FORM 1

61370 8 SPRUSON & FERGUSON

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

Shell Internationale Research Maatschappij B.V., a Netherlands Company, of Carel van Bylandtlaan 30, 2596 HR, The Hague, THE NETHERLANDS, hereby apply for the grant of a standard patent for an invention entitled:

Process for the Preparation of Activated Carbon

which is described in the accompanying complete specification.

Details of basic application(s):-

Basic Applic. No:	Country:	Application Date:
8803404	GB	15 February 1988

The address for service is:-

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DATED this THIRTEENTH day of FEBRUARY 1989

Shell Internationale Research Maatschappij B.V.

By: M.J. Anderson

Registered Patent Attorney

TO: THE COMMISSIONER OF PATENTS
OUR REF: 84914
S&F CODE: 61750

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5845/2

SPRUSON & FERGUSON

COMMONWEALTH OF AUSTRALIA
PATENTS ACT 1952

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT

In support of the Convention Application made for a patent for an invention entitled:

Process for the preparation of activated carbon.

I, Onno Aalbers, of Carel van Bylandtlaan 30, 2596 HR The Hague, the Netherlands, do solemnly and sincerely declare as follows:-

1. I am authorised by SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., the applicant for the patent to make this declaration on its behalf.

2. The basic application(~~s~~) as defined by Section 141 of the Act was/~~were~~ made in Great Britain
on 15th February, 1988
by Shell Internationale Research Maatschappij B.V.

3. Francisco RODRIGUEZ-REINOSO, a Spanish citizen of Departemento de Quimica Inorganica e Ingenieria Quimica, Universidad de Alicante, Alicante, Spain and Grahame Yarvic BUSS, a British citizen of 27 Albert Hill St., Didsbury, Manchester M20 ORF, England

~~(respectively~~), ~~is~~/are the actual inventor(s) of the invention and the facts upon which the applicant is entitled to make the application are as follows:

The Applicant is the assignee of the actual inventor(s).

4. The basic application~~(s)~~ referred to in paragraph 2 of this Declaration was/~~were~~ the first application~~(s)~~ made in a Convention country in respect of the invention the subject of the application.

DECLARED at The Hague this 4th day of January 1989

Onno Aalbers

TO: THE COMMISSIONER OF PATENTS
AUSTRALIA

(12) PATENT ABRIDGMENT **(11)** Document No. **AU-B-29887/89**
(19) AUSTRALIAN PATENT OFFICE **(10)** Acceptance No. **613708**

(54) Title
PROCESS FOR THE PREPARATION OF ACTIVATED CARBON

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(57) Claim

1. Process for the preparation of activated carbon, comprising providing carbonaceous cellulose material in a form having an average particle size of 1 to 3 mm, treatment of the material with an aqueous zinc chloride solution containing 0.25 to 4 parts by weight of anhydrous zinc chloride with respect to the amount of carbonaceous material, evaporation of the water to an extent suitable for ensuring even distribution of the zinc chloride in the carbonaceous material, filtering and drying, carbonization under an inert atmosphere at 400-700°C, removal of zinc chloride by washing with water and subsequent recovery of a dry granular activated carbon product.

2. Process according to claim 1, wherein the removal of zinc chloride is followed by activation at 700-1000°C in an oxidizing atmosphere.

12. Granulated microporous activated carbon having a surface area of at least $1800 m^2/g$ and a bulk density of at least $0.35 g/cm^3$ obtainable in a process as claimed in any one of claims 1 to 10.

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S & F Ref: 84914

FORM 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE:

Class   Int Class

Complete Specification Lodged:
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Related Art:

Name and Address of Applicant:	Shell Internationale Research Maatschappij B.V. Carel van Bylandtlaan 30 2596 HR The Hague THE NETHERLANDS
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Complete Specification for the invention entitled:

Process for the Preparation of Activated Carbon

The following statement is a full description of this invention, including the best method of performing it known to me/us

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ABSTRACT

PROCESS FOR THE PREPARATION OF ACTIVATED CARBON

Process for the preparation of activated carbon, comprising providing carbonaceous cellulose materials in particulate form and treating with an aqueous zinc chloride solution containing 0.25 to 4 parts by weight of zinc chloride with respect to the amount of carbonaceous material, evaporation of the water to distribute the zinc chloride evenly, carbonization in an inert atmosphere at 400-700 °C, removal of zinc chloride and subsequent recovery of a dry granular product.

The hard, granular activated carbon according to the invention has a very high surface area together with a relatively high density, making it especially suitable for use as a methane adsorbent.

