(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
5 June 2008 (05.06.2008)

PCT

(10) International Publication Number
WO 2008/065121 A1

(51) International Patent Classification:
C01B 31/02 (2006.01)

(21) International Application Number:
PCT/EP2007/062900

(22) International Filing Date:
27 November 2007 (27.11.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
06/55226 30 November 2006 (30.11.2006) FR
60/878,827 5 January 2007 (05.01.2007) US

(71) Applicant *(for all designated States except US)*: **ARKEMA FRANCE** [FR/FR]; 420, rue d'Estienne d'Orves, F-92700 Colombes (FR).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **PLEE, Dominique** [FR/FR]; 3, Allée du Martin Pêcheur, F-64140 Lons (FR). **DUBOIS, Jean-Luc** [FR/FR]; 190, rue du Coteau, F-69390 Millery (FR). **PIGAMO, Anne** [FR/FR]; 9, rue Saint Sidoine, F-69003 Lyon (FR).

(74) Agent: **LHOSTE, Catherine**; Arkema France, DRD/Département Propriété Industrielle, 420, rue d'Estienne d'Orves, F-92705 Colombes Cedex (FR).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

Published:
— *with international search report*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

(54) Title: PROCESS FOR SYNTHESIZING NANOTUBES, ESPECIALLY CARBON NANOTUBES, AND THEIR USES

(57) Abstract: The subject of the present invention is a process for synthesizing nanotubes, especially carbon nanotubes, by decomposition of a gas source, at a temperature ranging from 400 to 1200 °C in a reactor, by bringing it into contact with at least one (one or more) multivalent transition metals, the transition metal(s) being supported on a support having a specific surface area determined by the BET method of greater than 50 m^2/g, especially within the range from 70 m_2/g to 400 m_2/g. The support according to the invention is especially an inorganic support, for example an alumina having a multimodal porosity. The subject of the invention is also the nanotubes thus obtained and their use for improving the mechanical and/or electrical and/or thermal properties of materials, especially polymeric materials.

WO 2008/065121 A1

PROCESS FOR SYNTHESIZING NANOTUBES, ESPECIALLY CARBON NANOTUBES, AND THEIR USES

(Field of the Invention)

The subject of the present invention is a process for synthesizing nanotubes, especially carbon nanotubes, by chemical vapour deposition employing a fluidized catalyst bed. The subject of the invention is also the nanotubes synthesized and their use for improving the mechanical and/or electrical and/or thermal properties of materials, especially polymeric materials.

(Prior art and the technical problem)

Inorganic or carbon nanotubes are recognized at the present time as being materials having great advantages because of their mechanical properties, their very high aspect ratio (length/diameter ratio) and their electrical and thermal conduction properties. In particular, these nanotubes are nanotubes consisting of carbon, boron, nitrogen, metal dichalocogenide MX_2 (M = Mo, Nb, Hf, W; X= S, Se), metal oxide MO_x, such as TiO_2, ZnO, ..., by themselves or combined.

Nanotubes based on boron, nitrogen and/or carbon are composed of graphite sheets that are wound up and terminated by hemispheres consisting of pentagons and hexagons with a structure similar to fullerenes.

Nanotubes are known to be composed of either a single sheet - they are then referred to as single-walled nanotubes or SWNTs - or several concentric sheets - called multi-walled nanotubes or MWNTs.

Boron, nitrogen and/or carbon nanotubes may be produced by various processes, such as electrical discharge, laser ablation or chemical vapour deposition (CVD). In the case of metal-based nanotubes, sol-gel processes are used.

Among these techniques, CVD seems to be the only one capable of manufacturing boron, nitrogen and/or carbon nanotubes in large quantity, an essential condition for achieving a cost price allowing them to be used

industrially in bulk in materials based on polymers and/or resins, used in various industries, such as the automobile, electronics, optoelectronics, aeronautical and thermal or electrical protection industries.

In this CVD method, a source of nitrogen-containing, boron-containing and/or carbon-containing gas is injected at a relatively high temperature high temperature onto a catalyst, said catalyst possibly consisting of a metal supported on an inorganic solid. Among catalyst metals, mention may preferably be made of iron, cobalt, nickel, molybdenum, and among supports, alumina, silica and magnesia, or even carbon, are found.

Carbon sources that may be envisaged are methane, ethane, ethylene, acetylene, benzene, ethanol, methanol, acetone or even CO/H_2 synthesis gas (the HIPCO process).

