(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 089 840**
A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **83301552.2**

(51) Int. Cl.³: **C 10 C 3/00**

(22) Date of filing: **21.03.83**

(30) Priority: **24.03.82 JP 47903/82**

(43) Date of publication of application:
28.09.83 Bulletin 83/39

(84) Designated Contracting States:
BE DE FR GB IT NL

(71) Applicant: **TOA NENRYO KOGYO K.K.**
1-1 Hitotsubashi, 1-Chome Chiyoda-Ku
Tokyo(JP)

(72) Inventor: **Izumi, Takayuki**
1907-7, Aza-Tachigaeri Oaza-Kamekubo
Ohi-machi Iruma-gun Saitama-ken(JP)

(72) Inventor: **Naito, Tsutomu**
591-1, Aza-Hachiman Oaza Suneori
Tsurugashima-cho Iruma-gun Saitama-ken(JP)

(74) Representative: **Pitkin, Robert Wilfred et al,**
ESSO Engineering (Europe) Ltd. Patents & Licences
Apex Tower High Street
New Malden Surrey KT3 4DJ(GB)

(54) Process for producing an optically anisotropic carbonaceous pitch.

(57) A process for producing an optically anisotropic carbonaceous pitch comprises (a) heat treating a starting material which preferably comprises a carbonaceous heavy oil, at conditions which will favour the formation of an anisotropic pitch phase; (b) stopping said heat treating at an early stage in said formation; (c) maintaining the thus partially treated material at a temperature in the range 200 to 400°C; (d) subjecting the material from step (c) to a settling treatment, while maintaining the material in a molten state; (e) removing the anisotropic pitch phase which separates in step (d); and (f) su;bjecting at least a portiion of the remaining material to an after-treatment including a heat treatment for forming and/or concentrating an anisotropic pitch phase therein.

A preferred step (b) comprises stopping the heat treatment when a pitch is obtained having a globular optically anisotropic phase content of 5-50 wt.%, a quinoline-insoluble matter content of 2-20 wt.%, a quinoline-insoluble/benzene-soluble matter content of 5-40 wt.% and a softening point of the formed pitch as a whole of up to 200°C.

EP 0 089 840 A1

Field of the Invention

The present invention relates to a process for producing an optically anisotropic carbonaceous pitch suitable for the production of carbon fibers and other carbonaceous materials having a high strength and high modulus of elasticity.

Background of the Invention

In the recent energy-saving and resource-saving age, there have been eagerly demanded low-cost, high-performance carbon fibers for producing light-weight composite materials having a high modulus of elasticity required for the production of aircrafts, motorcars, etc. or molding carbonaceous materials having a high strength and high density by compression-molding into various products.

The composition and structure of optically anisotropic pitches suitable for the production of high-performance carbon fibers have not fully been elucidated. The relationship between physical properties of carbonaceous pitch and composition and structure thereof has been unclear. There has not been developed any satisfactory technique for obtaining pitches having satisfactory properties stably on an industrial basis.

Known optically anisotropic pitches such as those disclosed in Japanese Patent Laid-Open Nos. 19127/1974, 89635/1975 and 118028/1975 are produced by only a step of subjecting isotropic pitches to thermal decomposition/polycondensation reaction to make them heavier. An optically anisotropic phase (hereinafter referred to as AP) correspond substantially to quinoline-

insoluble matter (or pyridine-insoluble matter). If AP is increased to nearly 100%, the softening point of the pitch is raised remarkably and the spinning temperature is elevated to about 400°C or higher. Consequently, a gas is formed due to decomposition of the pitch and polymerization occurs during the spinning operation. Therefore, in these processes, the AP content is controlled below 90%, practically 50-70%, so as to prevent excessive spinning temperature elevation for preventing the remarkable thermal decomposition and thermal polymerization.

However, pitch compositions obtained by the conventional processes are heterogeneous, since they are mixtures of AP and a considerable amount of an optically isotropic phase (hereinafter referred to as IP). Therefore, they have defects that the fibers are broken in the course of the spinning and the fibers have uneven thickness and low strength.

Some of the pitches disclosed in Japanese Patent Publication No. 8634/1974 has an AP content of 100%. However, this is a special pitch having a specified chemical structure of the molecules. Such a pitch is produced by simple thermal polymerization of an expensive pure substance such as chrysene, phenanthrene or tetrabenzophenazine. It has a relatively well-controlled structural molecular weight. On the other hand, pitches produced from ordinary mixed starting materials have generally quite high softening points.

Pitches used as starting materials for the production of carbon fibers disclosed in Japanese Patent Publication No. 7533/1978 have a low softening point and spinning temperature and, therefore, they can be spun easily. However, their AP content is unclear. Further, these pitches obtained by polycondensation of staring

hydrocarbons in the presence of a Lewis acid catalyst such as aluminum chloride have a special composition and structure. Carbon fibers produced from them have a low strength and modulus of elasticity. Another problem is that it is difficult to completely remove the catalyst.

Pitches disclosed in Japanese Patent Laid-Open No. 55625/1979 are homogeneous ones comprising substantially 100% AP. They are produced also by only the thermal reaction of an isotropic pitch while the thermal decomposition/polycondensation reaction is carefully controlled. The pitches obtained by this process have a softening point of above about 330°C and spinning temperature of 370 to 400°C or higher. Under these temperature conditions, it is still difficult to spin the pitches stably on an industrial basis.

Pitches disclosed in Japanese Patent Laid-Open Nos. 160427/1979, 58287/1980, 130809/1980, 144087/1980 and 57881/1981 are produced by subjecting an isotropic pitch or a pitch containing only a small amount of AP to extraction with a solvent to extract a fraction comprising substantially AP and melting the same. By this process, optically anisotropic pitches having a narrow molecular weight distribution and a low quinoline-insoluble matter content are obtained. However, it is understood from the production process and data disclosed therein that the obtained pitches have generally a high softening point and a spinning temperature of as high as about 400°C is required.

As described above, homogeneous, optically anisotropic pitches having an AP content of approximately 100% produced by the known processes are expensive and they have generally high softening points and, accordingly, the stable spinning of them is difficult. On the other hand, pitches having a low softening point are heterogeneous excluding those having special compositions and structures produced from special starting materials, and spinning of them is also difficult. As a result, it is difficult to obtain carbon fibers having excellent qualities.