PROCESS FOR THE PREPARATION OF ACTIVATED CARBON

The application relates to a process for the preparation of activated carbon from carbonaceous cellulose materials.

Activated carbon can be prepared in a carbonization process (pyrolysis process) from a large number of different carbon-containing source materials, usually but not necessarily followed by an activation process (controlled oxidation). The adsorptive power of the ultimate product depends, among other factors, on the source material, as well as on the preparation procedure employed.

The carbonization process is usually conducted by heating the carbonaceous material in the absence of air at temperatures between 400 and 900 °C. In one known procedure, dehydrating salts, such as calcium chloride, magnesium chloride and zinc chloride, are used in the carbonization step. The dehydrating salt is mixed with the source material, e.g. wood, cellulose, peat etc., together with sufficient water to wet the entire mass thoroughly, after which it is dried and carbonized between 400 and 900 °C. The finished carbon is washed with water and acid, and the dehydrating salt may be recovered from the washings.

Although activated carbon prepared under suitable pyrolysis conditions can be used without further processing for some applications, usually the char is subsequently subjected to the action of an oxidizing agent, such as air, steam or carbon dioxide, at high temperatures.

Activated carbon can be used for many purposes, such as treating waste water, removing contaminants and purifying process streams. These purposes are all more or less related to the adsorption features of the carbon. At the present moment there is a growing interest in the use of activated carbon for gas adsorption, especially for the adsorption of methane (natural gas).

Methane is an excellent fuel for internal-combustion engines. It has high anti-knock value and produces an exhaust gas which is particularly free from toxic, noxious or otherwise detrimental components. Methane is gaseous at room temperature and low pressure. A particular problem is therefore encountered in the use of methane for internal-combustion engines for automotive vehicles, namely the safe storage of the methane in a sufficient amount to permit widespread use. Methane cannot be stored in a sufficient amount in a limited space to power the vehicle except under very high pressures and/or low temperatures. Such high pressures are dangerous and low temperatures are difficult to maintain in vehicles.

In German patent applications DE-2,302,403 and DE-2,923,561, methods are described to store, among others, methane, for use in powering automotive combustion engines, by providing a tank or vessel with an adsorbent for the gas. The adsorbent, e.g. molecular sieves, silica or coke, is capable of adsorbing methane at low pressures. The stored gas volume in DE-2,302,403 can be increased by 78% at a pressure of 70 bar which could be raised still higher for a further augmentation of storage capacity. This result, however, is not very attractive. In DE-2,923,561 a methane storage system is described using binder-free compacts of zeolites. A much higher methane-adsorption is obtained in this system. A disadvantage, however, of this system is the relatively expensive adsorption compound.

Activated carbon having a high surface area, and thus a high adsorption capacity, is already known from U.S. patent 4,082,694. However, the activated carbon obtained in the process described in this patent has a very small particle size, which makes its use as a methane storage compound impracticable, as withdrawal of the methane from the storage compartment would also result in withdrawal of small carbon particles, and plugging of the lines may be expected. It is of course possible to pelletise the small carbon particles; however this will make the carbon more expensive and usually this will influence its adsorption capacity in a negative way, for example by introducing an unwanted binder material. Further, some small carbon particles may become free, due, for instance, to shaking, resulting in the above-mentioned problems.

It has now been found that a relatively inexpensive methane adsorber having a very high methane adsorption capacity can be obtained by carbonization and activation of carbonaceous cellulose materials, for instance peach stones, olive stones and almond shells. The present application, therefore, relates to a process for the preparation of activated carbon, comprising providing carbonaceous cellulose material in a form having an average particle size of 1 to 3 mm, treatment of the material with an aqueous zinc chloride solution containing 0.25 to 4 parts by weight of anhydrous zinc chloride with respect to the amount of carbonaceous material, evaporation of the water to an extent suitable for ensuring even distribution of the zinc chloride in the carbonaceous material, filtering and drying, carbonization under an inert atmosphere at 400-700°C, removal of zinc chloride by washing with water and subsequent recovery of a dry granular activated carbon product.

Preferably, the removal of zinc chloride is followed by activation at 700-1000°C in an oxidizing atmosphere.

The activated carbon obtainable in the process of the present invention has a very high surface area (for example 2500 m^2/g or more (BET, in N_2)), together with a relatively high density (for example about 0.35 g/cm^3) and is highly microporous. Further the hard and granular particles have a relatively large particle size. The material is very pure and is resistant to dusting. These features make the activated carbon obtained according to the process of the invention highly suitable for use as a methane adsorbent, especially to be used for internal combustion engines of automotive vehicles. The material is also suitable for the adsorption of gasoline and other hydrocarbon vapours.

