AUSTRALIA

Patents Act

APPLICATION FOR A STANDARD/PETTY PATENT

(a) CONVENTION

GENERAL MOTORS CORPORATION

lodged at Sub-Office
30 Jul 1985
Melbourne

We (c) hereby apply for the grant of a Standard/Petty Patent for an invention entitled "Regulation of pyrolysis methane concentration in the manufacture of graphite fibres".

which is described in the accompanying complete specification.

(Note: The following applies only to Convention applications)

Details of basic application(s)

<table>
<thead>
<tr>
<th>Application No.</th>
<th>Country</th>
<th>Filing Date</th>
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<tr>
<td>642574</td>
<td>United States of America</td>
<td>20 August, 1984</td>
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<tr>
<td>685046</td>
<td>United States of America</td>
<td>21 December, 1984</td>
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Dated (i) 30 July, 1985

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COMMONWEALTH OF AUSTRALIA

Patents Act

DECLARATION FOR A PATENT APPLICATION

In support of the (a) Convention application made by GENERAL MOTORS CORPORATION (hereinafter called "the applicant") for a patent (c) for an invention entitled:-

REGULATION OF PYROLYSIS METHANE CONCENTRATION IN THE MANUFACTURE OF GRAPHITE FIBRES

1. Arthur Donald Haines, Chartered Patent Agent of Patent Section-Luton Office (F6) P.O.Box 3, Kimpton Road Luton Beds LU2 OSY, England do solemnly and sincerely declare as follows:-

1. I am authorized under a power of attorney from the applicant granted on 1st May 1981 to make this declaration on behalf of the applicant.


Michael Gerard Devour, a citizen of the United States of America, of 4675 Haverhill Detroit, Michigan 48224 United States of America.

Is/are the actual inventor(s) of the invention and the applicant is entitled to make the application by virtue of a service agreement(s) between the applicant and the inventor(s) as employee(s) and an assignment(s) from the inventor(s) to the applicant.

3. The basic application(s) for patent or similar protection on which the application is based is/are identified by country, filing date and basic applicant(s) as follows:

United States of America
20 August 1984 & 21 December 1984
Gary George Tibbetts
Michael Gerard Devour

4. The basic application(s) referred to in paragraph 3 hereof was/were the first application(s) made in a Convention country in respect of the invention the subject of the application.

Declared at: Luton, England

Dated: 23 July 1985

For and on behalf of
GENERAL MOTORS CORPORATION

[Signature]

Under Power of Attorney

A D Haines
MANUFACTURE OF GRAPHITE FIBRES VIA PYROLYSIS OF METHANE

GENERAL MOTORS CORPORATION

45598/85 (22) 30.7.85 (24) 20.8.84
642574 (32) 20.8.84 (33) US
685046 21.12.84 US

GARY GEORGE TIBBETTS AND MICHAEL GERARD DEVOUR

PO

Claim

1. A methane pyrolysis process for growing graphite fibres on a suitably nucleated ceramic surface, said process comprising flowing a hydrogen-base gas comprising 5 to 25 volume percent methane over said surface while heating the gas to a temperature sufficient to decompose the methane so as to form microscopic carbon filaments that project from the surface, and thereafter flowing a gas containing above 25 volume percent methane over said surface while heating at a temperature sufficient to decompose the methane so as to thicken the filaments into fibres.
COMPLETE SPECIFICATION
(ORIGINAL)

Application Number:
Lodged:

Complete Specification Lodged:
Accepted:
Published:

Priority
Related Art:

APPLICANT'S REF.: ADH/JCS/ 1736 Australia

Name(s) of Applicant(s): GENERAL MOTORS CORPORATION

Address(es) of Applicant(s): Grand Boulevard
Detroit, Michigan
United States of America

Actual Inventor(s):
Gary George Tibbetts,
Michael Gerard Devuour

Address for Service is: PHILLIPS, ORMONDE AND FITZPATRICK
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Melbourne, Australia, 3000

Complete Specification for the invention entitled:

REGULATION OF PYROLYSIS METHANE CONCENTRATION IN THE MANUFACTURE
OF GRAPHITE FIBRES.