After intensive investigations of optically anisotropic pitch compositions suitable for the production of high-performance carbon fibers, the inventors previously found that the optically anisotropic pitches have a well-developed laminate structure of condensed polycyclic aromatic compounds and a high molecular orientation, and actually, there are various kinds of optically anisotropic pitches. Among them, those having a low softening point and suitable for the production of homogeneous carbon fibers have a special chemical structure and composition. Namely, the inventors found that compositions, structures and molecular weights of a component O (i.e., n-heptane-soluble component) and a component A (i.e., n-heptane-insoluble/benzene-soluble component) are quite important. A process for producing such optically anisotropic pitches is disclosed in the specification accompanying European Patent Application 81305427.7.

Summary of the Invention

If a heavy hydrocarbon oil, tar or pitch obtained in petroleum industry or coal chemical industry used as a starting material of pitch is subjected to thermal reaction for making the same heavier, the softening point and viscosity of the pitch as a whole

at a given temperature are elevated generally with an increase in the AP content. With an AP content of approximately 100%, the softening point and viscosity of the pitch are very high and the molding process becomes difficult in many cases.

One of the reasons therefor is that AP formed in the initial stage of the thermal reaction stays in the reaction system for a long time and, therefore, polycondensation reaction proceeds excessively. Another reason is that AP formed in the initial stage of the thermal reaction consists of substances having softening points higher than those constituting AP formed thereafter.

If the pitch in a molten state is settled after the partial formation of AP in the heat treatment to make the pitch heavier and only AP forming a lower layer is taken out, an optically anisotropic pitch having a softening point far lower than that obtained without the settling step and a sufficiently high AP Our European Patent Application 81303276.0 discloses this process.
This process is characterized in that a starting material for the production of pitch is subjected to thermal decomposition/polycondensation, the reaction mixture is settled when the polycondensate having a given AP content has been obtained to deposit high-density AP to form a lower layer and the lower layer is separated from an upper layer (pitch mainly comprising IP of a low density).

After further investigations of the optically anisotropic pitch having such a low softening point, high AP content and excellent homogeneity, a main object of the present invention is to provide a process for producing an optically anisotropic carbonaceous

pitch having a low softening point and suitable for the production of carbon materials, particularly carbon fibers, having a high strength and a high modulus of elasticity.

Another object of the invention is to provide a process for producing a homogeneous optically anisotropic carbonaceous pitch having a high orientation and suitable for the production of carbon materials, particularly carbon fibers, having a high strength and a high modulus of elasticity.

Still another object of the invention is to provide a process for producing an optically anisotropic carbonaceous pitch having an excellent spinnability which can be spun at a temperature sufficiently lower than that at which remarkable thermal decomposition/polycondensation reaction occurs, resulting in carbon fibers having a high strength and a high modulus of elasticity.

A further object of the invention is to provide a process for producing an optically anisotropic carbonaceous pitch capable of forming the optically anisotropic carbonaceous pitch having a stable, high quality irrespective of variation of properties of the starting material and, therefore, capable of producing a high-quality carbon material in an economically advantageous manner.

Brief Description of the Drawings

The Figure is a graph showing changes in yield of a heat-settled lower layer AP △ and a softening point ○ thereof with time of the thermal reaction for making the pitch heavier.

α .....zone in which the settling is possible

β .....zone in which the settling is impossible.

Detailed Description of the Invention

First, the pitch was subject to an isothermal heat treatment for various times for making the same heavier and then the pitch was settled and the softening point of a lower layer (pitch of about 100% AP) was examined. The results are shown in an attached figure. In the Figure, a curve with symbols ○ shows a relationship between the heat reaction time and softening point of the lower layer (AP) after the heat-settling. It will be understood that the softening point is lowered initially with the thermal reaction time but is then elevated after 2 hr. A curve with symbols △ shows a relationship between the thermal reaction time and yield of the heat-settled lower AP layer. It will be understood that yield of the lower AP layer is increased with the thermal reaction time. Further, it is shown that if the thermal reaction for making the pitch heavier is carried out for longer than about 2.5 h, the separation by the settling becomes difficult.

From the results obtained in the above experiments, the inventors have found that, if the thermal reaction for making the pitch heavier is carried out for a short time, AP obtained in the initial stage is removed by the settling and an upper layer is again subjected to the thermal reaction or is again subjected to the heat-settling, an optically anisotropic pitch having a lower softening point and a higher AP content than those obtained without removing AP in the initial stage can be obtained.

AP formed in the initial stage of the above-mentioned thermal reaction may be removed by extraction with a solvent or filtration under heating under elevated pressure, in addition to the heat-settling process. However, both of the former processes are expensive and have practically difficult problems. The inventors considered, therefore, that the heat-settling process is the most excellent, inexpensive and easy process.

The precipitate formed in the initial stage of the thermal reaction can be settled easily at a low settling temperature in a short settling time, since the softening point of the whole pitch system and viscosity thereof at a settling temperature are extremely low in the initial stage.

By employing the process of the present invention wherein the precipitate formed in the initial stage of the thermal reaction is removed by settling, it becomes possible to remove also foreign matters in the form of solid particles contained in the starting material for the pitch, high-molecular carbonaceous materials and quinoline-insoluble matters of quite high molecular weights which are apt to be formed in the initial stage. Accordingly, an advantage is obtained that even if properties of the starting material are changed, the optically anisotropic pitch having a stable quality can be obtained.

The above-mentioned objects and other objects of the present invention can be attained by employing a process which comprises stopping the thermal reaction of a starting material for pitch for making the pitch heavier in the initial stage of the reaction, subjecting the pitch to a heat settling treatment to divide the pitch into two layers, removing and precipitated and concentrated lower heavy pitch layer and subjecting the

residual upper layer to an after-treatment including the thermal reaction for making the same heavier.

Meaning of the term "optically anisotropic phase (AP)" used herein is not necessarily standardized in the art or in various technical publications. In this specification, the term "optically anisotropic phase (AP)" refers to one form of pitch constituents which, when a section of a pitch mass solidified at around room temperature is polished and observed by means of a reflection-type polarizing microscope under crossed nicols, exhibits brilliance upon rotation of the sample or cross nicols, namely an optically anisotropic moiety. A moiety exhibiting no brilliance, i.e., having an optical isotropy, is called an optically isotropic phase (IP). A clear boundary is recognized between AP and IP. Foreign matters different from AP or IP such as dusts and bubbles are clearly distinguishable.

