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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
13 April 2006 (13.04.2006)

PCT

(10) International Publication Number
WO 2006/037368 A1

(51) International Patent Classification[7]: C10G 25/00, B01J 20/00

(21) International Application Number: PCT/EP2004/011361

(22) International Filing Date: 4 October 2004 (04.10.2004)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicants *(for all designated States except US)*: **PETROLEO BRASILEIRO S.A.-PETROBRAS** [BR/BR]; Avenida Republica do Chile, 65, Rio de Janeiro (BR). **ALBEMARLE NETHERLANDS B.V.** [NL/NL]; Stationsplein 4, NL-3818 LE Amersfoort (NL).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **MARQUES MOREIRA, Elizabeth** [BR/BR]; Rua Souza Lima 385/701, Copacabana, Rio de Janeiro, RJ- Brazil CEP 22081-010 (BR). **DE LACERDA ALVARENGA BAPTISTA, Claudia Maria** [BR/BR]; Rua Otavio Kelly 63/401, Tijuca, Rio de Janeiro, RJ-Brazil CEP 20511-280 (BR). **O'CONNOR, Paul** [NL/NL]; Hogebrinkerweg 9, NL-3871 KM Hoevelaken (NL). **SOARES CERQUEIRA, Henrique** [BR/BR]; Rua das Laranjeiras 585/703, Cosmo Velho, Rio de Janeiro, RJ- Brazil CEP 22240-002 (BR).

(74) Agent: **RASSER, J., C.**; Howrey LLP, Rembrandt Tower, Amstelplein 1, 31st Floor, NL-1096 HA Amsterdam (NL).

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

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2006/037368 A1

(54) Title: PROCESS FOR REDUCING THE ORGANIC ACID CONTENT OF HYDROCARBON FEEDSTOCKS

(57) Abstract: A process for reducing the organic acid content of a crude oil feed by contacting the oil feed with an adsorbent comprising anionic clay or a heat-treated form thereof in a reactor vessel under agitation and under a flow of inert gas at a temperature in the range of 200 to 500°C.

PROCESS FOR REDUCING THE ORGANIC ACID CONTENT OF HYDROCARBON FEEDSTOCKS

The present invention relates to a process for reducing the organic acid content of crude oil feeds.

The organic acids present in crude oils and petroleum fractions are mainly naphthenic acids. Naphthenic acids are predominantly monocarboxylic acids having one or more cycloaliphatic groups alkylated in various positions with short chain aliphatic groups and containing a polyalkylate chain terminating in the carboxylic acid function. They are represented by a general formula $C_nH_{2n-z}O_2$, where n indicates the carbon number and z specifies a homologous series. The z is equal to 0 for saturated acyclic acids and increases to 2 in monocyclic naphthenic acids, to 4 in bicyclic naphthenic acids, to 6 in tricyclic acids, and to 8 in tetracyclic acids. Naphthenic acids in the range of C_7 to C_{12} consist mainly of monocyclic acids. The more complex acids contain larger proportions of multicyclic condensed compounds.

The molecular weight of the naphthenic acids present in crude oils, as determined by mass spectrometry, generally varies between 200 and 700.

A significant quantity of crude oils has recently been found worldwide, particularly the recent offshore findings in Brazil. These crude oils, which exhibit a relatively high density and a high content of naphthenic acids, challenge downstream operations due to high corrosion rates. As a result, the price of the oil decreases sharply with the increase of the total acidity number (TAN).

The straightforward solution is to blend the high-acidity crude with low-acidic ones. Another option is the addition of a basic solution of corrosion inhibitors (US 5,182,013 and US 4,647,366), the drawback being the formation of a stable emulsion, which is difficult to separate from the treated crude. The pre-treatment of

crudes by making use of many different basic compounds to neutralize the acids present in the oil has also been investigated. Compounds like monoethanolamine (US 4,589,979), ethoxylated amine (US 5,961,821), ammonia (US 6,258,258), polymeric amines (US 6,281,328), aqueous solutions of hydroxides or ammonium hydroxide (WO 01/79386), or a mixture of alcohol with metal carbonates, hydroxides and/or phosphates (US 6,190,541) are disclosed as being effective. Nevertheless, the consumption of such compounds is a major inconvenience.

