March 26, 1974  YOSHIO SUETSUGU ET AL

PROCESS FOR PRODUCING NEEDLE-SHAPED COAL PITCH COKE

Filed Nov. 30, 1971

FIG. 1

FIG. 2

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PROCESS FOR PRODUCING NEEDLE-SHAPE COAL PITCH COKE

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Filed Nov. 30, 1971, Ser. No. 203,251
Claims priority, application Japan, Dec. 2, 1970, 45/105,980
Int. Cl. C10G 9/14

The present invention relates to a process for producing needle-like coal pitch coke suitable for use as an artificial graphite electrode. More particularly, the invention relates to the production of needle-like coal pitch coke of a high quality by coking a specific pitch obtained from purified coal tar or coking the purified pitch according to a delayed coking method.

Coke of a needle-like crystal structure useful as an artificial graphite electrode has been produced according to the so-called delayed coking method, wherein a petroleum heavy oil is heated and kept at a coking temperature to obtain raw coke and the obtained raw coke is then calcined. However, most available petroleum heavy oil generally contains many impurities such as metals, sulfur, etc., whereas relatively pure petroleum heavy oil low in impurities is difficult to obtain. Since petroleum coke produced from such impure petroleum heavy oil usually contains many impurities and even then is not suitable for manufacture of graphite electrode, such impure petroleum heavy oils having relatively high impurities have not usually been utilized for the production of petroleum coke of needle-like crystal structure. Furthermore, the output of petroleum heavy oil having preferable properties suitable for the production of needle-like crystalline structure coke is very low and such heavy oil is scarcely available commercially.

On the contrary coal tar pitch generally has an extremely low content of impurities such as metals, sulfur, etc., as compared with the petroleum heavy oil and is available in large quantities. However, conventional coal pitch coke which has been industrially produced from such coal tar pitch is usually rich in amorphous coke and needle-like crystal structure coke could not be obtained from said pitch coke.

After investigations on process for producing needle-like pitch coke of an excellent quality from coal pitch, the inventors have found that needle-like coal pitch coke of a high quality can be produced by heating pitch having a low content of quinoline-insoluble matter and containing a suitable quantity of light oil, to a temperature above 450°C., then introducing the heated pitch into a coking reactor at a rate (ton/hr.) less than

\[ \frac{T_c - 450}{34-D} \]

per m² of cross section of the coking reactor, wherein \( T_c \) represents temperature (°C.) of the starting pitch at an inlet of the coking reactor and \( D \) represents a ratio by weight of 400°C. fraction to the starting pitch, collecting mainly light oil and other minor constituents which do not take part in the coking reaction from the top of the reactor and keeping average temperature in the reactor above 400°C. for at least 20 hours after the beginning of the charge.

The inventors have also found that, for obtaining pitch of a low quinoline-insoluble matter content, it is effective that, prior to distillation of coal tar which is produced by dry distillation of coal (starting material), a tar oil is introduced in the coal tar, and then the resulting mixture is treated e.g. centrifuged to remove quinoline-insoluble matter contained in the coal tar or alternatively tar oil is blended with pitch obtained by distillation of the said coal tar in a usual manner, then the mixture is treated to remove quinoline-insoluble matter in the pitch.

The present invention has been accomplished on the basis of the above discovery. The object of the present invention is to provide pitch coke having needle-like crystalline structure suitable for use as artificial graphite electrode on various industries from coal pitch obtained from coal tar.

These and other objects and effects of the present invention will be made clear by the following descriptions.

At first preparation of coal pitch having a low quinoline-insoluble matter content to be used as starting materials for coke according to the present invention will be shown.

Various processes for producing coal pitch of a low quinoline-insoluble matter content have been proposed. The inventors have found that the following process is most effective.

The tar oil to be incorporated in coal tar or pitch obtained from coal tar in the invention means light oil by-produced in the production of coal coke or a distillation fraction thereof or a distillate obtained during distillation of coal tar, as for example, light oil, carbolic oil, naphthalene oil, wash oil, anthracene oil, mixtures thereof and aromatic compounds separated from the distillates such as benzene, toluene, xylene, phenols, naphthalene or methyl-naphthalene are included. Aromatic hydrocarbons obtained by cracking or reforming petroleum fractions such as naphtha can be also used as tar oil in the present invention.

The amount of the above tar oil to be blended to coal tar is preferably 5-50 wt. percent, particularly 10-40 wt. percent based on mixture of coal tar and tar oil.