AP comprises mainly molecules having such a chemical structure that the planarity of the polycyclic aromatic condensed rings are more highly developed than those of IP, the planar structures being aggregated and associated together to form a laminate structure. At a melting temperature, the optically anisotropic phase is considered to be in the form of a liquid crystal. Therefore, if it is extruded through a thin nozzle in the spinning step, the molecules are so arranged that the planar surfaces thereof are substantially in pallalel with the fiber axis. Consequently, the carbon fibers produced from the optically anisotropic pitch exhibit a high modulus of elasticity. The amount of AP or IP is determined by observing and taking a picture thereof by means of a polarizing microscope under crossed nicols and measuring an areal ratio of AP or IP. It is represented by vol.% in practice.

A difference in specific gravity between AP and IP is as small as about 0.05 at room temperature. Therefore, the vol.% may be considered to be substantially equal to a wt.% in the determination of these values.

"Optically anisotropic pitch" defined in this specification is a pitch having an AP content of 100% or an extremely high AP content and containing IP in the form of globular particles or islands of indeterminate forms.

As for homogeneity of the pitch, the one which exhibits a high homogeneity in the actual melt spinning step has a sufficiently low IP content determined as described above. In this pitch, solid particles having a diameter of at least 1 μ are not substantially detected therein in the observation of the section thereof with a reflection-type microscope. The pitch does not substantially form bubbles due to a volatile matter at the melt-spinning temperature. Such a pitch is referred to as substantially homogeneous, optically anisotropic pitch.

When a pitch having an IP content of higher than 20% or a pitch containing IP particles of a large size (even if content thereof is 20%) is spun, a breaking frequency of the fiber is high, a high-speed spinning is difficult, a sufficiently small fiber thickness cannot be obtained, the fiber thickness is uneven and, consequently, high-performance carbon fibers cannot be obtained, since the pitch subjected to the spinning is a mixture of those having quite different viscosities, i.e. a mixture of AP having a high viscosity and IP having a low viscosity. If infusible fine solid particles or low molecular weight volatile substances are contained in the pitch, the spinnability

of the pitch is deteriorated in the melt spinning step as a matter of course.

The term "softening point of pitch" herein refers to a temperature at which the pitch transfers from the solid state into a liquid state. The softening point is determined from a peak temperature of latent heat absorbed or released when the pitch is molten or solidified by means of a differential scanning calorimeter. This temperature coincides with that determined by the ring-and-ball method or micro melting point method with an error of $\pm$ 10°C in each pitch sample. The term "low softening point" herein refers to a softening point in the range from 230 to 320°C. The softening point is closely related to the melt-spinning temperature of the pitch (not necessarily the temperature of the pitch at the nozzle but the highest necessary temperature of the pitch in the spinning machine). In general spinning methods, a viscosity suitable for the spinning is realized at a temperature about 60-100°C higher than the softening point, though it varies depending on variety of the pitch used. If the softening point is higher than about 320°C, the spinning is effected at a temperature higher than 380°C at which the thermal cracking and polycondensation occur. Therefore, cracked gas and unmelted matter are formed, thereby deteriorating the spinning properties. In addition, the pitch fibers thus obtained contain bubbles and solid foreign matters disadvantageously. If the softening point is lower than 230°C, an infusibilization treatment of pitch fiber at a low temperature for a long period of time is required. Therefore, the treatment becomes complicated and expensive in such a case unfavorably.

A powdery pitch is charged in a cylindrical filter having an average pore diameter of 1 μ. Heat extraction is effected with n-heptane in a Soxhlet extractor for 20 h. An n-heptane-soluble matter obtained as above will be referred to as component 0. Then, it is heat-extracted with benzene for 20 h to obtain an n-heptane-insoluble/benzene-soluble matter which will be referred to as component A. The residual benzene-insoluble matter is treated by centrifugation according to JIS K-2425 with quinoline as solvent. A benzene-insoluble/quinoline-soluble matter (so-called β-resin) will be referred to as component B and a quinoline-insoluble matter will be referred to as component C. The fractionation may be effected by, for example, a method disclosed on page 45 of "Journal of Japan Petroleum Society" 20, (1) (1977).

Component C may be extracted and analyzed by, in addition to the above-described process, a process of ASTM D-2318-76 (wherein the extraction and filtration are effected at 75°C), a boiling quinoline process (wherein the extraction and filtration are effected using boiling quinoline) and a boiling pyridine method (i.e. Soxhlet extraction using pyridine). After experiments using various pitch samples, the inventors have found that data obtained by the JIS quinoline process, ASTM process and boiling pyridine process are substantially equivalent but according to the boiling quinoline process, insoluble matter data of as low as 1/2 to 3/4 of the data obtained by the other processes are obtained.

The term "heat settling" herein means precipitation and aggregation of a high-specific gravity phase into the direction of gravity force by maintaining the pitch in a molten state at a temperature necessary and sufficient for the precipitation and aggregation of the high-specific gravity phase including AP and other

infusible matters in a slightly or no turbulent flow. Therefore, this operation includes a standing method in a slightly turbulent stream, a heat centrifugal separation method and a liquid cyclone method.

The process of the present invention for producing the optically anisotropic pitch will be described in more detail.

The process of the present invention wherein a starting material for pitch is heated to convert the same into a heavy product and to form or to increase and concentrate AP phase-forming components is characterized in that the pitch satisfying certain conditions obtained in the initial stage of the heat treatment is subjected to the easy and low-cost heat setting treatment to precipitate and concentrate components contained in the pitch in the initial stage as high-specific gravity components, since the incorporation of them in the final pitch product is undesirable. Then the lower layer is removed, an upper layer pitch containing components of a low specific gravity in a large amount is used as a starting material in the next step and the pitch is further subjected to a heat treatment including the conversion thereof into a heavy product.

As the starting materials for the pitch, there may be used various carbonaceous heavy oils, tars and pitches obtained in petroleum or coal industry. Preferred starting materials are those specified in the specifications accompanying our European Patent Application No.82300420.5 and our Japanese Patent Application 135296/1981.

More particularly, the preferred starting materials are (1) oily products containing as main component a carbonaceous heavy oil having a boiling point of 250-540°C which products have an aromatic

carbon fraction in the aromatic oil and resin in the n-heptane-soluble matter of at least 0.6 and a number-average molecular weight of up to 1,000 or (2) tarry substances mainly comprising components having a boiling point of at least 540°C which tarry substances have an aromatic carbon fraction in the aromatic oil and resin of at least 0.7 and a number-average molecular weight of up to 1,000.