Thus, according to a further aspect of the invention, there is provided a granular microporous activated carbon having a surface area of at least 1800 m^2/g and a bulk density of at least 0.35 g/cm^3.

Suitable carbonaceous cellulose materials for use as precursor for the process of the invention are fruit pits, nut shells, cereals, wood, sawdust, peat etc. Preferably fruit pits and nut shells are used, more preferably peach stones, olive stones and almond shells, most preferably peach stones.

The precursor materials are crushed into small particles, suitably 1 to 3 mm average particle size, especially 1.7-2.8 mm.

The (crushed) precursor materials are advantageously washed with water, or more especially with an acidic aqueous solution, to remove residual organic matter and mineral matter. Suitable acidic solutions are for instance aqueous solutions of sulphuric acid, hydrochloric acid, hydrobromic acid, phosphorous acid, phosphoric acid and nitric acid. Organic acids such as formic acid and acetic acid may also be used.

Suitable concentrations of the acid may vary between 1 and 20%, more especially between 5 and 15%. A suitable washing time varies between 1 and 24 hours, more especially between 2 and 8 hours. The temperature is suitably chosen between 10 and 40 °C, more especially between 15 and 25 °C.

The aqueous zinc chloride solution used for impregnation of the carbonaceous precursor suitably contains between 50 and 5000 g/l $ZnCl_2$, especially between 250 and 2500 g/l, more especially between 400 and 1000 g/l. The amount of anhydrous zinc chloride with regard to the carbonaceous precursor is between 0.25 and 4 (w/w), more especially between 0.5 and 2. It is preferred to use a ratio of about 1. The temperature of the treatment varies preferably between 50 and 200 °C, more preferably between 70 and 160 °C. The reaction time is usually between 3 and 20 hours, preferably between 5 and 8 hours. The volume reduction of the reaction mixture after the zinc chloride treatment by partial evaporation of the water is suitably carried out by heating the reaction mixture to its boiling point and evaporating, for example, 20-95% of the amount of water, preferably 40-90% of the amount of water, more preferably 50-75% of the amount of water. It will be understood that the volume reduction is carried out to the extent necessary to ensure that the zinc chloride is evenly distributed in the carbonaceous material.

After the volume reduction the residue is filtered and dried. Drying may be performed at elevated temperature, e.g. 80-120 °C, during a sufficiently long period, e.g. 3-12 hours.

The carbonization step is carried out at temperatures between 400 and 700 °C, preferably about 500 °C, under an inert atmosphere, e.g. nitrogen or argon. The reaction time may vary between 1 h and 200 h, preferably between 2 h and 50 h, more preferably between 1 and 6 h. The temperature is preferably increased at a rate of between 1 and 7 °C/min, more preferably between 2 and 5 °C/min. The reaction mixture obtained after the carbonization step is washed with water to remove the zinc chloride. Preferably an acidic aqueous solution is used to remove also basic zinc compounds. A suitable acid is hydrochloric acid. The washings are continued until the zinc chloride is completely removed. The washings are preferably carried out between 30 and 50 °C.

Preferably, an activation step of the carbonaceous material obtained after carbonization is carried out at a high temperature using a steam or carbon dioxide atmosphere. The temperature is preferably increased at a rate of between 1 and 12 °C/min, more preferably between 2 and 10 °C/min.

The temperature during the activation procedure may vary between 700 and 1000 °C, preferably between 780 and 900 °C. The reaction time may vary between 10 h and 500 hrs, preferably between 15 and 400 hrs depending on the precursor, e.g. a minimum of 30 h for peach stones and 15 h for almonds.

The invention is illustrated by the following Examples, although it will be understood that the invention is not limited thereto.

Example I

Preparation of activated carbon from peach stones.

Peach stones were carefully cleaned and washed, and ground into small particles, having an average size of 1.7-2.0 mm. The particles were washed with an aqueous sulphuric acid solution (10%) for six hours, and thereafter with distilled water until zero acid removal, followed by drying at ambient temperature.

The particles were impregnated with a zinc-chloride solution (100 g $ZnCl_2$ in 135 g of H_2O for 100 g of dried peach stone precursor) at 85 °C for seven hours with continuous stirring (no loss of water). Thereafter the temperature was raised to the boiling point of the solution and the solution concentrated to 33% of its original volume. The residue was filtered and dried at 110 °C for twelve hours.