US 6,086,751 discloses reduction of the acidity by means of a moderate thermal treatment, at temperatures in the range of 320 to 420°C and reaction times of 2 hours. Under those conditions thermal cracking is minimized and most of the acids are converted to water and CO_2. The presence of water inhibits the decarboxylation reaction. It is therefore important to remove the water prior to the thermal treatment and to keep removing it (and the CO_2) as it is formed during the treatment.

Another possibility is pre-treatment of the crude oil under fixed bed hydrotreating conditions - temperature: 200-370°C, H_2 partial pressure: 50-500psi - for selectively converting low-molecular weight acids, which are thought to be the main cause of corrosion (US 5,871,636 and US 5,910,242). A Group VI metal or a Group VIII noble metal may be used as catalyst. The drawback to such a process is the investment (and catalyst) cost and the hydrogen consumption. According to US 5,928,501, a slurry reactor may also be used for the hydrogenation of naphthenic acids, achieving complete elimination of the acids using a similar catalyst and pressure, but at higher (380-450°C) temperatures.

Another approach is the use of adsorbents to adsorb the acids.

WO 04/005434 discloses a reduction of the naphthenic acidity of desalted and dewatered petroleum oils by using an adsorbent. Disclosed adsorbents include carbon black and spent or coked FCC catalysts.

US 5,389,240 discloses a fixed bed process for sweetening liquid hydrocarbon feedstocks. The first step in this process involves the removal of naphthenic acids; the second step is the removal of mercaptans from an alkaline environment. It is mentioned that petroleum fractions having an end boiling point up to about 600°C and TAN values of 0.003 to 4 mg KOH/g can be treated by this process. Disclosed petroleum feedstocks are kerosine, middle distillates, light gas oil, heavy gas oil, jet fuel, diesel fuel, heavy naphtha, lube oil, stove oil, and heating oil; with kerosine with a TAN of 0.01-0.06 mg KOH/g being preferred. The sulfur levels of these petroleum fractions is about 0.05-0.8 wt% (as S).

The first step involves flowing the feedstock in the presence of oxygen or air and at a preferred temperature of 30-80°C through a fixed bed of an adsorbent containing a metal oxide solid solution. The metal oxide solid solution contains a divalent and a trivalent metal oxide and is prepared by calcining a hydrotalcite-like material at a temperature between 400-750°C.

Although this document mentions that the reaction temperature during naphthenic acid removal may be as high as 400°C, the use of such a high temperature in said process will never be considered by those skilled in the art. First of all, such temperatures would result in thermal cracking of the petroleum fractions, which is in general undesired. Second, the use of such high temperatures in this oxygen-requiring process will result in the formation of (a) explosive mixtures of light cracking products and oxygen and (b) undesired O-containing compounds like phenols.

Crude oils contain far more heavy metal and hetero atom (S, N) contaminants than the petroleum fractions of US 5,389,240 do. Crude oil feeds usually have a sulfur

content of at least 1.5 wt% (as S), typically 2-3 wt%, although sulfur levels above 5 wt% are possible.

If the process of US 5,389,240 should be used for organic acid removal from crude oils, it is to be expected - because metal oxide solid solutions are good adsorbents for sulfur and nitrogen-containing materials – that sulfur and nitrogen-containing materials preferentially adsorb on the solid solutions before giving organic acids a chance to adsorb. Further, the heavy metals present in the crude oils are expected to poison the solid solution's adsorption sites. The same would be expected for anionic clays, the precursors of said solid solutions. Therefore, the process of US 5,389,240 cannot be used for the removal of organic acids from crude and heavy oils.

Unexpectedly, it has now been found that, under specific conditions, anionic clays and their heat-treated forms can be successfully used for the removal of organic acids from crude and heavy oils.

The present invention therefore relates to a process for reducing the organic acid content of crude oil feeds by contacting a crude oil feed with an adsorbent comprising an anionic clay or a heat-treated form thereof in a reactor vessel under agitation and under a flow of inert gas at a temperature in the range 200 to 500°C.

