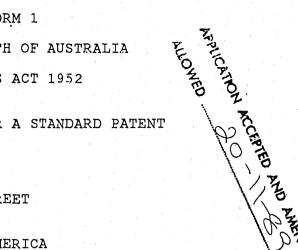
FORM 1

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952



APPLICATION FOR A STANDARD PATENT

I\We,

CONOCO INC.,

of

1000 SOUTH PINE STREET PONCA CITY 74601 OKLAHOMA UNITED STATES OF AMERICA

hereby apply for the grant of a standard patent for an invention entitled:

PRESSURE SETTLING OF MESOPHASE

which is described in the accompanying complete specification

Details of basic application(s):

application

Number of basic Name of Convention country in which basic application was filed

Date of basic application

AMENDMENTS

871978

09 JUN 86

My/our address for serviou is care of CLEMENT HACK & CO., Patent Attorneys, 601 St. Kilda Road, Melbourne 3004, Victoria, Australia.

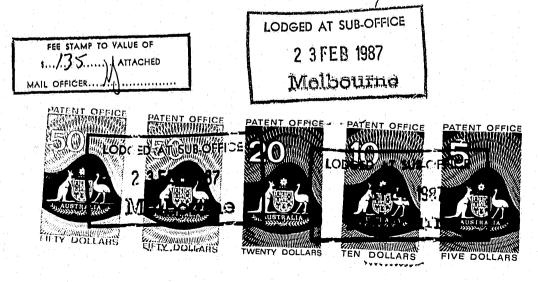
DATED this 23rd day of February 1987

US

CONOCO INC.,

CLEMENT HACK & CO.

The Commissioner of Patents. TO:



ICR No. 7250

Australia Patent Declaration Form

Forms 7 and 8

AUSTRALIA

Patents Act 1952

DECLARATION IN SUPPORT OF A CONVENTION OR NON-CONVENTION APPLICATION FOR A PATENT OR PATENT OF ADDITION

Name(s) of Applicant(s)	In support of the application made by <u>CONOCO INC.</u>
Title	for a patent for an invention entitled Pressure Settling of Mesophase
Name(s) and address(es) of person(s) making declaration	I/We,Julian B. Coon
	do solemnly and sincerely declare as follows:-
	 I am/we are the applicant(s) for the patent, or am/are authorised by the abovementioned applicant to make this declaration on its behalf.
Country, filing date and name of Applicant(s) for the or each basic application	2. The basic application(s) as defined by Section 141 of the Act was/were made in the following country or countries on the following date(s) by the following applicant(s) namely:- United States
	in_of AmericaOnJune 919_86 by_Hugh E. Romine
	inon19 by
	3. The said basic application(s) was/were the first application(s) made in a Convention country in respect of the invention the subject of the application.
Name(s) and address(es) of the or	4. The actual inventor(s) of the said invention is/are Hugh E. Romine, 804 Edgewood, Ponca City, Oklahoma
each actual	
See reverse side of this form for guidance in completing	5. The facts upon which the applicant(s) is/are entitled to make this application are as follows:- The APPLICANT is the assignee of the actual INVENTOR.
this part	DECLARED at Ponca City, OK this 9th day of February 19
	Calie & Pan B
	By: Julian B. Coon Vice President, - Petroleum R&D

This form may be completed and filed after the filing of a patent application but the form must not be

(12) PATENT ABRIDGMENT (11) Document No. AU-B-69152/87 (19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 593326

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(54)itle PRESSURE SETTLING OF MESOPHASE PITCH; PRODUCTION OF CARBON FIBRE International Patent Classification(s) (51)⁴ C10C 001/16 C10C 003/00 C10C 003/06 (21) Application No. : 69152/87 (22) Application Date : 23.02.87 (30) Priority Data (31) Number (32) Date (33) Country 871978 US UNITED STATES OF AMERICA 09.06.36 (43) Publication Date : 10.12.87 (44) Publication Date of Accepted Application : 08.02.90 (71) Applicant(s) CONOCO INC. (72) Inventor(s) HUGH E. ROMINE (74) Attorney or Agent **GRIFFITH HACK & CO, MELBOURNE** (56) Prior Art Documents US 4533461 (57) Claim

In a process for producing optically anisotropic 1. mesophase pitch wherein a heavy aromatic hydrocarbon feedstock is heat soaked until a substantial portion of the feedstock has been converted to optically anisotropic mesophase containing material, and in which optically anisotropic mesophase pitch is recovered from the heat soak material containing said pitch by gravity settling wherein the improvement comprises subjecting the heat soak material prior to the recovery of mesophase pitch therefrom to a pressure at least 30 kpa higher than the pressure at which the heat soak took place, whereby boiling of the heat soak material is reduced, gases formed by cracking of heat soak material during settling are substantially maintained in solution, and settling of the optically anisotropic mesophase pitch is onhanced.

