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3,326,796 PRODUCTION OF ELECTRODE GRADE PETROLEUM COKE

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This invention relates to a process for the production of petroleum coke suitable for use in the manufacture of carbon and graphite electrodes. More particularly it relates to the production of a coke exhibiting a crystalline needle-like structure from a feed stock which is a by-product of the production of unsaturated olefinic hydrocarbons from various starting materials such as refinery gases, light crude naphthas, ethyl benzene and low molecular weight hydrocarbons such as natural gas, ethane, propane, etc.

Petroleum coke is the residue resulting from the thermal decomposition or pyrolysis of high boiling hydrocarbons at temperatures in the range of about 350° C. to 500° C. High boiling virgin or cracked petroleum residues are typical charging stocks for the production of coke, the process often being carried out as an integral part of the overall petroleum refinery operation.

Many types and grades of petroleum coke are found to be unsuitable for use in the manufacture of large diameter, thermic electrodes because of certain adverse physical properties of the coke such as high coefficients of thermal expansion, high electrical resistivity, high sulfur content, etc. which affect the quality of the resultant electrode. Extensive research and study has been undertaken to develop so-called premium grade petroleum cokes, it being found that the properties and characteristics of these cokes render them suitable for the production of high quality electrodes.

Premium coke has heretofore been produced from one of two basic groups of starting materials. In an early development of coking, a few selected paraffinic crudes were found to have properties such that when they were distilled, the residues therefrom could be coked directly to produce high quality coke. More recently, as these select crudes have become more scarce, highly aromatic residues obtained from cracking or distillation of asphaltic crude distillates have been used as starting materials for coke production. Also, a premium coke can be obtained from these residues by one or more conditioning treatments prior to coking.

A description of processes for producing electrode grade coke from a residue obtained by the thermal cracking of certain hydrocarbon distillates obtained from asphaltic crude oils, followed by the delayed coking of the residue under controlled conditions is described in U.S. 2,775,549 to F. L. Shea, Jr. As stated in that patent, a coking stock suitable for the production of a premium coke is characterized by the absence of materials or components which would ordinarily produce inferior quality coke, such as asphaltic and naphtheic base oils. Such materials have a tendency to coke at a much lower temperature and at a faster rate than the rest of the coker feed thus resulting in premature and non-uniform coking. According to this patent, these materials can be removed from coker charge stocks prior to coking by a heat treating step or a solvent extraction process or both. The heat treatment may be carried out by charging the hydrocarbon residue into a still or other vessel and raising the temperature of the residue to 325°–550° C. at atmospheric pressure or above and holding the material at this temperature for a period of hours. At this temperature, these undesirable materials polymerize and form a sep-

arate phase which is insoluble in the main body of the residue and can be removed from the stock by filtration, centrifuging, or other mechanical means to produce a purified coking stock. Alternatively, the residue may be heat treated by distilling off between 80 and 95% of the residue, the distillate constituting the purified coking stock. Instead of heat treating, solvent extraction can be used to remove these undesirable components. This is accomplished by mixing the coking stock with a low boiling liquid paraffin such as propane, butane, pentane, etc., in an amount of 1 to 10 parts of solvent to 1 part of the coking stock. The undesirable asphaltic and naphthenic components being insoluble in the paraffinic hydrocarbon precipitate out and are removed by settling, distillation, or filtration. The purified material, after removal of the solvent by simple distillation, is then suitable for coking, which is carried out under carefully controlled conditions.

The coke produced by the Shea process is characterized by a striated appearance throughout the particles. These coke particles have a high metallic luster and a needle-like structure which is very noticeable when the coke is ground to a fine particle size. The needles produce an X-ray diffraction pattern showing a crystal orientation that is not present in the structure of regular coke. Normally the regular coke produced in conventional coking operations has a massive relatively dull gray-black appearance and is relatively porous. When crushed to a small particle size this coke breaks into lumps of irregular shape. The dimensions of the particles are about the same in all directions and it does not exhibit the crystalline or needle-like structure of the petroleum coke produced by Shea. If these pre-treatment steps are not carried out on most coking stocks, a petroleum coke of ordinary quality is produced and its use in the production of carbon and graphite electrodes is limited. Petroleum coke produced by the Shea process commands a premium price on the market and is in relatively short supply.

It is an object of this invention to produce a premium coke for large diameter thermic graphite electrodes by coking a material which has not heretofore been considered for such coke production.