Without wishing to be bound to any theory, it is thought that the success of the process is due to *in situ* regeneration of the adsorption sites. This *in situ* regeneration is probably due to decomposition of the organic - e.g. naphthenic – acids, thereby regenerating the adsorption sites.

Further, in this temperature range, acid adsorption seems to be favoured over adsorption of the sulfur contaminants.

Using the process of the invention, crude oils with a TAN up to 10 can be treated. Further, this process at the same time reduces the viscosity of the crude oil.

Crude oil feed

Crude oil feeds that may be used in the process of the invention include any organic acid-containing crude oil that is liquid or liquefiable at the temperature applied during the process. Both whole crudes, i.e. unrefined, undistilled crudes, and topped crudes may be used.

The crude oil feed preferably has a Conradson Carbon content of at least 3, more preferably of at least 5. Their sulfur content preferably is at least 1.5 wt% (as S), more preferably 2-3 wt%.

The Total Acid Number (TAN) of the crude oil feed preferably is up to 10, more preferably 2 to 5. This Total Acid Number refers to the amount of milligrams of KOH required for neutralizing one gram of oil and is determined using ASTM D-664-04.

The adsorbent

The adsorbent to be used in the process of the present invention comprises an anionic clay or a heat-treated form thereof. In addition, the adsorbent may contain a matrix material, such as alumina, silica, silica-alumina and/or magnesia. Other materials that may be present in the adsorbent include compounds containing metals selected from the group consisting of Ca, Ba, K, and Na.

The adsorbent preferably contains 50-100 wt%, more preferably 80 to 100 wt% of (heat-treated) anionic clay.

The adsorbent is preferably used in the form of shaped particles, such as microspheres, extrudates, beads, or pellets. These particles have a diameter of preferably 0.1-100 mm, more preferably 0.1-10 mm, and most preferably 0.1-3 mm.

The BET surface area of the (heat-treated) anionic clay preferably ranges from 60 to 300 m^2/g, more preferably from 150 to 250 m^2/g.

Anionic clays are layered structures corresponding to the general formula

$$[M_m^{2+} M_n^{3+} (OH)_{2m+2n}](X_{n/z}^{z-}). bH_2O$$

wherein M^{2+} is a divalent metal, M^{3+} is a trivalent metal, m and n have a value such that m/n = 1 to 10, preferably 1 to 6, and b has a value in the range of from 0 to 10, generally a value of 2 to 6, and often a value of about 4. X is an anion with valance z, such as CO_3^{2-}, OH^-, or any other anion normally present in the interlayers of anionic clays. It is more preferred that m/n should have a value of 2 to 4, more particularly a value close to 3.

In the prior art, anionic clays are also referred to as layered double hydroxides and hydrotalcite-like materials.

Anionic clays have a crystal structure consisting of positively charged layers built up of specific combinations of metal hydroxides between which there are anions and water molecules. Hydrotalcite is an example of a naturally occurring anionic clay in which Al is the trivalent metal, Mg is the divalent metal, and carbonate is the predominant anion present. Meixnerite is an anionic clay in which Al is the trivalent metal, Mg is the divalent metal, and hydroxyl is the predominant anion present.

In hydrotalcite-like anionic clays, the brucite-like main layers are built up of octahedra alternating with interlayers in which water molecules and anions, more particularly carbonate ions, are distributed. The interlayers may contain anions such as NO_3^-, OH, Cl^-, Br^-, I^-, SO_4^{2-}, SiO_3^{2-}, CrO_4^{2-}, BO_3^{2-}, MnO_4^-, $HGaO_3^{2-}$, HVO_4^{2-}, ClO_4^-, BO_3^{2-}, pillaring anions such as $V_{10}O_{28}^{6-}$ and $Mo_7O_{24}^{6-}$, monocarboxylates such as acetate, dicarboxylates such as oxalate, alkyl sulfonates such as lauryl sulfonate.