(11) AU-B-69152/87 (10) 593326

6. A process for producing optically anisotropic mesophase pitch comprising:

heat soaking a heavy aromatic hydrocarbon (a) feedstock at a temperature of from 350 to 475°C for a time of from 0.5 to 120 hours and at a first pressure until a substantial portion of said feedstock has been converted to mesophase pitch; subjecting said heat soaked feedstock (b) containing mesophase pitch to a pressure higher than said first pressure; allowing mesophase pitch to settle from (C) said heat soaked feedstock by gravity settlement; and separating and recovering said settled (d) mesophase pitch.

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AUSTRALIA ,

PATENTS ACT 19.2

COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE

Short Title:

Int. Cl:

Application Number: Lodged:

69152 87

Complete Specification-Lodged: Accepted: Lapsed: Published:

• Priority:

Related Art:

TO BE COMPLETED BY APPLICANT

Name of Applicant:

CONOCO INC.,

Address of Applicant: 1000 SOUTH PINE STREET •

PONCA CITY 74601 OKLAHOMA UNITED STATES OF AMERICA

Actual Inventor:

Í

Address for Service:

CLEMENT HACK & CO., 601 St, Kilda Road, Melbourne, Victoria 3004, Australia.

Complete Specification for the invention entitled: PRESSURE SETTLING OF MESOPHASE

The following statement i. a full description of this invention including the best method of performing it known to me:-

This document contains the amendments made under Section 49 and is correct for printing.

593326

Form 10

Case No. 7250

PRESSURE SETTLING OF MESOPHASE Background of the Invention

1. Field of the Invention

This invention relates to production of mesophase pitch suitable for manufacture of carbon fibers and other carbon artifacts. More particularly, the invention is directed to an improved settling process for separating mesophase pitch from a heat soaked heavy aromatic hydrocarbon feedstock.

2. The Prior Art

There has been a substantial effort in recent years to produce anisotropic pitch comprised of from 40 to 100 percent mesophase, which can then be spun into carbon fibers. One approach to production of mesophase involves heat soaking a heavy aromatic hydrocarbon feedstock at conditions such that a more dense mesophase material forms. Variations of the heat soaking process include sparging inert gas through the feedstock during heat soaking, agitating the feedstock during heat soaking, or a combination of sparging and agitation, as described in U.S. Patent 4,209,500 to Chwastiak.

U. S. Patent 4,317,809 to Lewis et al describes heat soaking a mesophase precursor material at high pressure, followed by additional heat soaking at atmospheric pressure with gas sparging.

U. S. Fatent 4,454,020 to Izumi et al describes heat soaking mesophase precursor material, separating a heavier anisotropic phase, and further heating the separated portion.

European Patent Application Publication No. 44,714 describes a basic heat soak and gravity separation process for producing mesophase pitch which involves cooling the heat soaked material enough to stop boiling so that settling of mesophase pitch readily occurs.

Many other descriptions of variations of the heat soaking procedure for producing mesophase appear in the literature, and the present invention is applicable in general to any process in which a mesophase forming feedstock is heat soaked to form mesophase and the thus formed mesophase recovered from the heat soaked feedstock. Specific mesophase-forming conditions of temperature, heat soaking time, feedstock composition, gas sparging, agitation and the like have heen extensively developed in the prior art, and are not a part of the present invention, as the present invention is generally applicable in

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any case where a mesophase-forming feedstock is heat soaked and mesophase pitch recovered therefrom, without regard to the specific conditions under which the mesophase is formed.

Summary of the Invention

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According to the present invention, mesophase pitch is recovered from a heat soaked mesophase precursor feedstock by applying a pressure higher than the heat soaking pressure to the heat soaked material, allowing more dense mesophase material to settle by gravity, and separating the settled material from the less dense heat soaked material.

The settling temperature can be the same as or lower than the heat soaking temperature, but should not be low enough that increased viscosity substantially impedes settling.

During the heat soaking stage, the feedstock undergoes cracking reactions leading to production of mesophase and other components, including gaseous components. These gaseous cracking components continue to evolve during the settling step, if settling is conducted at or near the heat soaking temperature, resulting in agitation of the material to be settled.

EPA Publication No. 44,714, referred to earlier, attempts to overcome this problem by cooling the heat soaked material to reduce gas evolution from cracking, as well as boiling of the material, such that settling is not hindered by gas movement through the settling material. This technique is subject to the drawback of increased viscosity with decreasing temperature, such that the time required for settling is increased.