It is another object of this invention to produce a needle-like coke by a simplified process which eliminates the necessity of pre-treating the coking stock to remove undesirable contaminants.

It is yet another object of this invention to produce an electrode-grade coke by the delayed coking of a material which is obtained as a residual by-product in the manufacture of certain olefinic hydrocarbons by cracking or dehydrogenation.

These and other objects which will become readily apparent upon a full disclosure of the invention are accomplished by treating a petroleum hydrocarbon, either aromatic or aliphatic, to produce an olefinic product and a residual by-product. The treatment consists of dehydrogenation, usually by cracking, to form olefinic gaseous or low boiling products and a residual by-product which I have found to be characterized by high aromaticity and the absence of readily cokable material. When coked in a delayed coker under carefully controlled conditions, it produces a coke having a needle-like structure.

In more detail, this invention relates to the cracking, and/or dehydrogenation, of a hydrocarbon feed to produce an unsaturated aromatic or aliphatic overhead product, and a resinous residual by-product. This by-product is highly aromatic, containing a high percentage of multiple ring hydrocarbons. It contains little or no readily cokable material which must be removed by heat treatment or solvent extraction. This by-product, with or without distillation, is heated uniformly to a temperature be-

tween about 300° and about 500° C. and is introduced into a thermally insulated coking vessel where it is converted into a premium grade petroleum coke characterized by a striated crystalline structure. The only agitation of the material in the vessel during coking is that caused by the movement of fresh feed into the vessel, and the escape of volatiles therefrom. These volatiles as they are produced, are removed from the coking vessel. Preferably, the high boiling constituents are recovered therefrom, and are recycled to the coker to increase the coke yield.

Typical of the processes which may be employed for producing ethylene and other unsaturated low boiling hydrocarbons from low boiling petroleum naphtha or lower boiling virgin distillates are disclosed in U.S. Patents Nos. 2,330,804, 2,354,892, 3,095,293, 2,525,276, 2,904,502 and 2,914,386. It is the tars or similar high boiling residues from these operations which are used to form coke according to my invention.

In a specific embodiment a crude petroleum naphtha having an API gravity of between 40 and 60, is separated from natural gas by a process such as scrubbing, and is converted to ethylene by cracking in a known manner. This cracking operation can be either thermal or catalytic. In thermal cracking, the naphtha feed is introduced into a tube still heater maintained at relatively low pressures and a temperature of about 800° C., where cracking occurs in the presence of steam. The main product which is ethylene, and a few other lightweight olefinic gases are separated from the residue, and are subjected to future separation and purification steps. In the catalytic cracking operation, lower cracking temperatures can be utilized by carrying out the reaction in the presence of an appropriate catalyst such as chromic acid deposited on bauxite, or orthophosphoric acid. In either process, a residual by-product is produced which is highly aromatic and is characterized by the absence of easily cokable material. This by-product is topped, if necessary to produce a coker feed stock having the following properties:

	Broad	Preferred
Benzene solubles.....	80 to 99%-----	92 to 99%.
Pentane solubles.....	20 to 50%-----	25 to 45%.
Sulfur.....	0.1 to 1.0%-----	0.2 to 0.7%.
Conradson carbon.....	20 to 60%-----	30 to 50%.
Specific gravity.....	1.17 to 1.20-----	1.17 to 1.20.
Softening point.....	40° to 65° C.-----	45 to 60° C.

This material is then coked uniformly at a temperature of between 300° and 550° C., preferably between 300° and 475° C., in a delayed coker under conditions whereby the formation of coke occurs with substantially no agitation of the feed stock except for that created by the fresh feed into the coker, and the escape of volatiles therefrom. The volatiles evolved during coking are removed as distillate from the coker. This distillate, or preferably the higher boiling fraction therefrom, can be recycled to the coker. This recycle can be mixed with fresh feed prior to or after passing through the heater, or can be introduced into the coker as a separate stream.

In another specific embodiment of the invention, an alkyl aromatic compound such as ethyl benzene is dehydrogenated to produce a vinyl aromatic product such as styrene, as exemplified in U.S. Patent No. 3,100,234, and a resinous aromatic residue. The dehydrogenation reaction is carried out at a temperature of between 600° and 800° C. in the presence of steam, a catalyst such as iron oxide and a promoter. The resinous residue is separated from the styrene product, is topped if necessary, and is then coked in a delayed coker at a uniform temperature of between 300° and 550° C. under conditions whereby agitation of the material in the coker is kept at a minimum. The resultant product is a premium grade needle-like coke.