When tar oil is blended with pitch, tar oil in a quantity corresponding to that of light oil which has been already removed by the coal tar distillation is added to pitch, to which additional tar oil is further added in such a quantity that tar oil content in the whole mixture will be 5-50 wt. percent, particularly 10-40 wt. percent like the above case of coal tar. However, in practice, the former tar oil which corresponds to quantity of light oil removed by coal tar distillation may be blended together with the latter additional tar oil. A tar oil having an average boiling point in the range of 80°-360°C. is preferably selected and used, because such tar oil has advantageous effects to the successive separating operation, particularly centrifugation of the mixtures.

Coal tar or pitch incorporated with tar oil in the above manner is then subjected to centrifugal operation to remove quinoline-insoluble matter contained in the coal
The centrifugation can be performed advantageously by using a centrifugal precipitator of separator plate type or decanter type having a centrifugal force higher than 1,000 G, preferably higher than 1,500 G. The centrifugal operation is advantageously performed at a temperature in the range of 70–200°C depending upon boiling point of tar oil used. By distillation of thus centrifuged tar, pitch of a low quinoline-insoluble matter content is obtained. When using pitch directly as a starting material, pitch treated in the above manners is used as the preferred starting material for pitch coke, because pitch containing less quinoline-insoluble matter can be obtained. In case pitch is used as starting material, pitch is usually collected by distillation after removal of quinoline-insoluble matter.

FIG. 1 is a flow sheet showing an embodiment of production of pitch to be used as starting material for production of pitch coke according to the present invention. FIG. 2 is a graph showing relation between production rate of needle-like pitch coke and operation conditions.

A flow sheet of a process for the production of pitch from coal tar, accompanying with removal of quinoline-insoluble matter from coal tar on an industrial scale using centrifugal separation will be described with reference to FIG. 1.

Coal tar from a coke oven is introduced in a receiver tank 1, from which coal tar is fed to a mixing tank 3 through a line 2. In the mixing tank 3, a tar distillate fraction having an average boiling point in the range of 80–360°C, which is a part of tar distillate from a tar distillation tower 11 and stored in a receiver tank 19, is introduced through a line 20 to blend with coal tar. The mixture is then introduced in a tube still 5 through a line 4, heated to a temperature in the range of 70–200°C, and thereafter introduced in a centrifugal precipitator 7 through a line 6. The oil-containing coal tar treated with the centrifugal precipitator is introduced in the tube still 5 through a line 8, wherein it is heated to a temperature of tar distillation and then introduced in the distillation tower 11 through a line 9, from which necessary tar oil fractions are taken out through lines 16, 17, and 18.

These tar oil fractions are used as starting materials for production of phenol, naphthalene, etc. Vapor from the top of the distillation tower 11 is introduced in an oil-cooler 13 through a line 12 and after cooling recycled into the distillation tower 11 through lines 14 and 15.

The residue containing quinoline-insoluble matter is discharged from the centrifugal precipitator 7 through a line 22 and water is also discharged through a line 21. 20 shows a still pot, in which soft pitch and medium pitch having low quinoline-insoluble matter content are obtained by adjusting discharging quantity of tar oil from, and said pitch being withdrawn through a line 23. As centrifugal precipitator, that of separator plate type or decanter type in which continuous separation is possible is advantageously used. Either a type of centrifugal precipitator which is capable of isolating water (water contained in tar), purified oil-containing tar and residue containing quinoline-insoluble matter or another type of centrifugal precipitator which is capable of isolating purified oil-containing tar and residue containing quinoline-insoluble matter may be used. In the latter case, water in coal tar is preferably removed previously.

However, the process for producing pitch of a low quinoline-insoluble matter content to be used in the process of production of pitch coke according to the present invention is not limited to the above technique. For example a pre-coated filter may be effectively used for separation of quinoline-insoluble matter from pitch. The essential requirement is the use of pitch from which quinoline-insoluble matter has been removed as much as possible as a starting material.

As described above, in the process of the present invention, quinoline-insoluble matter must be removed as much as possible. If a pitch from which quinoline-insoluble matter has not been removed is used as starting material pitch coke having a relatively low thermal expansion coefficient and good graphitizing property may be obtained. However the pitch coke having a desirable low thermal expansion coefficient and more excellent graphitizing property can be obtained by using a specific pitch from which quinoline-insoluble matter has been removed as much as possible and coking said pitch under a specific condition as described below.