The gaseous source of boron is for example borane (B_2H_6), and the gaseous source of nitrogen is especially pyridine, ammonia or ethylenediamine.

As prior art relating to the various types of nanotubes and their manufacture, the reader may refer to the doctoral thesis of Marie Castignolles: "Etudes de la synthèse et de la structure par microscopie et spectroscopie électroniques de nanotubes de carbone purs et dopés à l'azote [*Studies on the synthesis and structure, using electron microscopy and spectroscopy, of pure and nitrogen-doped carbon nanotubes*]", University of Montpellier II, defended on 15 June 2006.

As an example of the CVD method, the process described in document WO 86/03455A1 from Hyperion Catalysis International Inc. may be mentioned. The synthesis of carbon nanotubes (CNTs) is carried out by bringing a catalyst containing iron (for example Fe_3O_4, iron on a carbon support, iron on an alumina support or iron on a carbon-containing fibril support) into contact with a carbon-containing gaseous compound (preferably CO or one or more hydrocarbons), advantageously in the presence of a compound capable of reacting with carbon in order to produce gaseous products (for example CO, H_2 or H_2O). The catalysts are prepared by dry impregnation, by precipitation or by wet impregnation of a support.

The desire to increase the productivity by weight (quantity of nanotubes produced relative to the quantity of gas and catalyst used) or to achieve better

control of the quality of the nanotubes formed has led several authors to consider Co/Fe catalyst mixtures.

Thus, the article "Metal mixtures catalyzed carbon nanotubes", by Z. Konya, N. Nagaraju, A. Fonseca, J.B. Nagy, A. Tamasi and K.M. Mukhopadhyay, AIP Conference Proceedings, (1999), 486, 249-253, may be mentioned. This document explains that the Fe/Co catalyst mixtures are more effective for synthesizing MWNTs than Co or Fe by themselves on the aluminas used. These aluminas were prepared from hydrolysed aluminium isopropoxide or commercial alumina having a low specific surface area determined by the BET method.

Z. Fonseca *et al.* in "Synthesis of SWNT by catalytic decomposition of hydrocarbons", Chem. Commun. (1999), 1344-1344, teach that a Co/Fe catalyst mixture on silica or alumina results in better CNT yields than Fe by itself and that alumina is a better catalyst support than silica.

Controlling the diameter of nanotubes is mentioned in "XPS characterization of catalysts during production of multiwall carbon nanotubes" by Z. Konya, J. Kiss, A. Oszko, A. Siska and I. Kiricsi, Physical Chemistry, Chemical Physics (2001), 3(1), 155-158. Thus, this article mentions that the CNTs synthesized using a Co/Al_2O_3 or Fe/Al_2O_3 catalyst in the presence of acetylene have a diameter ranging from 20 to 40 nm, whereas they are finer (8 to 12 nm diameter) if an $Fe\text{-}Co/ Al_2O_3$ catalyst is used.

The article "Control of the outer diameter of thin carbon nanotubes synthesized by catalytic decomposition of hydrocarbons", by J. Willems, Z. Konya, JF. Colomer, G. van Tenderloo, N. Nagaraju, A. Fonseca and J.B. Nagy, CP 544, Electronic Properties of Novel Materials-Molecular Nanostructures, published by Kuzmany *et al.*, (2000), 242-245, shows that the outside diameter of the CNTs is controlled by the metal.

The object of the present invention is to provide a novel process that is effective for manufacturing nanotubes, especially carbon nanotubes, having good weight productivity and good reproducibility. This process also makes it

easier to purify the nanotubes, should this step be necessary for their application.

(Detailed description of the Invention)

The subject of the present invention is a process for synthesizing nanotubes, especially carbon nanotubes, by decomposition of a gas source, at a temperature ranging from 400 to 1200 °C in a reactor, by bringing it into contact with at least one (one or more) multivalent transition metals, the transition metal or metals being supported on a support having a specific surface area determined by the BET method of greater than 50 m^2/g.

The BET method is based on the molecular multilayer adsorption of gas at low temperature, well known to those skilled in the art.

In particular, the catalyst is brought into contact with the gases in a fluidized bed.

According to one embodiment of the invention, the specific surface area of the support is chosen to be in the range from 70 m^2/g to 400 m^2/g.