A good delayed coking stock is characterized by an initial boiling point above about 250° C. with not over about 25 to 30% boiling below 360° C. Because of variations in the properties of the naphtha feed and the operat-

ing conditions during the production of unsaturates, the bottoms produced therefrom may have a boiling point which is too low for the production of needle-coke due to the presence of low boiling components. The presence of these components in the stock when it is coked is inimical to the production of needle-coke inasmuch as they are readily volatilized at coking temperatures, and consequently tend to disrupt the desired uniform conditions in the coker. Therefore, it may be necessary to subject the bottoms from the catalytic cracker to a topping or stripping operation which removes the low boiling components by distillation. The stock may also be fractionated in a combination tower where several cuts are made to remove the lighter ends prior to feeding the bottoms to the heater and thence to the coker.

The process of delayed coking is characterized as a semi-continuous operation resulting in the destructive distillation of the coker feed. In operation, the usual coker feed such as a topped crude oil or other residue from a refinery operation, but which in this invention is the resinous by-product having the aforementioned properties, is heated to a temperature of between about 300° C. and about 550° C. in a tube still heater and is continuously introduced into the bottom of a coking drum, typically of the vertical type. The coking drum is maintained at a relatively low pressure, i.e. between atmospheric and 100 p.s.i. during coking. As the feed accumulates and heat soaks in the coking vessel, the hydrocarbon molecules crack and decompose into the smaller molecules having a lower boiling point while other molecules which are more reactive combine or polymerize to form larger molecules. As the cracking and polymerization progresses, the stock becomes more viscous and dense, while the decomposed molecules volatilize and are removed overhead. This process continues until the stock is solidified into coke.

To produce needle coke, it is necessary that the stock in the drum be maintained in a homogeneous condition, particularly immediately preceding solidification. Therefore, it is necessary that the coking condition be carefully controlled. Failure to so regulate these conditions will result in the production of coke lacking the desired properties, even from a suitable feed stock.

Maintaining thermal homogeneity of the stock in the coking drum is accomplished by preheating the drum with steam, etc., prior to the introduction of feed, insulating the drum to reduce heat loss, and uniformly heating the feed stock prior to its introduction into the coker. The stock is usually heated in a tube still heater typically used for heating of petroleum oils and reduced crudes in which the stock flows through tubes which are heated externally by convection and radiation from gas or oil fired burners.

As coking commences in the drum, the evolved volatiles are taken overhead as a relatively clean distillate. This distillate is preferably passed through a tower to remove any entrained coke particles or partially coked material which are then returned to the coker. The distillate, freed from entrained particles, is then fractionated or distilled by any one of a number of processes and the higher boiling components recycled to the coker. For instance, the distillate may be fractionated to produce an overhead, side streams, and bottoms which can be reheated and returned to the coker, or which can be mixed with fresh feed before or after passing through the tube still heater. Alternatively, coker distillate may be pumped directly to a combination tower where it is fractionated along with fresh feed to produce various overhead and side streams and bottoms. These bottoms are then fed to the coker preheater and thence to the coker. Other processes for treating the distillate, well known in refinery practices are also contemplated.

Usually two or more coking drums or chambers are operated in parallel, coking taking place in one drum while a decoking operation is being carried out in the other one. After a coking chamber has become filled to

a predetermined level with solidified coke, the feed is discontinued and switched over to an empty chamber. The filled chamber is then decoked by known means.

After removal, the coke may be calcined to produce carbon for graphite electrodes. This calcined coke is sized, mixed with a suitable binder such as coal tar pitch and is extruded or molded into shape. The green electrode thus produced can be baked to about 900° C. and graphitized to about 2500° to 3000° C. The final product has a lower coefficient of expansion and lower resistivity than electrodes produced from non-needle coke.

In some instances where the resinous feed material has inadvertently become contaminated with certain undesirable components it may be found necessary to subject it to solvent extraction, filtration, or a heat treating step in order to remove the unwanted or undesirable components therefrom. Such a process as described in U.S. 2,775,549 to F. L. Shea, Jr., is contemplated.