According to the present invention, an increased pressure is applied to the heat soaked material, sufficient to prevent or reduce boiling and to substantially maintain cracked gaseous components in solution, such that the settling occurs without the necessity of a viscosity-increasing cooling step.

It is an object of the invention to provide a process for rapidly settling mesophase pitch from heat soaked mesophase precursor. It is a further object to provide a process for controlling certain characteristics of mesophase pitch which is separated from a heat soaked mesophase procursor.

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The above as well as additional objects and advantages are obtained by the present invention, as will be apparent from the following detailed description.

The Drawings

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Figure 1 is a schematic flowchart showing a batch type process in accordance with the invention.

Figure 2 is a schematic flowchart showing a continuous type process in accordance with the invention.

Figure 3 is a schematic flowchart showing another variation 10 of a continuous type process in accordance with the invention. Description of the Preferred Embodiments

The term "mesophase" as used herein refers to an optically anisotropic material formed by any of several variations of a process in which a heavy aromatic hydrocarbon feedstock is heat soaked at conditions known in the art to produce a substantial amount of the optically anisotropic mesophase material.

Heavy aromatic hydrocarbon feedstocks suitable for formation of mesophase are also known in the art, and include, among others, petroleum pitch, decant oil and thermal tar.

A basic batch type version of the process of the invention is illustrated in Figure 1, where heavy aromatic hydrocarbon feedstock from tank 10 is pumped to heat soak vessel 12 where it is heated by any suitable means (not shown) until a substantial amount of mesophase has formed. During all or part of the heating, an inert sparge gas from line 14 may be sparged through the feedstock to remove lighter hydrocarbon components and to effect more efficient heat transfer. The sparging gas exits through line 16.

When the heat soak is completed, flow of sparging gas is stopped, the soak tank 12 is sealed, and soak tank 12 is then pressurized by gas from cylinder 18 to a pressure sufficient to prevent boiling of the contents and to maintain cracked gases in solution. With the system closed in and no appreciable gas movement through the heat soaked material, the more dense mesophase readily settles to the bottom of tank 12, and is withdrawn through mesophase recovery line 20.

A basic continuous type version of the process of the invention is illustrated in Figure 2, where feedstock from tank 30 is

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heated in heater 32 and passed to distillation or flash tower 34. The tower bottoms are fed through line 36 to soak tank 38, and sparge gas may be passed through the soak tank 38 via lines 40 and 42. If sparge gas is not used, vapors from tank 38 may be returned to tower 34 via line 44. Soak tank 38 may have internal baffles (not shown) or other flow control means to assure uniform residence time of the feedstock in tank 38. The heat soaked material from soak tank 38 is passed to settling tank 46 via line 48. Settling tank 46 may also include internals (not shown) to assure appropriate residence time and to direct settled mesophase to mesophase recovery line 50. The non-mesophase material may be removed from settling tank 46 via line 52, or recycled to soak tank 38 via line 54. An increased pressure in settling tank 46 may be maintained by gas pressure from gas cylinder 56.

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A more elaborate continuous type version of the process of the invention in which two different mesophase products are recovered is illustrated in Figure 3. The system depicted in Figure 3 is similar to the Figure 2 version, but includes a second settling tank 60 which is fed with non-mesophase material from first settling tank 46 via line 62. Second settling tank 60 normally is maintained at a lower temperature and pressure than first settling tank 46. Pressure in tank 60 may be controlled with gas cylinder 64, and unsettled material may be returned to heater 32 via recycle line 66. Settled mesophase from tank 60 is recovered via line 68. Elements of Figure 3 which are common with Figure 2 have like identification numbers.

Temperature is an important variable during pressure settling due to the strong temperature dependence of the solubility of mesophase in isotropic heavy aromatic pitch. Decreased settling tamperature increases the yield of mesophase while lowering its average molecular weight. Through proper temperature control, two distinct types of mesophase pitch or blends thereof can be isolated. Setcling at or near the soaking temperature yields a relatively high melting, highly coalesced mesophase pitch. This material is almost entirely comprised of anisotropic mesophase. Subsequent cooling of the saturated heat soaked feedstock leads to precipitation and settling of "new" lower melting mesophase pitch which is less highly

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coalesced. This lower melting mesophase pitch is generally 50 to 90 weight percent anisotropic material.

Thus, the embodiment illustrated in Figure 3 enables a "tailoring" of mesophase product which is not possible in a single settling step operation.

Example I

This example illustrates production of two mesophase pitch products having different properties using a process as depicted in Figure 3.