Among supports according to the invention, it is particularly useful to use inorganic supports, for example a support consisting of at least one alumina, the intraparticle porosity of which is multimodal, as determined by the mercury porosimetry method.

According to one particular embodiment of the invention, the support is a multimodal alumina (having 2 or more than 2 porosity peaks), the total mercury pore volume of which is greater than 0.9 cm^3/g, said alumina having at least one porosity peak in the range from 50 to 3000 nm.

According to one particular embodiment, the supports can be impregnated with an amount of transition metal(s) ranging up to 50% by weight of the final catalyst and especially in a range from 10 to 50% by weight of the final catalyst.

Advantageously, the size of the support particles is chosen so as to allow good fluidization of the catalyst during the CNT synthesis reaction. In practice, to ensure correct productivity, the support particles preferably have a mean diameter D_{50} ranging from 20 to 500 µm. According to one particular embodiment

of the process of the invention, the catalyst is prepared by impregnating the support particles, especially in a stream of dry gas, with an impregnation solution containing at least one transition metal salt, especially an iron and/or cobalt and/or molybdenum salt, at a temperature lying within the range from room temperature to the boiling point of the solution. The amount of impregnation solution is chosen so that the support particles are, at all times, in contact with a sufficient amount of solution to ensure formation of a film of the impregnation solution on the surface of the support particles. In particular, when the transition metal is iron, the iron impregnation solution may be an aqueous iron nitrate solution.

According to the invention, before the nanotubes are synthesized, the catalyst is calcined in a furnace, especially at a temperature between 300 and 750 °C, for the purpose of purifying them and, for example, denitrifying them.

The fact of working "dry", that is to say having at all times just the quantity of liquid needed to create a liquid film on the surface of the catalyst support particles, prevents aqueous discharges (for example aqueous nitrate discharges when the impregnation solution contains iron nitrate; after impregnation, the product obtained is heated to between 300°C and 400°C in a gas, whether inert or not, in order to remove the nitrates).

According to one particular embodiment of the invention, the catalyst is reduced *in situ* in the synthesis reactor and the catalyst does not see air again before the synthesis of the nanotubes. The iron thus remains in metallic form.

According to the invention, the carbon source may be chosen from any type of carbon-containing material, such as methane, ethane, propane, butane or any other aliphatic alkane containing more than 4 carbon atoms, cyclohexane, ethylene, propylene, butane, isobutene or any other aliphatic alkane containing more than 4 carbon atoms, benzene, toluene, xylene, cymene, ethyl benzene, naphthalene, phenanthrene, anthracene, acetylene or any other alkyne containing more than 4 carbon atoms, formaldehyde, acetaldehyde, acetone, methanol, ethanol, carbon monoxide, by themselves or as a mixture.

According to the invention, the boron source is for example borane (B_2H_6).

According to the invention, the nitrogen source is for example pyridine, ammonia or ethylenediamine.

The gas source and its composition fixes the composition of the nanotubes. Thus, a carbon source allows carbon nanotubes to be manufactured.

The subject of the present invention is also nanotubes, especially carbon nanotubes, obtained by the above process. The nanotubes thus obtained are multi-walled nanotubes having an external diameter lying within the range from 10 to 30 nm.

These nanotubes may be used as agents for improving the mechanical and/or electrical and/or thermal conductivity properties, especially in compositions based on polymers and/or resins.

These nanotubes may be used in many fields, especially in electronics (depending on the use temperature and their structure, they may be conductors, semiconductors or insulators); in the mechanical field, for example for the reinforcement of composites, for example in the automotive field, aeronautical field (CNTs are one hundred times stronger and six times lighter than steel) and in the electromechanical field (they can elongate or contract by charge injection). For example, mention may be made of the use of CNTs in macromolecular compositions intended for example for the packaging of electronic components, for the manufacture of fuel (petrol or diesel) lines, antistatic coatings, in thermistors, in electrodes for the energy sector, especially for supercapacitors, as agents dispersed in aqueous media, such as electromagnetic screening, etc.

Because the catalyst support has multimodal porosity, the method of purifying the nanotubes, in order to remove the catalyst residues, for example using an acid solution, is made easier owing to greater accessibility to the support.

The present invention will now be illustrated by particular examples of its implementation described below. It should be pointed out that the purpose of these examples is not in any way to limit the scope of the present invention.

EXAMPLES:

The instrument used for carrying out the BET specific surface area measurements was a Micromeritics ASAP® 2000 machine.