The following statement is a full description of this invention, including the best method of performing it known to applicant(s):
REGULATION OF PYROLYSIS METHANE CONCENTRATION
IN THE MANUFACTURE OF GRAPHITE FIBRES

Background of the Invention

This invention relates to a methane pyrolysis process for manufacturing graphite fibres of a type suitable for filler in plastics composites.

United States Patent No. 4,391,787 (Tibbetts) describes a method for manufacturing thin, straight graphite fibres by natural gas pyrolysis carried out within a thin-wall stainless steel tube surrounded by wet hydrogen gas. The fibres are preferably 5 to 15 microns in diameter and up to several centimetres long and are well suited for plastics filler. In this process, fibre growth is attributed to a complex interaction between the chromium-bearing steel and methane at elevated temperature. European patent application No. 0 132 909A describes a method for growing the fibres on a ceramic surface, but only after natural gas pyrolysis is initiated adjacent stainless steel. Stainless steel is relatively expensive and has a limited useful life at fibre-growing temperatures. Furthermore, unavoidable carburization of the stainless steel unproductively removes carbon and reduces yield.

Fibre growth is believed to proceed in two sequential stages. During a first stage, pyrolytic carbon interacts with metallic nuclei to form long, thin filaments less than 100 nanometres in diameter. Suitable nuclei are derived from a deposit produced by evaporation of ferric nitrate solution, as described in European patent application No. 0 132 909A. Once nucleated, the filament grows rapidly in length. However, for reasons not fully understood, the filament then ceases to lengthen. Thereafter, additional
pyrolytic carbon thickens the filament into a fibre that is several microns in diameter. It is believed that pyrolysis reactions initiated between the stainless steel and the natural gas in some manner control the nature and the concentration of carbonaceous precursors in the gas stream to favor first filament formation and then thickening.

Therefore, it is an object of this invention to provide an improved process for growing graphite fibres by natural gas pyrolysis on a ceramic surface that does not require that pyrolysis be initiated adjacent stainless steel.

More generally, it is an object of this invention to provide an improved process for growing graphite fibres by pyrolysis of a methane gas, wherein the methane concentration in the gas is regulated first at a value particularly conducive to reactions that nucleate and lengthen filaments and thereafter at a relatively richer value for thickening the filaments into fibres. Although other parameters such as temperature, gas flow rate and nuclei characteristics also affect fibre growth, regulation of the methane concentration during each step improves the overall process by increasing yield, maximizing fibre length and reducing growing time.

Summary of the Invention

In accordance with a preferred embodiment of this invention, graphite fibre growth on a suitably nucleated ceramic surface by natural gas pyrolysis is improved by regulating the methane concentration in the reactant gas during each stage of the fibre growing process. The growing surface is pretreated by
evaporating ferric nitrate solution to deposit an iron compound. A methane gas is passed over the surface while heating the gas at a temperature sufficient to decompose the methane. During an initial period, the gas comprises natural gas diluted with hydrogen so that the prepyrolysis methane concentration is between 5 and 15 volume percent. As used herein, methane concentration is designated by reference to the concentration in the gas mixture prior to heating to pyrolytic temperatures, it being understood that pyrolysis reduces the methane concentration by producing other carbonaceous species. This gas stream may commence either while the surface is being heated to a predetermined reaction temperature or after the temperature has been achieved. In either event, the iron compound on the growing surface, when exposed to the hydrogen-base gas at elevated temperature, decomposes to form minute ferrous particles that are suitable nuclei. The nuclei react with carbon derived from the methane to produce long, thin cylindrical carbon filaments that project from the surface.

After the filaments have achieved ultimate length, the methane concentration is increased to grow the microscopic filaments radially and form macroscopic fibres. During this step, the gas phase suitably contains at least 25 volume percent methane and is preferably undiluted natural gas. The flow of enriched gas is continued for a time sufficient to grow fibres of a desired diameter, which diameter is preferably 5 to 15 microns for fibres intended for use as plastics filler.

The yield of product fibres is optimized by
maximizing the number and length of filaments during the initial step, since the subsequent thickening step does not significantly increase the number or length of the filaments. The reaction of the nuclei and the pyrolytic carbon to grow the filaments depends upon many reaction parameters including temperature and gas flow rate. However, in accordance with this invention, it has been found that the filament-forming reaction is particularly sensitive to the methane concentration in the initial gas. If the methane concentration is too high, the number and average length of filaments is reduced, presumably because excess carbon prematurely terminates the filament-forming reaction. On the other hand, if the methane concentration is too low, carbon is not supplied at a rate sufficient to sustain the reactions and achieve maximum length.