If these starting materials for pitch are subjected to the thermal reaction at a temperature of 370-500°C, preferably 380-430°C, to effect mainly thermal cracking and thermal polycondensation and to convert the materials into heavy products and then volatile matters are removed from the cracked products, AP is formed and increased in amount and finally an optically anisotropic pitch is obtained. However, according to the improved process of the present invention for producing the pitches having higher and stable qualities, and thermal reaction is stopped in the initial stage and the reaction mixture is transferred to the characteristic heat settling step.

The time at which the pitch is transferred to the heat settling step is such that the pitch contains quinoline-insoluble matter and benzene-insoluble matter as minor components, has not so high softening point and contains two phases having different specific gravities in a molten state. More concretely, the pitch to be subjected to the heat settling should have a quinoline-insoluble matter content of about 2-20 wt.%, a quinoline-soluble/benzene-insoluble matter content of about 5-40 wt.%, a softening point of up to 200°C and a relatively high specific gravity phase content of 5-50 wt.% (in a molten state at a temperature about 100°C higher than the softening point). The pitches having the above-described properties may be obtained

by slightly heat-treating the above-mentioned starting materials under broad conditions without limiting the properties so strictly as shown above, or they can be obtained directly from other processes or other pitch makers.

If the pitch to be subjected to the heat settling is heat-treated excessively and its quinoline-insoluble matter content or benzene-insoluble matter content is far higher than the range shown above, the amount of the lower layer pitch to be discarded in the heat settling becomes large and finally, the yield of the intended product is lowered unfavorably. If the softening point is higher than about 200°C, a high temperature and long residence time are required in the heat settling step unfavorably.

On the other hand, if the heat treatment is insufficient and the pitch has (1) a quinoline-insoluble matter content or benzene-insoluble matter content lower than the above-mentioned range and (2) too low content of a high-specific gravity phase, the separation of the lower layer becomes insufficient or a large amount of the upper layer is discarded together with the lower layer in the heat settling step and the object of the present invention cannot be attained in many cases.

Then, the above-described carbonaceous material for pitch is prepared or got in the market and is subjected to the heat settling treatment. In the heat settling step, thermal reactions such as thermal cracking and thermal polymerization proceed slowly at a sufficiently mild temperature range in which the pitch can be kept in a molten, sufficiently fluid state. More concretely, a temperature in the range from 200 to 400°C is employed, though it varies depending on the softening point and viscosity of the pitch to be treated. This

step is characterized in that the pitch per se can be settled directly in a molten state according to the precipitation due to gravitation, while a solvent or additive may be incorporated therein.

A temperature as high as above 400°C is not preferred in this step, since at such a high temperature, troubles are caused in the system by bubbling or evaporation of products formed by the thermal cracking. Another reason therefor is that coking of the metal surface of the settling vessel would be caused, since the liquid phase is not stirred or the flow is only slight. At a temperature lower than 200°C, a sufficiently fluidity cannot be obtained even if the pitch subjected to the settling treatment has a softening point far lower than 200°C. At such a low temperature, problems are posed that a long residence time is required for the settling or that the phase separation does not occur at all, or that the lower layer cannot be taken out easily.

In the settling step, the object can be attained by maintaining the pitch in a molten state at the above-mentioned temperature for a given time even without stirring. However, as a matter of course, the pitch may be stirred slowly or the whole pitch may be allowed to flow in such a manner that the phase precipitation is not inhibited for the purpose of effecting the separation continuously or for the purpose of obtaining a uniform temperature distribution throughout the system.

In the heat settling step, the separation of the phase having a higher specific gravity is effected for the purpose of concentrating and removing a major part of the phase having a higher specific gravity from the pitch. It is unnecessary to completely precipitate

100% of the phase as the lower layer or to completely remove 100% of the lower layer.

The upper layer pitch obtained after the heat settling followed by the removal of the lower layer still contains only a small amount of the phase having a higher specific gravity. However, this phase does not exert significant influences on the final product, since it is one of the original constituents of the pitch. The higher the degree of concentration of the lower layer phase of a higher specific gravity, the better in the heat settling step. However, a degree of concentration of about 70-90% is satisfactory in general. The amount of the phase having a higher specific gravity still remaining in the upper layer after the separation is preferably small. The object can be attained, however, if the amount is as small as 5-30% based on the amount thereof contained prior to the settling.

Process for the preparation of the pitch to be subjected to the heat settling treatment is not particularly limited in the present invention. However, there may be mentioned two preferred processes for preparing the pitch by subjecting various carbonaceous heavy oils, tar or pitch obtained in petroleum or coal industry to the heat treatment as described below.

One of the processes comprises heating a starting material for the production of pitch to a temperature in the range from about 370 to 460°C, preferably 400 to 430°C while an inert gas is introduced above the pitch surface or in the liquid pitch phase to cause bubbling and to accelerate the removal of low molecular weight volatile matter, stopping the thermal reaction when the pitch residue having a globular AP content of 5-50%, a quinoline-insoluble matter content of 2-20 wt.% and a softening point of the pitch

as a whole of up to 200°C has been obtained, and transferring the reaction product from the reaction vessel to the subsequent heat settling step. The heat settling is effected preferably at a temperature in the range from 250 to 400°C.

The other improved process for preparing the pitch to be heat-settled comprises heating a starting material for the production of pitch to a temperature in the range from 370 to 460°C, preferably from 400 to 430°C to effect a thermal reaction without the introduction of inert gas or rather in a closed system. This process may be effected under elevated pressure without forcing to remove volatile matters but under accelerated reflux of the starting material or oil formed by the cracking. More concretely, the starting material sealed or continuously introduced in a high pressure thermal reaction vessel or tube is heated to the above-mentioned temperature. The pressure is elevated by low molecular products formed by the thermal cracking. The reaction is continued while the pressure is controlled until a pitch having a quinoline-insoluble matter content of 2-10 wt.% a benzene-soluble matter content of at least 60 wt.% and a softening point of up to 150°C has been obtained. The pitch is taken out of the reaction tank and transferred to the subsequent heat settling step. In another analogous process, the thermal reaction is carried out at the above-described reaction temperature under atmospheric pressure without particular acceleration of the removal or volatile matters but rather under the reflux of a major part of the starting material and low-molecular weight substances into the reaction system at the bottom of the reactor to control the quinoline-insoluble matter content of the resulting pitch to 2-10 wt.%, the benzene-soluble matter content to at least 60 wt.% and the softening point to up to 150°C.