The machine used to carry out the mercury porosimetry measurement was a Micromeritics AUTOPORE® machine operating from 3 to 4000 bar.

➢ **Preparation of the catalysts:**

Counter-example

A catalyst containing 35% iron by weight was prepared by impregnation of Puralox® SCCA 5-150 alumina from Sasol using the following protocol:

300 g of alumina were introduced into a jacketed 3-litre reactor heated to 100°C, a stream of air being passed therethrough. By means of a pump, 1600 ml of an iron solution containing 545 g/l of iron nitrate nonahydrate was then continuously injected. Since the intended (mass of metal/mass of final catalyst) ratio was 35% by weight of iron in metallic form, the iron solution was added over a period of 23 h and the rate of addition of this solution was equal to the rate of evaporation of the water. The catalyst was then heated at 100 °C in an oven for 16 h.

Initially, the particles of this alumina had a median diameter of about 85 µm and the surface area and porosity characteristics indicated below:

BET surface area (m^2/g)	148
Hg total pore volume (cm^3/g)	0.87

Example 1 (Ref: 2017 C27) (according to the invention)

An alumina was prepared by spray drying, without prior micronization, a suspension consisting of water, a calcined alumina (Sasol Puralox® UF 5/230) and a pseudoboehmite (Sasol Dispersal® 40). After calcination to convert the pseudoboehmite into γ-alumina, the catalyst was prepared as explained in the counter-example.

Example 2 (Ref: 2017 C01) (according to the invention)

An alumina was prepared by milling a bimodal alumina from Norton, supplied in the form of extrudates 5 mm in length having a BET surface area of 252 m^2/g.

Example 3 (Ref: 2017 C54) (according to the invention)

An alumina was prepared by spray drying, with prior micronization, a suspension consisting of water, a calcined alumina (Sasol Puralox® UF 5/230)

and a pseudoboehmite (Eurosupport Versal® 250). The solids content was 21.3% by weight. After calcination to convert the pseudoboehmite into γ-alumina, the catalyst was prepared as explained in the counter-example.

Example 4 (Ref: 2017 C70) (according to the invention)

An alumina was prepared by spray drying, with prior micronization, a suspension consisting of water, a calcined alumina (Sasol Puralox® UF 5/230) and a pseudoboehmite (Sasol Pural® 400). The solids content was 42.5% by weight. After calcination to convert the pseudoboehmite into γ-alumina, the catalyst was prepared as explained in the counter-example.

Example 5 (Ref: 2017 C94) (according to the invention)

An alumina was prepared by spray drying, without prior micronization, a suspension consisting of water and a pseudoboehmite (Sasol Versal® 250). The solids content was 26% by weight. After calcination to convert the pseudoboehmite into γ-alumina, the catalyst was prepared as explained in the counter-example.

Example 6 (Ref: 2017 C93) (according to the invention)

An alumina was prepared by spray drying, without prior micronization, a suspension consisting of water and a pseudoboehmite (Sasol Versal® 250). The solids content was 15% by weight. After calcination to convert the pseudoboehmite into γ-alumina, the catalyst was prepared as explained in the counter-example.

Example 7 (Ref: 1870 C161) (according to the invention)

An alumina was prepared by milling a bimodal alumina in the form of extrudates 1.2 mm in length from Norton.

The main data regarding these aluminas are given in Table 1 below.

Table 1

	Total Hg pore volume (cm^3/g)	1st porosity peak (nm)	2nd porosity peak (nm)	D_{50} particle size (µm)	BET specific surface area (m^2/g)
Puralox® SCCA 5-150 counter-example	0.87	9		85	148
Example 1 2017 C27	1.19	8	50	105	156.8
Example 2 2017 C01	2	8	500	83	252
Example 3 2017 C54	1.73	8	200	91	208
Example 4 2017 C70	1.23	8	500	96	155
Example 5 2017 C94	3.53	8	1500	107	228
Example 6 2017 C93	3.27	8	2000	87	249
Example 7 1870 C161	1.05	7	600		254.8

D_{50}: Apparent mean diameter of 50% of the particle population.

Example 8 (according to the invention)

An alumina was prepared by spray drying, without prior micronization, a suspension consisting of water and a pseudoboehmite (Sasol Versal® 250). The solids content was 15% by weight. After calcination to convert the pseudoboehmite into γ-alumina, the catalyst was prepared by adding a solution composed of cobalt acetate dihydrate and iron nitrate, so as to have a total metal content of 35 wt% with a Co/Fe ratio = 1.