It is to be noted further that even if pitch from which quinoline-insoluble matter has been removed is used as starting material, on an industrial scale, the desirable pitch coke of a high quality having low thermal expansion coefficient and excellent graphitizing property cannot be obtained, unless the following specific coking method is employed.

In other words, pitch coke of high qualities can be obtained only when the pitch low in quinoline-insoluble matter has been coked by means of a specific coking procedure according to the present invention.

Preparation of pitch coke from pitch of low quinoline-insoluble matter content according to the present invention will be described below.

According to the present invention, the needle-like coke is produced by delayed coking a pitch of low quinoline-insoluble matter content under special conditions as described below to obtain raw coke and then calcining the produced raw coke.

Among properties of the resulting coke product, crystal structure thereof largely depends upon preparation conditions of the raw coke. It is considered that the factors controlling crystal structure of the coke product are properties of starting pitch used for preparation of raw coke, heating conditions of the starting pitch and reaction conditions in a coking reactor.

According to the discovery of the inventors, it is observed that one of important factors influencing the crystal structure of coke is the light oil content in starting pitch of low quinoline-insoluble matter content. In other words, it has been confirmed that the ratio of amorphous coke to needle-like crystalline coke in the product varies depending upon content ratio of a fraction boiling out at temperatures below 400°C in starting pitch.

Light oil content is significant also for minimizing coking troubles caused during heating of starting pitch. However, light oil content in starting pitch is determined in consideration of desirable yield of needle-like crystal in the produced coke, coking troubles caused during coke production and productivity.

In coking of such a starting pitch on an industrial scale, it is quite difficult to heat a large quantity of pitch charged in a coking reactor to a temperature at which the coking reaction is initiated. Therefore, according to the process of the present invention, starting pitch is heated previously in a tubular furnace as employed in the production of petroleum coke and the preheated pitch is introduced in a reactor. In the stage of heating the starting pitch, occurrence of coking reaction which causes so-called coking troubles such as lowering in thermal conductivity of heating tubes must be checked as much as possible and, on the other hand, in the successive stage of coking reaction, the temperature must be elevated to a point sufficient for carrying out the coking reaction. Thus, both the above two requirements contrary to each other must be satisfied. The temperature in the heating stage, i.e. the temperature of starting pitch at the inlet of the coking reactor, also, is one of important factors influencing crystal structure of the resulting coke. The starting pitch should have a temperature above 450°C at the inlet of the coking reactor. At a temperature of heated starting pitch above 450°C, it is possible to obtain needle-like coke if other conditions such as light oil.
content of starting pitch and introduction conditions of the starting pitch into the coking reactor are satisfied. For minimizing coking troubles in the heating stage, a proper quantity of light oil as described above or steam is introduced in starting pitch thereby to make flow of the starting pitch turbulent, or to decrease the residence period of the pitch in the heating device, while homogeneous heating is effected.

As to quantity of steam to be added, the least possible quantity is desirable for producing needle-like coke according to the present invention, and minimum quantity thereof necessary to preventing coking troubles is added. Starting pitch thus heated is introduced in the reactor until pitch taking part in the coking reaction reaches to a regular quantity. Thus introduced preheated starting pitch passes through the pitch accumulated in the reactor to keep the temperature of the reacting zone in the reactor constant. During the introduction, a part of pitch taking part in the coking reaction stays in the reactor and the remainder mainly composed of light oil and steam is withdrawn from the top of the reactor. During this procedure, coking reaction of pitch staying in the reactor proceeds. In order to carry out the coking reaction completely, average temperature in the reactor must be kept above 400 °C for at least 20 hours after initiation of the introduction of the starting pitch. Quantity of the starting pitch introduced is also one of the factors influencing crystal structure of coke.

Upon cooling the resulting raw coke, it is finely divided by high pressure water or the like, taken out from the reactor and calcined in a known calcination apparatus, such as a rotary kiln, to obtain calcined coke.

As to crystal structures, change in structure of crystal was not observed in the calcination stage. Thus it is considered that the stage of producing raw coke is significant for the structure. Although the crystal structure of the calcined coke can be examined with the naked eye, for the raw coke it is preferable to use polarization with a microscope. Each of factors influencing to crystal structure of coke has been described above. After detailed investigations of interrelations of these factors, the inventors have found on the basis of numerous experimental results that a certain relation lies between rate of needle-like coke production and each of factors.