When the reaction is carried out in the closed system, pressure exhibit no direct effect on the acceleration of the reaction and the pressure may be elevated for the purpose of inhibiting the removal of volatile matter in the cracking products or unreacted reaction material from the reaction system. However, it is preferred to control the pressure to 1 to 50 kg/cm by means of a leak valve when the reaction temperature is around 430°C, since pressure is preferably as low as possible.

As a matter of course, the liquid phase should be stirred sufficiently or allowed to flow in the preparation of the pitch to be subjected to the heat settling so that the two phases formed in this step are not separated clearly from each other and uniform temperature distribution can be obtained.

When the reaction is carried out in the closed system, pressure exhibit no direct effect on the acceleration of the reaction and the pressure may be elevated for the purpose of inhibiting the removal of volatile matter in the cracking products or unreacted reaction material from the reaction system. However, it is preferred to control the pressure to 1 to 50 kg/cm^2 by means of a leak valve when the reaction temperature is around 430°C, since pressure is preferably as low as possible.

As a matter of course, the liquid phase should be stirred sufficiently or allowed to flow in the preparation of the pitch to be subjected to the heat settling so that the two phases formed in this step are not separated clearly from each other and uniform temperature distribution can be obtained.

The process for producing the pitch to be subjected to the heat settling by the heat treatment in the above-mentioned closed system or in an atmospheric pressure system wherein the removal of volatile matters is not accelerated is characterized in that the pitch contains a large amount of low-molecular weight substances and, therefore, the subsequent heat settling can be effected at a lower temperature. More particularly, the object can be attained at a temperature of 150-400°C, preferably 200-350°C, under easy operating conditions without causing thermal reaction.

Now, the description will be made on the after-treatment of "pitch containing a large amount of the phase having a lower specific gravity" obtained by the heat settling.

Process for the after-treament is not particularly limited. Any process capable of increasing an AP content in the pitch while a softening point is not elevated significantly may be employed. After investigations, the inventors have found that two processes which will be described below are particularly preferred.

One of the processes comprises subjecting the "pitch containing a large amount of the phase having a lower specific gravity" to the heat treatment to convert the same into heavy product at 300-420°C after the heat settling treatment. This treatment is continued until the IP content of the residual pitch has been reduced to less than 20%. Namely, this treatment is effected mainly for concentrating the AP-forming pitch contained in the "pitch containing a large amount of the phase having a lower specific gravity" obtained by the heat settling and also for forming fresh AP by the thermal chemical reaction. In an embodiment of this process, the lighter pitch obtained by the heat settling

is subjected to the thermal reactions mainly comprising thermal cracking and thermal polycondensation reactions at a temperature of 350-420°C, preferably 370-420°C while an inert gas is introduced into the reaction system or under reduced pressure to convert the light pitch partially into heavy components and also to distill another part of the light pitch from the reaction system, whereby the pitch is made gradually heavier. Thus, the AP-forming components are concentrated. This thermal treatment is finished when an intended pitch having an AP content of at least 80%, a softening point in the range from 230-320°C and a quinoline-insoluble matter content of no higher than 70%, preferably no higher than 50 wt.% and particularly no higher than 40 wt.% is obtained.

The other process for the heat treatment for converting the pitch into heavy product comprises dividing the reaction step into two steps, i.e., a thermal chemical reaction step and a distillation step in which the thermal reaction proceeds only slightly. The lighter pitch obtained by the heat settling is subjected to the thermal chemical reactions mainly comprising thermal cracking and thermal polycondensation at 370-420°C, preferably 390-400°C in a closed system or under such reflux conditions that the removal of volatile matter is not particularly accelerated. Then, the resulting pitch is subjected to thermal cracking/polycondensation reaction under mild conditions at a temperature in the range from 300-370°C, preferably 320-350°C and low-molecular substances are removed under reduced pressure or with introduction of an inert gas to obtain a pitch having an AP content of at least 80%, a softening point in the range from 230-320°C and a quinoline-insoluble matter content of no higher than 70 wt.%, preferably no higher than 50 wt.% and particularly no higher than 40 wt.%.

According to this process, pitches of various properties can be obtained by suitably combining the thermal chemical reaction temperature with residence time or conditions of the volatile matter-removing operation with the residence time. As compared with the process wherein the volatile matters is removed simultaneously, this process is characterized in that a stable operation can be effected under sufficiently broad conditions, a continuous or semi-continuous treatment is possible and an intended product can be obtained in a high yield.

In an improved embodiment of this process, the thermal reaction at 370-420°C is omitted and the AP content of the pitch can be increased only by a low-temperature heat treatment carried out at a low temperature under reduced pressure or with introduction of an inert gas. More particularly, the light pitch obtained by the heat settling is treated at a temperature of 300-370°C, preferably 300-350°C under reduced pressure or with introduction of an inert gas for a long residence time. By this treatment, heavy AP-forming components contained in the pitch are thermally cracked and polycondensed slowly and a major part of excessive low-molecular weight substances is distilled off to obtain a pitch having an AP content of at least 80% usually at least 90%, a softening point in the range from 230-320°C and a quinoline-insoluble matter content of no more than 40 wt.%.

This process has an advantage that the operation in each step is easy, though it takes a long time for the treatment.

As a matter of course, it is preferred that the pitch is stirred sufficiently or the liquid phase is allowed to flow so as to maintain a uniform pitch

temperature and to avoid the phase separation in the heat treatment for making the pitch heavier.

The inert gas used in the above-mentioned step is one which does not remarkably chemically react with the pitch at a temperature around 400°C. As practical inert gases, N_2, Ar, steam and low-molecular weight hydrocarbons can be used.

Another process for the after-treatment of the light pitch obtained by the heat settling comprises subjecting the light pitch obtained by heat settling to the heat treatment for making the same heavier, stopping this treatment halfway, subjecting the pitch again to the heat settling and taking "pitch containing a large amount of a high-specific gravity phase" in the lower layer as the intended product.