- **Preparation of the carbon nanotubes:**

Example 9 (according to the invention)

The denitrification operations, corresponding to the step of purifying the catalysts obtained according to the counter-example and examples 1 to 8, were carried out at 350°C in an oven under a stream of air for 2 h. About 2.5 g of catalyst thus denitrified was introduced, as a layer, into a reactor having a

diameter of 5 cm and an effective height of 1 m, fitted with a separator intended to prevent fine particles from being entrained towards the top of the reactor. The reactor was heated for about 30 minutes up to 650°C and then the catalysts were reduced under 25 vol% H_2/75 vol% N_2 for 30 minutes. The nitrogen was then replaced with ethylene, the reaction was left to continue for 1 hour and then the nanotubes formed were collected. In all cases, the total N_2, H_2/N_2 or C_2H_2/H_2 flow rates were constant at 160 Sl/min.

After the nanotubes formed were discharged and collected, the productivity was determined by loss of ignition of the CNTs and the quality of the CNTs determined by electron microscopy.

The results are given in Table 2 below:

Table 2

Catalyst of the example	Productivity (g of CNT/ g of catalyst)	Type of CNT formed
Counter-example	12	MWNT / ∅: 10-30 nm, no other forms of C
3	15	MWNT / ∅: 10-30 nm, no other forms of C
4	14	MWNT / ∅: 10-30 nm, no other forms of C
5	16.5	MWNT / ∅: 10-30 nm, no other forms of C
6	16	MWNT / ∅: 10-30 nm, no other forms of C
7	11	MWNT / ∅: 10-30 nm, no other forms of C
8	18.5	MWNT / ∅: 8-16 nm, no other forms of C

MWNT: multi-walled nanotubes; ∅: diameter of the nanotubes.

Except for the counter-example, all the other catalysts were γ-alumina/iron catalysts exhibiting two peaks in the region of pores smaller in size than 5 μm.

Table 2 shows that the best productivity is obtained with catalysts having a multimodal porosity.

Table 2 also shows that the combination of iron and cobalt results in better CNT productivity and smaller CNTs.

It may also be seen that the amount of catalyst has no influence on the productivity nor on the reproducibility of the CNTs in terms of diameter and structure.

CLAIMS

1. Process for synthesizing nanotubes, especially carbon nanotubes, by decomposition of a gas source, at a temperature of between 400 and 1200 °C, by bringing it into contact with at least one or more multivalent transition metals, characterized in that the transition metal or metals are supported on a support having a BET specific surface area of greater than 50 m^2/g.

2. Nanotube synthesis process according to Claim 1, characterized in that the transition metal or metals are supported on a support having a BET specific surface area lying within the range from 70 m^2/g to 400 m^2/g.

3. Nanotube synthesis process according to Claim 1 or 2, characterized in that the transition metal or metals are supported on an inorganic support.

4. Process according to one of the preceding claims, characterized in that the support consists of at least one alumina whose intraparticle porosity is multimodal.

5. Process according to one of the preceding claims, characterized in that the support is an alumina, the total mercury pore volume of which is greater than 0.9 cm^3/g, said alumina having at least one porosity peak in the range from 50 to 3000 nm.

6. Process according to one of the preceding claims, characterized in that the amount of transition metal(s) represents up to 50% by weight of the final catalyst.

7. Process according to one of the preceding claims, characterized in that the amount of transition metal(s) lies within the range from 10 to 50% by weight of the final catalyst.

8. Process according to one of the preceding claims, characterized in that the support particles have a mean diameter lying within the range from 20 to 500 µm.

9. Process according to one of the preceding claims, characterized in that the catalyst is prepared by impregnating the support particles with an impregnation solution containing at least one transition metal salt.

10. Process according to one of the preceding claims, characterized in that said catalyst is prepared by impregnating the support particles at a temperature lying within the range from room temperature to the boiling point of the solution, the support particles being at all times in contact with a sufficient amount of impregnation solution to ensure formation of a film of the impregnation solution on the surface of the support particles.

11. Process according to one of the preceding claims, characterized in that the catalyst is prepared by impregnating the support particles with an iron impregnation solution.

12. Process according to one of the preceding claims, characterized in that the catalyst is calcined in a furnace before the nanotubes are synthesized.