The relation may be shown by the following empirical formula and it was confirmed that results of the experiments agreed with the line shown in FIG. 2.

$$N = C + R(T_s - 450) \times \frac{Q}{X \times D}$$

wherein $N$ represents rate of needle-like coke production (percent) as described below, each of $C$ and $R$ represents a constant value of approximately $-41.5$ and $3.3$ respectively, $T_s$ represents temperature of starting pitch at an inlet of coking reactor (°C), $Q$ represents quantity of introduced starting pitch (tons/hr.) per $1 \ m^2$ cross section of the coking reactor and $D$ represents ratio by weight of distillate lighter than 400 °C for the starting pitch.

The rate of needle-shaped coke production (percent) means percentage by weight of needle-like crystal in the calcined coke obtained by calcining raw coke produced under fixed conditions, which is determined by taking up crystals of particle sizes above $5 \ mm$, dividing the particles into needle-like crystal and amorphous ones under the naked eye and calculating from weights of the crystal and amorphous ones.

"Coal pitch cokes of high quality" in this invention means those having $N \geq 70%$. Accordingly, as clearly shown in FIG. 2, needle-like coke of the present invention produced if ($T_s - 450)/Q \times D$ is above 34 units. In other words, rate needle-like coke production of above 70% can be obtained by adopting an introduction quantity of starting pitch $Q$ (t./hr./m.²) smaller than a calculated value ($T_s - 450)/34 \times D$.

Thus, according to the present invention, production of a desired rate of needle-like coke from a coal pitch of a low quinoline-insoluble matter content is possible by utilizing a delayed coking method of excellent productivity and high operational easiness.

Like coal pitch coke produced in a conventional chamber type coke oven, coke obtained according to the present invention has a low impurity content (i.e. ash and sulfur contents), and particularly, contents of vanadium, silicon and iron which are serious for coke to be used as electrode are extremely small as compared with petroleum coke. This is considered to be due to the fact that coal pitch of a low quinoline-insoluble matter content is used as starting material. Surprisingly, another merit in quality of the product of this invention is that ash and sulfur contents of coke obtained according to the present invention are smaller than those of coke obtained from the same coal pitch by a chamber type coking oven.

The table clearly shows advantages in quality judged from composition of coke obtained according to the present invention.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Pitch coke obtained by</th>
<th>Pitch coke obtained by</th>
<th>Pitch coke obtained by</th>
<th>Pitch coke obtained by</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a chamber</td>
<td>a chamber</td>
<td>a chamber</td>
<td>Petroleum coking oven</td>
</tr>
<tr>
<td>Water</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Solid carbon</td>
<td>99.5-0.95</td>
<td>99.3-0.95</td>
<td>99.0-0.96</td>
<td>99.0-0.96</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.2-0.35</td>
<td>0.2-0.35</td>
<td>0.2-0.35</td>
<td>0.2-0.35</td>
</tr>
<tr>
<td>Ash</td>
<td>0.1-0.2</td>
<td>0.1-0.2</td>
<td>0.1-0.2</td>
<td>0.1-0.2</td>
</tr>
<tr>
<td>Fec.</td>
<td>0.027</td>
<td>0.04-0.05</td>
<td>0.04-0.05</td>
<td>0.04-0.05</td>
</tr>
<tr>
<td>ADF</td>
<td>0.03</td>
<td>0.04-0.05</td>
<td>0.04-0.05</td>
<td>0.04-0.05</td>
</tr>
<tr>
<td>Fd</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Tests</td>
<td>0.93</td>
<td>0.94</td>
<td>0.94</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Per cent.</td>
<td>1,000-500</td>
<td>1,000-500</td>
<td>1,000-500</td>
<td>1,000-500</td>
</tr>
</tbody>
</table>

1 P.p.m.

The process of the present invention will be made more clear from the following example. It should be understood that the following example is given in order to illustrate the present invention but it by no means limits the scope of the invention.

EXAMPLE

For confirming effect of removing quinoline-insoluble matter in coal tar according to the present invention, the following experiments were carried out.