It is also contemplated that two or more of these resinous by-products from separate and distinct catalytic or thermal cracking operations may be blended in order to form a desirable premium stock. Likewise the resinous by-product may be mixed with a residuum or a cracked crude oil or other petroleum oil which would ordinarily be suitable only for the production of regular petroleum coke, in order to upgrade the latter and make a coking mixture which is suitable as a premium coking blend. The respective ratios of the two materials can easily be determined.

In order to more fully clarify and exemplify the invention but with no intentions of being limited thereby, the following example is presented:

Example I

A 52° API light crude naphtha was subjected to catalytic cracking at high pressure in the presence of steam to produce ethylene, other low boiling gases and a resinous residue having the following properties:

Softening point (Ring and Ball), ° C.	45
Specific gravity (at 15° C.)	1.180
Conradson carbon	percent 36.5
Ash	do 0.02
Sulfur	do .38
Benzene soluble	do 98.0

This residue has a dark brown-black color and a glossy resin-like appearance. In an ASTM (D-20) distillation, 44% by weight of the material distilled. An analysis of the overhead showed it to be a highly aromatic material containing substantial amounts of phenanthrene, anthracene, fluorene and various derivatives of these cyclic compounds.

The resinous residue was charged to a still and heated at atmospheric pressure to a temperature of about 435° C., held there for 15 hours, heated to 460° C. at a rate of 2½° C./hr., and then to 560° at 33° C./hr. The yield of coke produced was 55% based upon the weight of the original feed to the still. The coke has a sulfur content of 0.14%, an ash of 0.04%, had a needle-like crystalline appearance, and, when made into an all flour (50%-200 mesh) test electrode, the electrode had a coefficient of thermal expansion (CTE) of 8.8×10^{-7} .

I have found that needle coke produced by the methods described and claimed herein is particularly suitable, after calcination, for the manufacture of large thermic graphite electrodes (18" diameter and greater) which are used by steel producers in the operation of electric furnaces. Further, this provides an alternate source for this type of coke which has not heretofore been available.

Although certain variations and limitations have been set forth as well as preferred embodiments of my inven-

tion, it is my intention to be limited only by the appended claims.

I claim:

1. A process for producing a premium grade coke having a needle-like structure from a resinous by-product having a softening point of from 40° to 65° centigrade derived from the manufacture of unsaturated hydrocarbons by the cracking of petroleum naphtha and characterized by high aromaticity and the substantial absence of readily cokable material, which consists essentially of heating the resinous by-product uniformly to a coking temperature and coking it under conditions of thermal homogeneity and without agitation except for the natural movement of vapors evolved during coking.

2. A process for producing a premium grade coke having a needle-like structure consisting essentially of: cracking a low boiling petroleum hydrocarbon feed to produce unsaturated hydrocarbons which are gaseous at standard pressure and temperature, and a high boiling residual by-product having a softening point of from 40°-65° centigrade and characterized by high aromaticity and the substantial absence of readily cokable material, heating the residual by-product uniformly to coking temperature, and coking it under conditions of thermal homogeneity and without agitation except for the natural movement of vapors evolved during coking.

3. A process according to claim 2 wherein the low boiling cracking feed is a crude naphtha having an API gravity above 40.

4. A process of producing a premium grade coke having a needle-like structure from a resinous by-product resulting from the catalytic cracking of a petroleum hydrocarbon selected from the group consisting of petroleum naphtha having an API gravity of at least 40, and low boiling lightweight paraffinic and alkyl aromatic gases; said by-product having the following properties:

Benzene solubles, percent	80 to 90
Pentane solubles, percent	20 to 50
Sulfur, percent	0.1 to 1.0
Conradson carbon	20 to 60
Specific gravity	1.17 to 1.20
Softening point, ° C.	40 to 65

and further characterized by a high aromaticity and the substantial absence of readily cokable material, which consists essentially of heating the resinous by-product uniformly to a coking temperature and coking it under conditions of thermal homogeneity and without agitation except for the natural movement of vapors evolved during coking.

5. A process for producing a premium grade coke with a needle-like structure consisting essentially of: dehydrogenating an alkyl aromatic hydrocarbon to produce a vinyl aromatic hydrocarbon and a resinous residual by-product and characterized by high aromaticity and the substantial absence of readily cokable material, heating the by-product uniformly to a coking temperature and coking it under conditions of thermal homogeneity and without agitation except for the natural movement of vapors evolved during coking.

6. A process according to claim 5 wherein the alkyl aromatic hydrocarbon is ethyl benzene.

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