13. Process according to one of the preceding claims, in which the catalyst is reduced *in situ* and does not see air again before the synthesis of the nanotubes.

14. Process according to any one of the preceding claims, characterized in that the gas source is a carbon source.

15. Nanotubes that can be obtained by the process as defined in any one of the preceding claims.

16. Use of the nanotubes, especially carbon nanotubes, obtained according to any one of Claims 1 to 14 as agents for improving the mechanical and/or electrical and/or thermal conductivity properties, especially in compositions based on polymers and/or resins.

17. Use according to the preceding claim of the compositions based on polymers in fuel lines, antistatic coatings or in electrodes for the energy sector.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/062900

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B31/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 03/002456 A (TOULOUSE INST NAT POLYTECH [FR]; SERP PHILIPPE GILLES [FR]; FEURER ROS) 9 January 2003 (2003-01-09) * comparative example1 * * comparative example7 * page 3, line 31 - page 4, line 22 page 5, line 1 - line 3 page 6, line 23 - line 27 page 9, line 3 - line 7 page 9, line 13 - line 21 claims 1,5,8,10,12,15,28	1-6,8-17

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
31 March 2008	08/04/2008

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Rigondaud, Bernard

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/062900

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2006/008385 A (TOULOUSE INST NAT POLYTECH [FR]; KALCK PHILIPPE [FR]; SERP PHILIPPE [F) 26 January 2006 (2006-01-26) claims 1,11,12,16-20 page 3, line 16 - line 26 page 6, line 29 - page 7, line 8 page 7, line 19 - line 21 page 7, line 28 - line 30 page 8, line 3 - line 8 examples 1-4	1-8, 14-17
A	EP 1 449 885 A (ATOFINA [FR]) 25 August 2004 (2004-08-25) paragraphs [0001] - [0006]	1,17
A	WO 2005/037745 A (CONOCOPHILLIPS CO [US]; ESPINOZA RAFAEL L [US]; JOTHIMURUGESAN KANDASW) 28 April 2005 (2005-04-28) page 3	1,4,5
A	EP 1 640 065 A (INST FRANCAIS DU PETROL [FR]) 29 March 2006 (2006-03-29) the whole document	1,4,5
A	EP 0 353 129 A1 (RHONE POULENC CHIMIE [FR]) 31 January 1990 (1990-01-31) column 1	1,4,5

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2007/062900

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 03002456 A	09-01-2003	AT 284839 T	15-01-2005
		CA 2455086 A1	09-01-2003
		CN 1549792 A	24-11-2004
		DE 60202290 D1	20-01-2005
		DE 60202290 T2	08-12-2005
		EP 1399384 A2	24-03-2004
		ES 2235083 T3	01-07-2005
		FR 2826646 A1	03-01-2003
		JP 4033833 B2	16-01-2008
		JP 2004532180 T	21-10-2004
		MX PA03011876 A	26-03-2004
		RU 2299851 C2	27-05-2007
		US 2004234445 A1	25-11-2004
WO 2006008385 A	26-01-2006	BR PI0512398 A	04-03-2008
		CA 2570587 A1	26-01-2006
		CN 101018736 A	15-08-2007
		EP 1771379 A1	11-04-2007
		FR 2872150 A1	30-12-2005
		JP 2008503435 T	07-02-2008
		KR 20070059050 A	11-06-2007
EP 1449885 A	25-08-2004	CN 1539882 A	27-10-2004
		JP 4042857 B2	06-02-2008
		JP 2004250707 A	09-09-2004
		KR 20040074615 A	25-08-2004
		US 2005131147 A1	16-06-2005
WO 2005037745 A	28-04-2005	NONE	
EP 1640065 A	29-03-2006	CN 1762597 A	26-04-2006
		FR 2875716 A1	31-03-2006
		JP 2006095524 A	13-04-2006
		US 2006067877 A1	30-03-2006
EP 0353129 A1	31-01-1990	BR 8903789 A	20-03-1990
		CA 1340845 C	07-12-1999
		DE 68901318 D1	27-05-1992
		DK 372789 A	30-01-1990
		ES 2032667 T3	16-02-1993
		FR 2634757 A1	02-02-1990
		GR 3005141 T3	24-05-1993
		JP 2074520 A	14-03-1990
		JP 2098287 C	02-10-1996
		JP 8000694 B	10-01-1996
		SU 1836139 A3	23-08-1993