A flashed thermal tar feedstock is heated to about 460°C and passed to a flash tower maintained at about 375 kPa. The flash tower bottoms (deep flashed thermal tar) are passed to a heat soak tank maintained at about 375 kPa and about 440°C. Residence time of the deep flashed thermal tar in the heat soak tank is about six hours. Heat soaked thermal tar is pumped from the soak tank to a first settling tank maintained at about 620 kPa without substantial cooling of the heat soaked material. Residence time in the first settling tank is about ten minutes. The increased pressure essentially prevents boiling in the settling tank, and about 35 percent by volume of the heat soaked material settles out as "old" mesophase pitch which is essentially 100 percent anisotropic material having a melting point of about 450°C. Unsettled material from the first settling tank is passed to a second settling tank maintained at a pressure of 375 kPa and a temperature of about 250°C with a residence time of about twenty minutes. A "new" mesophase pitch in an amount of about 50 percent of the feed to the second settling tank, comprising about 75 percent anisotropic material and having a melting point of about 200°C, is Unsettled material from the second settling tank is recovered. recycled to the heater feed.

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This example illustrates that high melting mesophase can be quickly settled from heat soaked feedstock using an increased pressure, and a low melting mesophase can be precipitated from the remaining saturated heat soaked material.

There are many variations and embodiments of the invention 35 which will be apparent to those skilled in the art of making mesophase. Directionally, much is known as to the effects of varying such things as feedstock, soaking time and temperature, sparging,

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agitation, cooling of soaked feedstock, and the like. Soaking temperatures of from 350 to 475°C and soaking times of from 0.5 to 120 hours are generally considered to be the practical limits for the process, with shorter times within that range generally being used with temperatures nearer the higher limit. The conditions for a particular run may be influenced by factors such as time available, feedstock properties, equipment limitations, desired product properties, etc., as is known in the art. However, the prior art has not recognized that rapid settling can be effected by increasing pressure on a heat soaked mesophase-containing feedstock, and further has not recognized that rapid initial settling of mesophase, made possible by use of increased settling pressure, provides a capability for producing mesophase pitches having specific desired properties such as low melting point.

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The essential novel feature which permeates all the embodiments of the invention is the use of an initial settling pressure greater than the pressure at which the feedstock was heat soaked. The heat soaking pressure can be higher, lower or equal to atmospheric pressure, and the settling pressure needs to be sufficiently higher than the soaking pressure to retard or eliminate boiling in the soak tank and to keep in solution any gases generated by cracking after the soaking is completed. A pressure as little as 30 kPa above the soaking pressure can be effective in some cases, and in other cases it may be desirable to use a pressure as much as 2 MPa higher than the soaking pressure.

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

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1. In a process for producing optically anisotropic mesophase pitch wherein a heavy aromatic hydrocarbon feedstock is heat soaked until a substantial portion of the feedstock has been converted to optically anisotropic mesophase containing material, and in which optically anisotropic mesophase pitch is recovered from the heat soak material containing said pitch by gravity settling wherein the improvement comprises subjecting the heat soak material prior to the recovery of mesophase pitch therefrom to a pressure at least 30 kpa higher than the pressure at which the heat soak took place, whereby boiling of the heat soak material is reduced, gases formed by cracking of heat soak material during settling are substantially maintained in solution, and settling of the optically anisotropic mesophase pitch is enhanced.

2. The process of claim 1 wherein said heat soaked material is retained in a heat soaking vessel, and the pressure in said vessel is increased prior to recovery of settled mesophase pitch therefrom.

3. The process of claim 1 wherein said heat soaked material is transferred from a heat soaking vessel to a settling vessel maintained at a higher pressure than said heat soaking vessel, and mesophase pitch is recovered from said settling vessel.

4. The process of claim 3 wherein the remaining heat soaked material in said settling vessel, after recovery of mesophase pitch therefrom, is returned to said heat soaking vessel and further heat soaked.

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5. The process of claim 3 wherein the remaining heat soaked material in said settling vessel, after recovery of mesophase pitch therefrom, is transferred to a second settling vessel from which additional settled mesophase pitch is recovered.

6. A process for producing optically anisotropic mesophase pitch comprising:

(a) heat soaking a heavy aromatic hydrocarbon feedstock at a temperature of from 350 to 475 °C for a time of from 0.5 to 120 hours and at a first pressure until a substantial portion of said feedstock has been converted to mesophase pitch;
(b) subjecting said heat soaked feedstock

containing mesophase pitch to a pressurehigher than said first pressure;(c) allowing mesophase pitch to settle from

said heat soaked feedstock by gravity settlement; and

(d) separating and recovering said settled mesophase pitch.

DATED THIS 8TH DAY OF NOVEMBER, 1989 CONOCO INC.

By Its Patent Attorneys:

GRIFFITH HACK & CO.

Fellows Institute of Patent Attorneys of Australia.



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