In general, a prepyrolysis methane concentration between 5 and 15 volume percent produces abundant filaments of suitable length for forming the product fibres. It is believed that, for a predetermined temperature, there is a specific methane concentration that is particularly conducive to the filament-forming reactions. For example, at 1050°C, the optimum methane concentration is found to be about 11 percent. However, the optimum concentration is sensitive to temperature and other reaction parameters. Further, the temperature and other reaction parameters may vary, for example, even between different regions of a growing surface. In one aspect of this invention, the methane concentration is varied over a range intended to provide an optimum concentration for a plurality of reaction conditions, including temperature
fluctuations. Thus, for a reaction temperature within a preferred range between 1000°C and 1100°C, the methane concentration may be varied from a value below 10 volume percent to above 12 volume percent, and more preferably from below 9 volume percent to above 13 volume percent.

Once nucleated, filament formation is completed within a short time. Continued exposure to the gas stream containing methane within the range conducive to filament formation does not thicken the filaments at an appreciable rate, even for periods of two hours or more. In accordance with this invention, the methane concentration in the gas stream is increased in a second step to radially enlarge the filaments into fibres. The diameter of the product fibres is related to the duration of this second step. However, the length is not significantly increased. In general, a concentration greater than about 25 percent thickens the fibres at a suitable rate. Higher methane concentrations are preferred to maximize the rate of carbon deposition and thereby to minimize the time required to achieve a desired diameter. Thus, regulation of the methane concentration in accordance with this invention not only maximizes the number and length of precursor filaments, and thus the yield and length of product fibres, but also reduces the time required to produce fibres of a particular diameter, thereby reducing the overall reaction time.

Detailed Description of the Invention

The method of this invention is illustrated by the following examples.
Example I

Graphite fibres were grown within a cylindrical tubular mullite reactor having a gas inlet at one end and a gas outlet at the opposite end. The longitudinal midsection of the reactor was enclosed within a coaxial cylindrical furnace such that the reactor ends extended beyond the furnace for making gas line connections thereto. The furnace had a helical electrical resistance heating element encompassing the midsection for heating the midsection to reaction temperature. The reactor inner diameter was about 52 millimetres. The midsection within the furnace was about 70 centimetres long.

Fibres were grown on an alumina body inserted into the reactor midsection so that a surface of the body was exposed to the gas therein. Prior to insertion, the surface of the body was pretreated by applying to it a 1.5 M aqueous ferric nitrate solution and drying the surface to deposit an iron salt thereon.

A mixture of natural gas and dry hydrogen was delivered to the reactor through the inlet. Gas was exhausted from the reactor outlet, thereby establishing a gas stream through the reactor at slightly above atmospheric pressure. Bottled natural gas was employed from Airco, Inc. under the designation methane grade 1.3 and was about 96 volume percent methane. The flow rate of natural gas through the reactor was adjusted to 48 cubic centimetres per minute (cc/min). The hydrogen flow rate was adjusted to about 452 cc/min. Thus, the methane concentration in the gas stream was estimated to be about 9.2 volume percent.

After air had been purged from the reactor, the furnace midsection was heated to about 700° C. Thereafter, the reactor flow rate of methane was reduced to 10 percent. Although the reactor temperature was maintained at about 1,300° C, it was considered as about 1,000° C. The reactor was heated with an air-purged furnace. The hot fibres were removed from the reactor by pulling.
the furnace was heated, whereupon the reactor midsection and the gas therein was heated at a rate of about 7°C per minute to a temperature of 1130°C and maintained at that temperature. The flow of the 9.2 percent methane gas was continued for about one hour. Thereafter, the natural gas flow rate through the reactor was increased to 380 cc/min and the hydrogen flow rate was increased to 995 cc/min, so that the methane concentration was increased to about 28 volume percent. After about one hour, the furnace was shut off and the reactor was cooled to room temperature. Although gas flow was discontinued during cooling, the reactor was not opened to air to avoid oxidation of the hot fibres. An abundance of graphite fibres was found on the body surface. The average fibre length was about 1.5 centimetres, although numerous fibres as long as about 3 centimetres were found. The average diameter was about 10 microns. The fibres were considered comparable to those described in United States Patent No. 4,391,787 and were suitable for use as plastics filler.