Dried material (100 g) was introduced into a horizontal furnace in which a nitrogen flow was maintained (80 cm^3/min) and the temperature was raised to 500 °C (2 °C/min), whereafter the temperature was kept at 500 °C for three hours. After cooling the residue was washed with diluted hydrochloric acid (7 %w) for ten minutes. This was repeated until complete elimination of zinc chloride was obtained (which was tested by the use of a $NH_4OH/(NH_4)_2S$ solution). The sample was then washed with water and dried at 110 °C.

The washed and dried material (30 g) was thereafter activated in a furnace in which a carbon dioxide flow was maintained (80 cm^3/min) by raising the temperature to 825 °C (5 °C/min), whereafter the temperature was kept at 825 °C for 150 h. Yield of activated carbon: 12% in respect to precursor. The resulting granular material had a bulk density of 0.36 g/cm^3 and a surface area of 2500 m^2/g.

Example II

Preparation of activated carbon from olive stones. The same procedure was used to prepare activated carbon from olive stones as was described in Example I, except that an activation time of 111 h was used. Yield: 17%. The resulting granular product had a bulk density of 0.41 g/cm^3 and a surface area of 2200 m^2/g.

Example III

Preparation of activated carbon from almond shells. The same procedure was used to prepare activated carbon from almond shells as was described in Example I, except that an activation time of 75 h was used. Yield: 18%. The resulting granular product had a bulk density of 0.43 g/cm^3 and a surface area of 1900 m^2/g.

Example IV

Testing of activated carbons. Figure 1 shows the characteristic isotherms for the materials of Examples I, II and III when tested for butane adsorption at 0 °C. The results are given as liquid volume per adsorbent bulk volume (V/v) vs fraction of saturated vapour pressure (P/Po).

Example V

Alternative preparation of activated carbon from peach stones.

Peach stones were prepared as described in Example I except that the stones were ground to an average particle size of 2.0-2.8 mm.

Dried particles (100 g) were impregnated with zinc chloride solution (200 g $ZnCl_2$ in 135 ml of water). After heating at 85 °C for 7 hours with continuous stirring, the mixture was boiled to dryness. The product was heated under nitrogen flow (80 cm^3/min) at a final temperature of 700 °C for 2 hours. After cooling and washing with hydrochloric acid and water, a dry sample was obtained of bulk density 0.34 g/cm^3 and a surface area of 1500 m^2/g.

The claims defining the invention are as follows:

1. Process for the preparation of activated carbon, comprising providing carbonaceous cellulose material in a form having an average particle size of 1 to 3 mm, treatment of the material with an aqueous zinc chloride solution containing 0.25 to 4 parts by weight of anhydrous zinc chloride with respect to the amount of carbonaceous material, evaporation of the water to an extent suitable for ensuring even distribution of the zinc chloride in the carbonaceous material, filtering and drying, carbonization under an inert atmosphere at 400-700°C, removal of zinc chloride by washing with water and subsequent recovery of a dry granular activated carbon product.

2. Process according to claim 1, wherein the removal of zinc chloride is followed by activation at 700-1000°C in an oxidizing atmosphere.

3. Process according to claim 2, wherein the activation is carried out in a carbon dioxide atmosphere.

4. Process according to claim 2 or 3, wherein the activation is carried out for 15 to 400 hrs.

5. Process according to any one of the preceding claims, wherein the carbonaceous cellulose material is selected from fruit pits and nut shells.

6. Process according to claim 5, wherein the carbonaceous cellulose material is selected from peach stones, olive stones and almond shells.

7. Process according to claim 6, wherein the carbonaceous cellulose material is peach stones.

8. Process according to any one of claims 1 to 7, wherein the carbonaceous cellulose material is washed with an acidic solution for 3 to 10 hours prior to zinc chloride treatment.

9. Process according to any one of claims 1 to 8, wherein the zinc chloride treatment is carried out at a temperature between 50 and 200°C for 3 to 20 hours.

10. Process according to any one of claims 1 to 9, wherein the carbonization is carried out for 1 to 6 hours.

11. Activated carbon when prepared according to a process according to any one of claims 1 to 10.

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12. Granulated microporous activated carbon having a surface area of at least $1800 m^2/g$ and a bulk density of at least $0.35 g/cm^3$ obtainable in a process as claimed in any one of claims 1 to 10.