In this process, the heat treatment for making the pitch heavier is carried out in the same manner as above at the same temperature as above. However, the pitch having an AP content of at least 80%, a softening point of 230-320°C and a quinoline-insoluble matter content of no more than 70% is not approached directly by this treatment only. This treatment is stopped halfway when a pitch having an AP content of 20-70%, preferably 30-50%, a quinoline-insoluble matter content of up to 25 wt.%, preferably up to 20 wt.%, a quinoline-soluble/benzene-insoluble matter content of at least 25 wt.%, preferably at least 30 wt.% and a softening point of the pitch as a whole of up to 250°C has been obtained. Then, the pitch is again subjected to the heat settling at a temperature in the range from 330 to 400°C to precipitate and aggregate AP spheres of a higher specific gravity and to form a lower layer. The lower layer pitch comprising substantially AP is separated from the upper layer pitch comprising mainly

IP. The pitch thus obtained may be subjected further to a finishing treatment, if necessary. The optically anisotropic pitch obtained as above has an AP content of at least 80% usually at least 90%, a softening point in the range from 230 to 320°C and a quinoline-insoluble matter content of no more than 70 wt.%.

According to this process, it is possible to obtain an optically anisotropic carbonaceous pitch more excellent than that obtained by the above-mentioned process wherein the after-treatment is effected only by the heat treatment for making the pitch heavier. Namely, the pitch obtained by this process has a higher AP content and lower softening point and it has higher spinnability and gives carbon fibers and graphite fibers having more excellent properties.

In the heat treatment for making the pitch heavier in this process, the temperature, reactor, flowing method and stirring method may be the same as those described above and the residence time is shorter than the above.

The second heat settling in this process may be effected in the same manner as in the first heat settling except that the temperature range is different. The second heat settling step is effected at a temperature of 330-400°C for maintaining the viscosity of the whole system sufficiently low and for precipitating spherical particles or masses of AP to form the lower layer while the aggregation and aging of AP are accelerated, since the pitch subjected to the second heat settling treatment has been made considerably heavier. If a temperature below 320°C is employed in this step, the aggregation, precipitation and separation of lower layer AP become difficult. At a temperature above 410°C, a residence time of several minutes is required

generally, though AP is separated in such a short time in some cases. If the residence time is as long as above, a violent thermal reaction occurs to elevate the softening point of the resulting pitch unfavorably.

The following examples and comparative examples will further illustrate the present invention.

Example 1

A pitch having about 20% AP content and softening point of 168°C was used as starting material, said AP comprising globular particles having a diameter of up to about 100 μ. The pitch had a quinoline-insoluble matter content of 14.9 wt.% and a quinoline-soluble/benzene-insoluble matter content of 30.1 wt.%.

300 g of the starting pitch was charged in a 500 mℓ cylindrical glass vessel and left to stand in a nitrogen atmosphere in a muffle furnace at 360°C for 1 h. After cooling, the glass vessel was broken to obtain about 36 g of a lower layer, i.e., relatively brittle, dim pitch and about 260 g of an upper pitch layer.

The lower layer pitch was optically anisotropic and comprised nearly 100% AP. This pitch had a quinoline-insoluble matter content of 65.6 wt.% and a softening point of 295°C. This pitch will be referred to as pitch a.

The upper layer pitch comprised mainly IP containing about 10% of AP in the form of globular particles having a diameter of up to about 10 μ. This pitch had a softening point of 156°C, a quinoline-insoluble matter content of 4 wt. % and a quinoline-soluble/benzene-insoluble matter content of 48.6 wt.%.

200 g of the upper layer pitch was allowed to react at 400°C for 4 h while 2 ℓ/min of nitrogen gas was introduced above the pitch surface in a 500-mℓ stainless steel reaction vessel. 156 g of an optically anisotropic pitch having an AP content of about 95%, a softening point of 273°C, a quinoline-insoluble matter content of 35.7 wt.% and a quinoline-soluble/benzene-insoluble matter content of 24.0 wt.% remained. This pitch will be referred to as pitch b.

Pitches a and b obtained as above were tested by charging each of them in a spinning apparatus having a nozzle of 0.5 mm diameter and subjected to the tests. Pitch a could not be spun at all at a spinning temperature of up to 370°C. At 380°C, pitch a could be spun at a take-up speed of 300 m/min by extruding the same under a nitrogen gas pressure of 200 mmHg. The breaking frequency was less than once per 10 min. Pitch b could be spun at take-up speed of 500 m/min at 355°C under nitrogen gas pressure of about 100 mmHg. The breaking frequency was less than once per 30 min.

The two pitch fibers obtained from the two pitches respectively were maintained in an oxygen stream at 200°C for 2 h and then in an oxygen stream at 240°C for 30 min, and heated to 1500°C at a temperature-elevation rate of 50°C/min in argon gas and immediately thereafter, they were left to cool to obtain carbon fibers. Diameters of 16 samples of each of the two carbon fibers were measured and then tensile strength and modulus in tension of them were determined. Averages of the values were calculated. The carbon fibers obtained from pitch a had an average diameter of 14 μm, average strength of 16 GPa and average modulus of elasticity of 1.4×10^2 GPa. The carbon fibers obtained from pitch b had an average diameter of 8.7 μm, average

strength of 26 GPa and average modulus of elasticity of 2.3×10^2 GPa. Comparative Example 1

200 g of the same starting material as in Example 1 was allowed to react in a 500-mℓ stainless steel reaction vessel at 400°C for 4 h while a ℓ/min of nitrogen gas was introduced above the pitch surface in the vessel. An optically anisotropic pitch having an AP content of about 95% was obtained. The pitch had a quinoline-insoluble matter content of 61.1 wt.%, a benzene-insoluble/quinoline-soluble matter content of 23.0 wt. % and a softening point of as high as 330°C. The pitch could not be spun with the same spinning apparatus as in Example 1.

Example 2

300 g of the same starting material as in Example 1 was settled in the same manner as in Example 1. 200 g of an upper layer pitch was heat-treated for making the same heavier at 400°C for 2 h in a 500 mℓ stainless steel reaction vessel while 2ℓ/min of nitrogen gas was introduced therein to obtain 168.4 g of an intermediate pitch. The pitch had a softening point of 212°C, a quinoline-insoluble matter content of 9.5 wt.%, a benzene-insoluble matter content of 55.2 wt.% and an AP globular particle content of about 45%. Then, 100 g of the pitch was charged in a 200-mℓ glass cylindrical vessel and settled again at 380°C for 2 h to divide the pitch into upper and lower layers. The amount of the lower layer pitch was about 22 g. It had an AP content of 99%, a quinoline-insoluble matter content of 33.3 wt.% and a softening point of 244°C. The pitch could be spun with the same spinning apparatus as in Example 1 at 320°C without breaking of the fiber for a long time.