Example II

The tubular mullite reactor and the electric-al furnace were similar to Example I except that the reactor inner diameter was 19 millimetres and the heated midsection was about 30 centimetres long. An air-purgable antechamber was provided adjacent the reactor outlet for introducing the alumina body into the reactor while avoiding air contamination. The reactor was heated to about 1050°C while passing argon gas therethrough. After the reaction temperature had been achieved, the alumina body was inserted into the hot
zone of the reactor from the antechamber. The body surface had been treated using 0.15 M ferric nitrate solution in a manner similar to Example I. After the body was positioned near the middle of the reactor hot zone, argon gas flow into the reactor was discontinued, and the flow of a dilute methane gas was initiated. Methane of high purity was premixed with, by volume, 1 percent nitrogen and 2 percent ethane to produce a formulation representative of commercial grade natural gas, but having a controlled composition to permit evaluation of the method of this invention without concerns for variations in commercial natural gas composition. The synthesized natural gas flowed into the reactor at about 4.4 cc/min and was diluted by hydrogen introduced at a rate of about 35.6 cc/min. Thus, the methane concentration in the gas stream was estimated to be about 10.7 volume percent. This gas flow was continued for about 20 minutes, which time was deemed sufficient to permit filaments to sprout and grow to maximum length. Thereafter, the flow of hydrogen through the reactor was discontinued, and the flow rate for the synthesized natural gas was increased to about 40 cc/min for about 40 minutes. Gas flow through the reactor was then discontinued and the reactor was cooled. Examination of the alumina body revealed an abundance of graphite fibres having an average fibre length of about 4 millimetres and an average diameter of about 10 microns.

Example III

In this example, the prepyrolysis methane concentration in the gas stream was varied during the filament-forming stage over a suitable range to
optimize fibre growth despite variations in reaction conditions.

The apparatus and method were substantially as in Example II except for the following differences. The body surface was treated with 0.1M ferric nitrate solution. After the reactor had been heated to about 1050°C, the flow of dilute methane gas was commenced. Initially, the gas entering the reactor consisted of 3.6 cc/min synthesized natural gas and 36.4 cc/min hydrogen, corresponding to a methane concentration of about 8.7 percent. The gas formulation was varied over a period of about one-half hour by uniformly increasing the natural gas flow rate and concurrently decreasing the hydrogen flow rate, so that the total gas flow rate remained substantially constant. After one-half hour, the gas flowing into the reactor consisted of 5.4 cc/min natural gas and 34.6 cc/min hydrogen, corresponding to a methane concentration of about 13.1 volume percent. Thereafter, the natural gas was passed undiluted into the furnace at a rate of about 40 cc/min for about 15 minutes. The product fibres were approximately 3 to 4 microns in diameter.

Example IV

Example III was repeated, except that during the filament-forming step the initial gas consisted of 4 cc/min synthesized natural gas and 36 cc/min hydrogen, corresponding to a prepyrolysis methane concentration of 9.7 volume percent. The gas composition was uniformly adjusted to 4.8 cc/min natural gas and 35.2 cc/min hydrogen over one-half hour. Thereafter, undiluted natural gas was flowed into the furnace to produce the fibres.
As illustrated in these examples, the method of this invention comprises a preferred first step during which methane diluted with hydrogen interacts with the ferric nitrate deposit to form thin, long microscopic filaments. At the elevated temperature, the hydrogen-base gas is believed to reduce the ferric nitrate deposit and form minute iron particles. These particles interact with pyrolytic carbon to grow the filaments. Hydrogen is preferred for the diluent to assist in reducing the ferric nitrate deposit. Also, since hydrogen is also a major byproduct of methane pyrolysis, the presence of a large hydrogen proportion may aid in regulating methane pyrolysis in accordance with well known chemical principles to prevent uncontrolled sooting.

Once nucleated, the filaments lengthen at a very rapid rate. However, this lengthening ceases after only a short time for reasons that are not fully understood. It is believed that filament formation is substantially completed within a few minutes, although the first step is preferably extended to assure maximum opportunity for filament growth.