About 45 g. of oil-containing coal tar prepared by incorporating 10-30 parts of tar oil described below in 90-70 parts of dehydrated coal tar were placed in a centrifugal precipitator tube, which was placed in an oil bath and heated to about 100 °C. Then the heated centrifugal precipitator tube was placed in a rotor previously heated 100 °C. Centrifugation was started immediately. After attaining centrifugal force of 1,500 G (rotor 6,000 rpm.), centrifugation was continued for about 5 minutes. During the operation, quinoline-insoluble matter in coal tar was precipitated at the bottom of the centrifuge precipitation tube. After completion of the centrifugation, the tube was inclined to decant the supernatant liquid. The supernatant liquid and the residual precipitate were analyzed for quinoline-insoluble matter content. The results were as shown in Table 2. Analysis of quinoline-insoluble matter content was performed according to the specification of JIS K-2421.
TABLE 2 Percent

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Proportion (wt. percent)</th>
<th>QI content (percent)</th>
<th>Yield</th>
<th>QI Yield</th>
<th>QI</th>
<th>Rate of QI removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Coal tar A 90%; tar naphtha 10%</td>
<td>3.3</td>
<td>92.8</td>
<td>Trace</td>
<td>9.2</td>
<td>38.5</td>
</tr>
<tr>
<td>2</td>
<td>Coal tar B 85%; tar naphtha 15%</td>
<td>2.8</td>
<td>92.8</td>
<td>Trace</td>
<td>7.2</td>
<td>35.0</td>
</tr>
<tr>
<td>3</td>
<td>Coal tar B 80%; tar naphtha 20%</td>
<td>1.8</td>
<td>93.0</td>
<td>0.4</td>
<td>7.0</td>
<td>38.0</td>
</tr>
<tr>
<td>4</td>
<td>Coal tar B 75%; tar naphtha 25%</td>
<td>1.8</td>
<td>93.6</td>
<td>Trace</td>
<td>6.4</td>
<td>45.5</td>
</tr>
<tr>
<td>5</td>
<td>Coal tar B 70%; tar naphtha 30%</td>
<td>1.8</td>
<td>92.2</td>
<td>0.3</td>
<td>7.8</td>
<td>26.0</td>
</tr>
<tr>
<td>6</td>
<td>Coal tar B 65%; tar naphtha 35%</td>
<td>1.8</td>
<td>92.2</td>
<td>0.3</td>
<td>7.4</td>
<td>37.8</td>
</tr>
<tr>
<td>7</td>
<td>Coal tar B 60%; tar naphtha 40%</td>
<td>1.8</td>
<td>94.1</td>
<td>0.2</td>
<td>5.9</td>
<td>38.8</td>
</tr>
</tbody>
</table>

Notes:
In the Table QI represents quinoline-insoluble matter.
Rate of QI removal = ([QI in starting material (percent)] - [QI in supernatant liquid (percent)]) x 100

For reference, results of removal of quinoline-insoluble matter (QI) in the similar treatment of coal tar alone without tar oil dilution are shown in Table 3.

TABLE 3

<table>
<thead>
<tr>
<th>Run No.</th>
<th>QI content of coal tar</th>
<th>Supernatant liquid</th>
<th>Residue</th>
<th>Rate of QI removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Coal tar A 3.5</td>
<td>92.2</td>
<td>1.2</td>
<td>7.8</td>
</tr>
<tr>
<td>b</td>
<td>Coal tar B 3.3</td>
<td>98.9</td>
<td>2.5</td>
<td>3.1</td>
</tr>
</tbody>
</table>

By comparison of Tables 2 and 3, effect of removing quinoline-insoluble matter in coal tar according to the present invention is clearly recognized.

Properties of tar oils used in Table 2 were as follows:

<table>
<thead>
<tr>
<th>Name</th>
<th>Average boiling point (°C)</th>
<th>Distillation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tar light oil</td>
<td>162; FD-170°C; (above 60%)</td>
<td></td>
</tr>
<tr>
<td>Carvola oil</td>
<td>190; 170-200°C; (above 60%)</td>
<td></td>
</tr>
<tr>
<td>Naphthena oil</td>
<td>220; 200-250°C; (above 60%)</td>
<td></td>
</tr>
<tr>
<td>Wash oil</td>
<td>255; 250-260°C; (above 60%)</td>
<td></td>
</tr>
<tr>
<td>Tar naphtha</td>
<td>113; FD-160°C; (above 60%)</td>
<td></td>
</tr>
</tbody>
</table>

Note: Average boiling point means a temperature at which 50 wt. percent distillation has been effected according to Engler distillation.

In case of pitch, the same effect of removing quinoline-insoluble matter as above is also obtained.