Comparative Example 2

200 g of the same starting material as in Example 1 was heat-treated for making the same heavier at 400°C for 2 h in a 500-mℓ stainless steel reaction vessel while 2 ℓ/min of nitrogen gas was introduced therein to obtain 181.3 g of an intermediate pitch. The intermediate pitch had a softening point of 224°C, an AP globular particle content of about 45%, a quinoline-insoluble matter content of 23.0 wt.% and a quinoline-soluble/benzene-insoluble matter content of 30.1 wt.%.

100 g of the intermediate pitch was charged in a 200-mℓ glass cylindrical vessel and settled at 380°C for 2 h to divide the pitch into upper and lower layers. The amount of the lower layer pitch was about 28 g. It had an AP content of approximately 100%, a softening point of 286°C, a quinoline-insoluble matter content of 74.2 wt.% and a quinoline-soluble/benzene-insoluble matter content of 1.4 wt.%. The pitch was spun in the same manner as in Example 1. The optimum spinning temperature was 370°C and the breaking occurred considerably frequently.

Referential Example

A pitch having a boiling point of above 450°C (under atmospheric pressure) obtained by reduced pressure distillation of a tar obtained by catalytic cracking of petroleum was used as starting material. 20ℓ of the pitch was heat-treated at 430°C for 2 h under a 30 ℓ/min nitrogen gas stream in a 50- stainless steel reaction tank to obtain the starting material used in Example 1.

Example 3

600 g of the same starting tar as in Referential Example was charged in a 1-ℓ stainless steel autoclave. After purging with nitrogen gas, the temperature was elevated and the tar was heat-treated at 430°C for 3 h. The pressure was controlled to about 5 kg/cm^2 by discharging a gaseous cracked product through a leak valve. After completion of the reaction, the contents of the autoclave were cooled to 250°C, the pressure was reduced and the stirring was stopped at 250°C. After cooling, the autoclave was opened and the contents thereof were decanted at 150°C. A pitch in the form of a slurry remained on the walls and at the bottom. About 522 g of the pitch was obtained. The pitch had a softening point of up to 100°C, a quinoline-insoluble matter content of about 2.4 wt.% and a benzene-soluble matter content of 86 wt.%. 400 g of the pitch was transferred to a 500 mℓ stainless steel reactor and treated at 360°C for about 5 h while 6ℓ/min of nitrogen gas was introduced therein to obtain 152 g of residual pitch. This pitch had a softening point of 221°C, an AP content of about 40%, a quinoline-insoluble matter content of 8.7 wt.% and a quinoline-soluble/benzene-insoluble matter content of 42.4 wt.%. Then, 100 g of this pitch was charged in a 200-mℓ glass cylindrical vessel and settled at 380°C for 2 h. Upper and lower layers were formed clearly. 24 g of lower layer pitch was obtained. This pitch had a softening point of 261°C, an AP content of approximately 100%, a quinoline-insoluble matter content of 32.6% and a quinoline-insoluble/benzene-soluble matter content of 30.8%. The pitch could be spun at a spinning temperature of 350°C easily for longer than 30 min without breakage in the same manner as in Example 1.

Example 4

400 g of the same starting tar as in Referential Example was subjected to the thermal reaction at 450°C for 3 h without introduction of nitrogen gas in a 500-mℓ stainless steel reactor to obtain 233 g of a residual pitch. The pitch was heterogeneous and contained a small amount of solid slurry even at 250°C. It had a softening point of 92°C, a quinoline-insoluble matter content of 4.2 wt.% and a quinoline-soluble/benzene-insoluble matter content of 30.2 wt.%. Then, the pitch was settled at 250°C for 30 min. 196 g of a supernatant layer was taken by decantation and heat-treated at 330°C for 10 h while 6 ℓ/min of nitrogen gas was introduced in a 500-mℓ stainless steel reactor without reflux tube. A residual pitch had an AP content of about 97%, a quinoline-insoluble matter content of 25.9 wt.%, a quinoline-soluble/benzene-insoluble matter content of 40.7 wt.% and a softening point of 271°C.

CLAIMS:

1. A process for producing an optically anisotropic carbonaceous pitch characterised by the steps of:

(a) heat treating a starting material which preferably comprises a carbonaceous heavy oil, at conditions which will favour the formation of an anisotropic pitch phase;

(b) stopping said heat treating at an early stage in said formation;

(c) maintaining the thus partially treated material at a temperature in the range 200 to 400°C;

(d) subjecting the material from step (c) to a settling treatment, while maintaining the material in a molten state;

(e) removing the anistropic pitch phase which separates in step (d); and

(f) subjecting at least a portion of the remaining material to an after-treatment including a heat treatment for forming and/or concentrating an anisotropic pitch phase therein.

2. A process as claimed in claim 1, wherein said heat treating step (a) comprises the step of subjecting the starting material to a thermal reaction at a temperature in the range from about 370 to 460°C in an inert gas stream; and wherein step (b) comprises the step of stopping the thermal reaction when a pitch is obtained having a globular optically anisotropic phase content of 5-50 wt.%, quinoline-insoluble matter content of 2-20 wt.%, a quinoline-insoluble/benzene-soluble matter content of 5-40 wt.% and a softening point of the formed pitch as a whole of up to 200°C.

3. A process as claimed in claim 1, wherein step (a) comprises the step of subjecting the starting material to a thermal reaction at a temperature in the range 370 to 460°C, and step (b) comprises the step of stopping the thermal reaction when a pitch is obtained having a quinoline-insoluble matter content of 2-10 wt.%, a benzene-soluble matter content of at least 60 wt.% and a softening point of the formed pitch as a whole of up to 150°C.

4. A process as claimed in claim 2 wherein the starting material is a heavy hydrocarbon oil, tar or pitch by-product of petroleum or coal.

5. A process as claimed in claim 2 or claim 4, wherein the settling step (d) is effected at a temperature in the range 250 to 400°C.

6. A process as claimed in claim 3, wherein the settling step (d) is effected at a temperature in the range 200 to 350°C.

7. A process as claimed in any one of claims 2 to 6, wherein said thermal reaction is carried out at a temperature in the range of from 400 to 430°C.