Upon thermal treatment at a temperature above about 200°C, anionic clays are transformed into so-called solid solutions, i.e. mixed oxides that are re-hydratable

to anionic clays. At higher temperatures, above about 800°C, spinel-type structures are formed. These are not re-hydratable to anionic clays.

The thermally treated anionic clays that can be used in the process of the present invention include solid solutions and spinel-type materials, with solid solutions being preferred.

For the purpose of the present invention various types of (thermally treated) anionic clays are suitable. Examples of suitable trivalent metals (M^{3+}) present in the (thermally treated) anionic clay include Al^{3+}, Ga^{3+}, In^{3+}, Bi^{3+}, Fe^{3+}, Cr^{3+}, Co^{3+}, Sc^{3+}, La^{3+}, Ce^{3+}, and combinations thereof. Suitable divalent metals (M^{2+}) include Mg^{2+}, Ca^{2+}, Ba^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Mo^{2+}, Ni^{2+}, Fe^{2+}, Sr^{2+}, Cu^{2+}, and combinations thereof. Especially preferred anionic clays are Mg-Al and Ca-Al anionic clays.

Anionic clays with any type of stacking can be used, e.g. conventional $3R_1$ stacking or the $3R_2$ stacking described in WO 01/012550.

Suitable anionic clays can be prepared by any known process. Examples are co-precipitation of soluble divalent and trivalent metal salts and slurry reactions between water-insoluble divalent and trivalent metal compounds, e.g. oxides, hydroxides, carbonates, and hydroxycarbonates. The latter method provides an inexpensive route to anionic clays.

Process conditions

The process according to the present invention is conducted in a slurry phase reactor, by mixing the adsorbent with the crude oil feed. The adsorbent/oil weight ratio in the slurry preferably is in the range of 0.01 to 1, more preferably 0.02 to 0.08.

The process is conducted under an inert gas flow. Suitable inert gases include nitrogen and argon.

During the process, light gases may be produced, such as butanes and lighter, H_2O, CO, and CO_2. This gas formation may be due to decomposition of the organic acids and/or some cracking of the crude oil feed.

The temperature in the reactor ranges from 200°C to 500°C, preferably from 250 to 400°C, and more preferably from 300 to 350°C. The latter range is preferred, because it results in minimized thermal cracking of the crude oil feed. Above this temperature, gas production and coke deposition will increase.
On the other hand, some thermal cracking of the crude oil may be desired and higher temperatures are then preferred.

The pressure in the reactor is preferably atmospheric, more preferably in the range of 0.1 to 1.0 MPa.

The crude oil feed is preferably contacted with the adsorbent for a period of 15 minutes to 5 hours, more preferably 30 to 120 minutes.
After this period, the adsorbent may be removed from the oil feed using a conventional solid/liquid separation technique, such as decantation or centrifugation. The oil fraction can then be further refined, whereas the adsorbent may be regenerated by calcination, i.e. controlled burning in the presence of air, at a temperature of 200-400°C.
Alternatively, the adsorbent and oil feed are not separated, and the slurry obtained from the process of the invention can be submitted to further refining during which the adsorbent may be present as a useful additive.

FIGURE

Figure 1 illustrates a laboratory scale installation suitable for performing the process of the invention.

EXAMPLES

General test procedure

The adsorbent was loaded in the reactor (2), which was then closed and purged with a stream of nitrogen at a flow rate of 100 mL/min for nearly 30 minutes. Cooling water was turned on and the adsorbent was heated up to 80°C.

A Campos Basin oil, Rio de Janeiro, Brazil, having TAN of 3.2 mg KOH/g (1 kg), - pre-heated at 80°C in a reservoir (1) - was drained towards the interior of reactor (2) with the aid of nitrogen. The flow rate of nitrogen was then reduced to 5 mL/min and reactor (2) was heated to the contacting temperature, under constant agitation with an impeller (3) at about 300 rpm.

The condenser (5) and the cold finger (6) were used to condense the light gases formed. The volume of gas evolving during the process, minus the volume of purge gas, was measured by a humid gas meter (7) and collected in sample bags (8) for chromatographic analysis.