The filaments formed in the first step have submicron diameters, but are thickened into fibres in a subsequent step. Thus, each product fibre is derived from a filament, although only a fraction of the total number of filaments resists breakage and is suitably oriented and lengthened so as to mature into fibres. Since the thickening step does not significantly add to the length or produce additional fibres, it is useful to consider the yield of fibres as being the total length of fibres per growing surface area, which
in turn is related to the population and length of the precursor filaments. It has been found that the methane concentration during the filament-forming step critically affects the fibre yield.

The optimum methane concentration depends upon the reaction temperature. At 1050°C, the prepyrolysis methane concentration that produces an optimum fibre yield is about 11 volume percent. Deviation from the optimum value reduces yield but may produce suitable results. In Example II, the reaction temperature was held constant throughout the fibre growing process. Example II was repeated at different reaction temperatures, while varying methane concentration to determine the optimum concentration at each temperature. At 1000°C, the optimum methane concentration was found to be about 12.5 volume percent. At 1100°C, the optimum was about 8 volume percent. At 1150°C, the optimum was about 5.5 volume percent. Above 1200°C and below 950°C few fibres were formed under the conditions of Example II. In general, a methane concentration between about 5 and 15 volume percent produces precursor filaments sufficient to form a high density of suitably long fibres.

The practice of this invention is not limited to maintaining a constant prepyrolysis methane concentration during the filament formation step, but may advantageously be carried out by varying the methane concentration over a suitable range to obtain optimum fibre yield despite fluctuations in temperature or differences in other reaction conditions. Reaction conditions may vary not only over the time of the reaction, but also between different regions within the
reactor. At 1050°C, it is believed that filament growth is optimized using about 11 volume percent methane, as in Example II. However, a high yield of fibres may be obtained with methane concentrations within a preferred range between 9 and 13 volume percent. Thus, as illustrated in Example III, the methane concentration may be gradually increased to sweep over the preferred range. The prepyrolysis methane concentration may be adjusted initially to a value of less than 9 percent and gradually increased to a value greater than 13 percent. Alternatively, the methane concentration may be suitably varied over a narrower range from below to above the optimum methane concentration, as in Example IV. The rate at which the methane concentration is increased is suitably slow enough to permit filaments to form, which occurs rapidly when optimum conditions are achieved. In general, varying the methane concentration over a period of time of between about 10 and 30 minutes is sufficient.

Preferred conditions comprise a temperature between about 1000°C and 1100°C and a methane concentration between about 8 and 13 volume percent. Although Example II comprises isothermal reactions, it is believed that filaments may be formed at temperatures as low as about 600°C, although such low temperatures evidently are not sufficient to thicken the filaments. Thus, commencing methane gas flow during warm-up, as in Example I, may accelerate filament formation, particularly since the filament-lengthening reaction may be favored at lower temperatures. It has been found that fibres grow within the
reactor after the gas has been heated at the reaction temperature for 10 to 20 seconds. Optimum growth occurs after the gas is heated for about 15 seconds.

The relatively low methane concentration employed in the first step to promote filament formation is not sufficient to enlarge the filaments radially at a rate sufficient to form the fibres within a practical time. I. Example II, continued exposure to 10.7 volume percent methane gas at 1050°C for times as long as two hours does not significantly increase the diameter. Thus, the method of this invention comprises a second step wherein the methane concentration in the gas stream is increased. At this increased concentration, pyrolysis produces abundant carbonaceous species that suitably deposit on the peripheral surfaces of the filaments to thicken the filaments into fibres. In general, it is found that a methane concentration greater than about 25 volume percent thickens at an appreciable rate. However, it is preferred to maximize the methane concentration in the gas phase, for example, by using undiluted natural gas, to improve efficiency and maximize the radial growth rate. For a particular methane concentration in the second step, it is believed that the average diameter of the fibres produced increases linearly as a function of time, so that the diameter is conveniently determined by the duration of the second step. In general, fibre diameters of between 5 and 100 microns are suitable for plastics filler, with fibres having diameters between 5 and 15 microns being preferred.