Then, the pitch obtained by distillation of coal tar from which quinoline-insoluble matter had been removed in the above manner was blended with light oil collected at the top of the coking reactor, and then added with 1.2 wt. percent of steam. And, subsequently at once, the mixture was heated in a tubular furnace and introduced in a coking reactor. Relation between rate of needle-like coke in the resulting coke (N) and reaction conditions (i.e., properties of starting pitch (D), temperature of starting pitch at the inlet of coking reactor (T), and quantity of starting pitch per a unit cross section of reactor (Q)) is shown in Table 4.

TABLE 4

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Property of starting yield</th>
<th>wt. ratio of distillate D lighter than 400°C</th>
<th>Temperature at inlet of reactor (°C)</th>
<th>Quantity Introduced Ql (m³/hr, m³/l)</th>
<th>(T - 450°) Ql/D (°C/L)</th>
<th>Ratio of needle-like coke production (percent)</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>0.580</td>
<td>478</td>
<td>1.19</td>
<td>41.3</td>
<td>95</td>
<td>Example of the present invention.</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>0.555</td>
<td>478</td>
<td>1.19</td>
<td>38.8</td>
<td>95</td>
<td>Doa.</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>0.585</td>
<td>478</td>
<td>1.19</td>
<td>38.8</td>
<td>95</td>
<td>Doa.</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>0.573</td>
<td>478</td>
<td>1.35</td>
<td>43.9</td>
<td>90</td>
<td>Doa.</td>
</tr>
</tbody>
</table>

Note: Run No. 3 is a run of coking process in which quinoline-insoluble matter is not removed. Run No. 4 is a run of another coking process in which quinoline-insoluble matter was removed from the pitch, but other conditions were different from that of the present invention. In the above table, period of introduction is 24 hours, and average temperature in reactor is kept about 10°C lower than that at inlet of the reactor and also pressure in the reactor is kept at 2-3 kg/cm² G.

Each of needle-like coke in run Nos. 2 and 3 in Table 4 was calcined in an ordinary manner and then subjected to graphitizing treatment at 2300°C in a Tammman furnace under argon gas atmosphere. The results of measurement of real specific gravity and thermal ex-7676

pansion coefficients at 100-400°C with a dilatometer are shown in Table 5.

TABLE 5

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Real specific gravity</th>
<th>Coefficient of thermal expansion parallel to the needle-like crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2.22</td>
<td>0.05x10^-5</td>
</tr>
<tr>
<td>3</td>
<td>2.19</td>
<td>0.05x10^-5</td>
</tr>
</tbody>
</table>

Note: Real specific gravities were measured according to the specification of JIS K 2222.

What is claimed is:
1. In a delayed coking process for the preparation of coal pitch coke, the improvement which comprises blending coal tar with a tar oil in an amount of from 5 to 50%, by weight of the mixture of coal tar and tar oil, separating from said blend a pitch-containing liquid substantially free of quinoline-insoluble material, subjecting said pitch-containing liquid to coal tar distillation to produce coal pitch substantially free of quinoline-insoluble material, heating said coal pitch to a temperature above 450°C, introducing said heated coal pitch into a delayed coking reactor at a surface velocity which, expressed in tons/hour/meter of reactor cross-section, is less than

(T0 - 450°C)/34D

where T0 is the temperature in degrees centigrade of the heated pitch, and D is the weight ratio of the pitch components volatilizing at temperatures up to 400°C to total components, maintaining said coal pitch in said reactor at a temperature above 400°C for at least twenty hours while removing volatile products formed, and recovering coke having a ratio of crystalline needle-like structure to amorphous structure, for particles of a size greater than 1 mm, of at least 70%.

2. The process as defined in claim 1 wherein said separation is effected in a centrifuge.

3. The process as defined in claim 1 wherein said separation is effected through filtration at elevated temperatures.
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9. The process as defined in claim 5 wherein the light oil is petroleum oil.

10. The process as defined in claim 4 wherein said separation is effected in a centrifuge.

7. The process as defined in claim 5 wherein the light oil is petroleum oil.

8. The process as defined in claim 4 wherein said separation is effected in a centrifuge.

5. The process as defined in claim 4 wherein said coal pitch is blended with light oil and diluted with steam prior to heating.

6. The process as defined in claim 5 wherein the light oil is tar oil.

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U.S. Cl. X.R.

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