The process was conducted for 60 minutes, after which the TAN of the treated oil was measured. To this end, a sample of the treated oil feed was centrifuged at ambient temperature for 5 minutes at 2,000 rpm and the TAN of the liquid phase was determined using a Metrohm™ titration processor employing ASTM Method D-664.

EXAMPLES 1-5 AND COMPARATIVE EXAMPLES 6-9

The general test procedure described above was applied in order to test the suitability of (thermally treated) anionic clays for the removal of naphthenic acids from crude oils. Different contacting temperatures and adsorbent/oil weight ratios were used: see Table 1.

The adsorbent used was a powder containing 100 wt% of either Mg/Al anionic clay or a solid solution prepared by calcining this anionic clay at 350°C (Example 4) or

400°C (Example 5). The anionic clay had a specific surface area of about 200 m^2/g.

In Table 1, the results are compared with those of kaolin (i.e. a cationic clay), coke fines, and two blank tests, Comparative Examples 6-9, respectively. The blank tests only involved the thermal treatment, without any adsorbent.

The results clearly indicate that anionic clays can be used to reduce the acid content of crude oils. Solid solutions obtained by calcination of anionic clay are even more suitable.
The Table further shows that a contacting temperature of 350°C is preferred above one of 250°C.

Table 1

Example	T (°C)	Adsorbent	Adsorbent/oil (wt/wt)	TAN (mg KOH/g oil)
1	250	anionic clay	0.1	1.35
2	350	anionic clay	0.1	0.32
3	350	anionic clay	0.02	0.53
4	350	anionic clay calcined at 350°C	0. 1	0.13
5	350	anionic clay calcined at 400°C	0.1	0.12
6	350	kaolin	5	1.5
7	350	coke fines	0.02	1.29
8	250	blank	0.00	3.20
9	350	blank	0.00	1.52

CLAIMS

1. A process for reducing the organic acid content of a crude oil feed by contacting the oil feed with an adsorbent comprising an anionic clay or a heat-treated form thereof in a reactor vessel under agitation and under a flow of inert gas at a temperature in the range of 200 to 500°C.

2. A process according to claim 1 wherein the crude oil feed and the adsorbent are used in an adsorbent/oil weight ratio of from 0.01 to 1.

3. A process according to claim 2 wherein the adsorbent/oil weight ratio ranges from 0.02 to 0.08.

4. A process according to any one the preceding claims wherein the crude oil feed is contacted with the adsorbent for a time period of from 15 minutes to 5 hours.