13. Activated carbon according to claim 12, which has been derived from peach stones, olive stones or almond stones.

14. The use of activated carbon in accordance with claim 11, 12 or 13 for the adsorption of gas.

15. The use of activated carbon in accordance with claim 11, 12 or 13 for the adsorption of natural gas and/or gasoline vapours.

16. Process for the preparation of activated carbon, substantially as hereinbefore described with reference to any one of the Examples.

17. Activated carbon whenever prepared by the process of claim 16.

DATED this SIXTEENTH day of MAY 1991
Shell Internationale Research Maatschappij B.V.

Patent Attorneys for the Applicant
SPRUSON & FERGUSON

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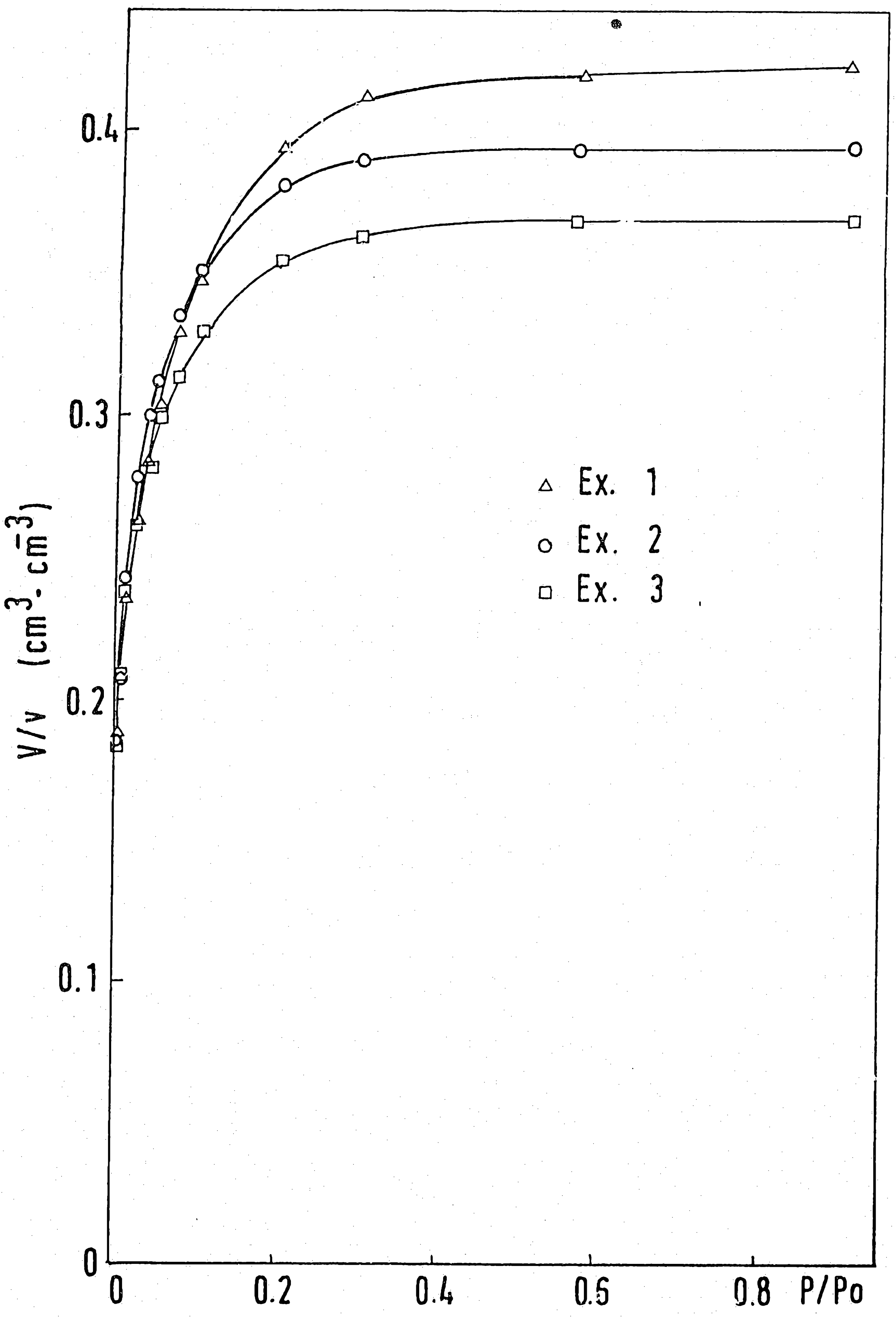

FIG. 1