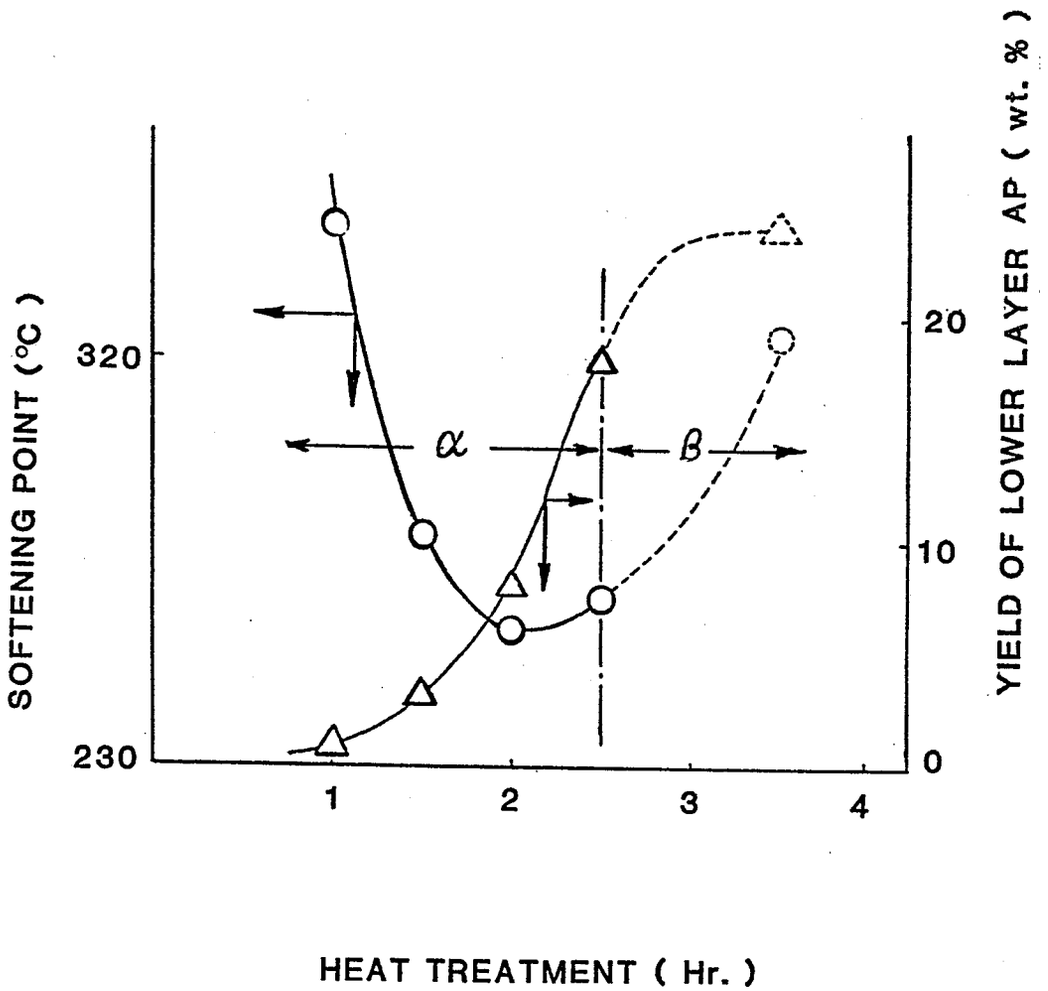
8. A process as claimed in any preceding claim wherein the after-treatment of step (f) includes a heat treatment step for making the material heavier, said heat treatment being continued until an optically isotropic phase content of 0-20 wt.% has been attained.

9. A process as claimed in any one of claims 1 to 7, wherein the after-treatment step (f) comprises a heat treatment step for making the material heavier, which step (f) is carried out at a temperature in the range 300 to 420°C, preferably 350 to 420°C, in an inert gas stream, and continued until said material has a globular optically anisotropic phase content of 20-70 wt.%, a quinoline-insoluble matter content of no higher than 25 wt.%, a quinoline-soluble/benzene-insoluble matter content of at least 25 wt.% and a softening point of up to 250°C; and further comprises a second settling step carried out at a temperature in the range of from 330-400°C, and a discharging step wherein a lower layer of the settled material mainly comprises globular optically anisotropic phase which is discharged.

10. A process as claimed in claim 9, wherein the heat treatment step (f) for making the material heavier is continued until a pitch having a globular optically anisotropic phase content of 30-50 wt.%, a quinoline-insoluble matter content of up to 20 wt.% and a quinoline-soluble/benzene-insoluble matter content of at least 30 wt.% has been formed.

11. A process as claimed in claim 8, wherein the heat treatment for making the material heavier in the after-treatment step (f) further comprises a step of accelerating the thermal chemical reaction at a temperature in the range 370 to 420°C and a subsequent step of performing a thermal chemical reaction at a lower temperature in the range 300 to 370°C in an inert gas stream.

12. A process as claimed in any preceding claim, where the optically anisotropic carbonaceous pitch product has a softening point in the range 230 to 320°C, a globular optically anisotropic phase content of at least 80 wt.%, an isotropic phase content of up to 20 wt.% and quinoline-insoluble matter content of not more than 70 wt.%, preferably not more than 40 wt.%.


SOFTENING POINT (°C)
320
230
1
2
3
4
α
β
20
10
0
YIELD OF LOWER LAYER AP (wt. %)
HEAT TREATMENT (Hr.)

European Patent Office

EUROPEAN SEARCH REPORT

0089840
Application number

EP 83 30 1552

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
D,X	EP-A-0 044 714 (TOA NENRYO KOGYO K.K.) * Page 5, lines 23-36; page 6, line 1 - page 8, line 5; page 9, lines 21-35; page 10, lines 1-14; page 13, lines 27-35; page 14, lines 1-34; page 15, lines 1-35; page 16, lines 1-10; page 17, lines 2-19, 28-35; page 18, lines 1-18; page 24, lines 17-35; page 25, lines 1-14 *	1,2,4, 5,7,8, 12	C 10 C 3/00
E	GB-A-2 086 932 (KOA OIL CO.) * Page 2, lines 51-62, 75-78 *	1	
A	FR-A-2 424 954 (EXXON)		
D,E	EP-A-0 055 024 (TOA NENRYO KOGYO K.K.) * Page 28, lines 20-37; page 29, lines 1-28 *	1,2	TECHNICAL FIELDS SEARCHED (Int. Cl. ³) C 10 C D 01 F
D,E	EP-A-0 057 108 (TOA NENRYO KOGYO K.K.) * Page 29, lines 26-37; page 30, lines 1-27 *	1	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	09-05-1983	KERRES P.M.G.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO Form 1503. 03.82