5. A process according to claim 4 wherein the time period is from 30 to 120 minutes.

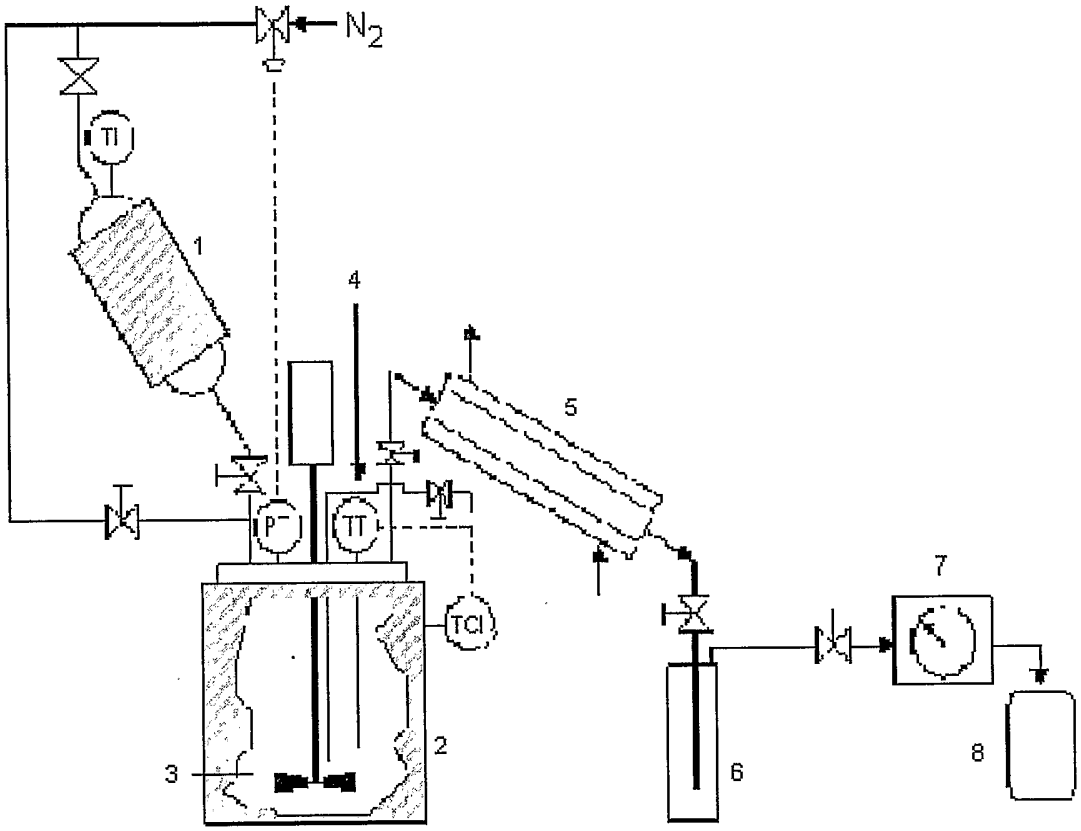
6. A process according to any one of the preceding claims wherein the pressure in the reaction vessel is from 0.1 to 1.0 MPa.

7. A process according to any one of the preceding claims wherein the adsorbent comprises 50 to 100 wt% of (heat-treated) anionic clay.

8. A process according to any one of the preceding claims wherein the adsorbent has a BET surface area of between 60 and 300 m^2/g.

9. A process according to any one of the preceding claims, followed by separating the adsorbent from the oil feed and regenerating the adsorbent by calcination.

Figure 1



5

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/011361

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C10G25/00 B01J20/00

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)
IPC 7 C10G B01J

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2004/005434 A (PETROLEO BRASILEIRO S.A.- PETROBRAS; BENSON, JOHN, EVERETT) 15 January 2004 (2004-01-15) cited in the application the whole document	1-9
Y	US 2002/092812 A1 (STAMIRES DENNIS ET AL) 18 July 2002 (2002-07-18) page 1, paragraph 7	1-9
Y	EP 0 278 535 A (AKZO N.V) 17 August 1988 (1988-08-17) the whole document	1-9
Y	US 5 389 240 A (GILLESPIE ET AL) 14 February 1995 (1995-02-14) cited in the application the whole document	1-9

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in 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
9 June 2005	17/06/2005

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	Cagnoli, M

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP2004/011361

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2004005434 A	15-01-2004	BR 0202552 A	25-05-2004
		AU 2003244845 A1	23-01-2004
		WO 2004005434 A1	15-01-2004
		US 2004026299 A1	12-02-2004
US 2002092812 A1	18-07-2002	AT 279375 T	15-10-2004
		BR 0207085 A	20-01-2004
		CA 2437604 A1	19-09-2002
		CN 1529677 A	15-09-2004
		DE 60201577 D1	18-11-2004
		WO 02072474 A1	19-09-2002
		EP 1358127 A1	05-11-2003
		ES 2229105 T3	16-04-2005
		JP 2004529839 T	30-09-2004
EP 0278535 A	17-08-1988	AT 60874 T	15-02-1991
		AU 609763 B2	09-05-1991
		AU 1021288 A	14-07-1988
		BR 8707099 A	02-08-1988
		CA 1314862 C	23-03-1993
		DE 3861771 D1	21-03-1991
		EP 0278535 A1	17-08-1988
		GR 3001934 T3	23-11-1992
		JP 2678276 B2	17-11-1997
		JP 63182031 A	27-07-1988
		US 4866019 A	12-09-1989
		US 4946581 A	07-08-1990
		US 4952382 A	28-08-1990
US 5389240 A	14-02-1995	NONE	