 325°–550° C., which comprises mixing said residuum with a low boiling paraffin hydrocarbon to form a precipitate, separating the dissolved residuum, removing said low boiling hydrocarbons, coking the thus treated residuum in a quiescent pool maintained without agitation except for the natural movement of vapors evolved during coking, and recovering the coke formed.

8. A process for manufacturing needle-like coke which comprises heating a heavy petroleum residue at a temperature of about 325° to about 550° C. for at least five hours to form a precipitate, separating the liquid oil from the insoluble material formed, and subjecting the liquid oil to coking conditions in a quiescent pool maintained without agitation except for the natural movement of vapors evolved during coking, and recovering the coke thus formed.

9. A process for producing needle-like coke which comprises removing from a high boiling petroleum residuum those components which readily form an insoluble phase upon heating at about 350° to about 550° C., coking the resulting material in a coking operation comprising the steps of first heating a stream of the material to a coking temperature, then continuously passing it into a coking zone, maintaining a liquid body thereof in said zone at a coking temperature and converting it to coke, said material being heated and coked without agitation except

that incident to the natural movement of the material and of vapors in said steps, and at a rate and under conditions of thermal homogeneity precluding sharp temperature gradients within the material during said heating and coking which would cause localized premature coking of minor portions of said material with resultant contamination of the body of material prior to its solidification, and recovering a coke of needle-like structure.

10. The process of claim 9 wherein the components which readily form said insoluble phase are removed by forming a charging stock for catalytic cracking, subjecting said charging stock to catalytic cracking conditions of temperature and pressure, separating gas, gasoline, recycle stock and a high boiling aromatic residue, and coking said residue under the defined conditions.

11. The process of claim 9 wherein the components which readily form said insoluble phase are removed by forming a charging stock for catalytic cracking, subjecting said charging stock to catalytic cracking conditions of temperature and pressure, separating gas, gasoline and recycle stock, subjecting said recycle stock to thermal cracking to produce gas, gasoline, gas oil and a high boiling aromatic residue and coking said residue under the defined conditions.

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