The rate at which filaments thicken into fibres is also dependent upon other reaction parameters
including temperature and flow rate. In general, the flow rate may be increased during the second step to increase the rate at which pyrolytic carbon is supplied to the growing surface. Also, while temperatures as low as 600°C are suitable for forming filaments, temperatures near 1200°C or higher enhance the thickening reactions.

In the described embodiments the ceramic surface was initially treated with ferric nitrate solution. It is believed that the ferric nitrate deposit decomposes at moderately elevated temperatures to a mixture of iron oxides, which iron oxides thereafter further decompose at elevated temperatures in the presence of a hydrogen-base reducing gas to form metallic nuclei suitable for forming filaments. However, nuclei derived from other sources may be substituted. For example, fibres have been grown using nuclei derived from submicron magnetite particles. Also, iron particles derived from thermal decomposition of iron carbonyl produce fibres. Iron particles having diameters less than 0.1 micron are commercially available and are suitable nuclei.
The claims defining the invention are as follows:

1. A methane pyrolysis process for growing graphite fibres on a suitably nucleated ceramic surface, said process comprising flowing a hydrogen-base gas comprising 5 to 15 volume percent methane over said surface while heating the gas to a temperature sufficient to decompose the methane so as to form microscopic carbon filaments that project from the surface, and thereafter flowing a gas containing above 25 volume percent methane over said surface while heating at a temperature sufficient to decompose the methane so as to thicken the filaments into fibres.

2. A methane pyrolysis process for manufacturing graphite fibres according to claim 1, by growing the fibres on a surface of a ceramic substrate bearing suitable iron-base nuclei, in which said hydrogen-base gas is a hydrogen gas stream including a prepyrolysis methane concentration between 5 and 15 volume percent, the gas stream is heated to a temperature between 600°C and 1200°C to decompose the methane in the gas stream and to grow said microscopic elongated carbon filaments, and the gas containing above 25 volume percent methane is heated at a temperature between 950°C and 1200°C.

3. A methane pyrolysis process for manufacturing graphite fibres according to claim 1, by growing the fibres on a surface of a ceramic substrate bearing an iron oxide deposit reducible to form suitable iron-base nuclei, in which said hydrogen-base gas is formed by diluting natural gas with hydrogen, the hydrogen-base gas is heated to a temperature between 950°C and 1200°C to decompose the methane in
the gas stream and to grow said microscopic elongated carbon filaments, and the gas having a prepyrolysis methane concentration above 25 volume percent comprises natural gas, said gas being heated at a temperature within said range of 950°C to 1200°C for a time sufficient to thicken the filaments into fibres.

4. A methane pyrolysis process for manufacturing graphite fibres according to claim 1, in which the ceramic surface is a surface of a ceramic substrate bearing an iron oxide deposit of the type formed by evaporation of a ferric nitrate solution, the hydrogen-base gas initially comprises methane from a natural gas source which is diluted with hydrogen to form a gas stream having a concentration of methane between 8 and 13 volume percent, said gas stream and the ceramic surface being heated at a temperature between 1000°C and 1100°C, and said gas containing above 25 volume percent methane is a substantially undiluted natural gas stream which is passed in contact with the filament-bearing ceramic surface at a temperature within the range of 1000°C to 1100°C for a time sufficient to radially grow the filaments into fibres having diameters between 5 and 15 microns.

5. A methane pyrolysis process for manufacturing graphite fibres according to any one of the preceding claims, in which a predominantly hydrogen gas stream having a prepyrolysis methane concentration less than a predetermined optimum filament-forming concentration is initially passed over said surface, the prepyrolysis methane concentration in said gas stream is gradually increased to above said optimum filament-forming concentration at said decomposition
temperature over a time sufficient to form said filaments, and then the prepyrolysis methane concentration in said gas stream is further increased to above 25 volume percent so as to thicken the filaments into the fibres.

6. A methane pyrolysis process for manufacturing graphite fibres according to claim 5, in which the initial gas stream comprises a natural gas source blended with hydrogen so as to have a prepyrolysis methane concentration which is less than 9 volume percent, the methane concentration in said stream is gradually increased to a prepyrolysis concentration above 12 volume percent over a period of between 10 and 30 minutes, and then a substantially undiluted natural gas stream is passed in contact with the filaments on said surface for a time sufficient to radially grow the filaments into fibres having diameters between 5 and 15 microns.

DATED: 30 July, 1985

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