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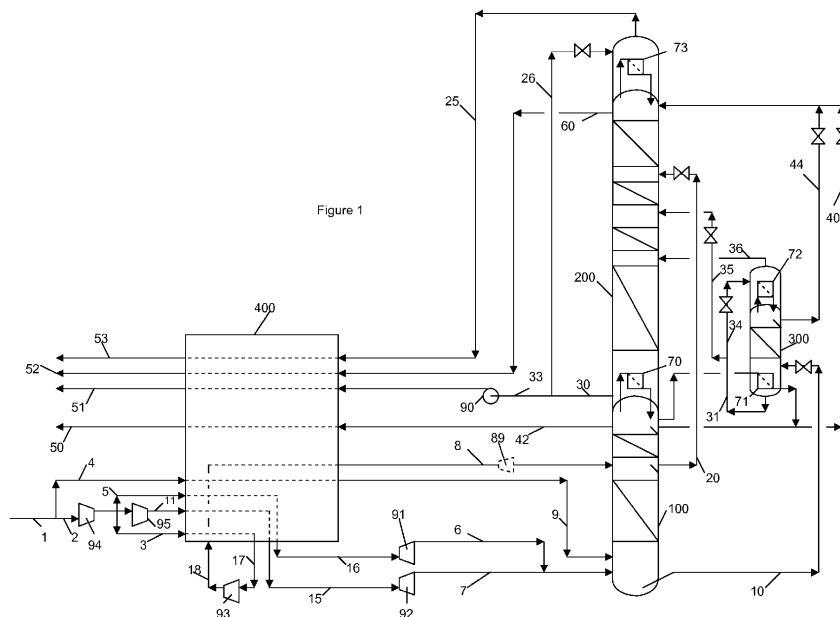
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(54) **Process and apparatus for the separation of air by cryogenic distillation**

(57) In a process for the separation of air by cryogenic distillation, purified air is cooled in a heat exchanger (400) and sent to a first column (100) of a column system operating at between 9 and 17 bars abs, oxygen rich liquid (30) is removed from the bottom of the second column, pressurized, vaporized in the heat exchanger and removed as a pressurized gaseous oxygen product (51), nitrogen rich fluid (42, 60) is removed from at least one column of the column system, warmed in the heat exchanger and removed as a gaseous nitrogen product (50),

52), the ratio between the gaseous nitrogen product and the pressurized gaseous oxygen product being greater than 3.6, oxygen rich liquid (26) is removed from the bottom of the second column, expanded and vaporized in a top condenser (73) of the second column to produce a waste stream (25, 53), nitrogen rich gas from the top of the second column is condensed in the top condenser and sent back to the second column and nitrogen rich gas from the top of the first column is condensed in a bottom vaporizer (70) of the second column and sent back at least in part to the first column.



Description

[0001] The present invention relates to a process and apparatus for the separation of air by cryogenic distillation.

[0002] An Integrated Gasified Combined Cycle is usually selected to generate clean energy from coal. This clean energy production technique is especially suited for new coal-based power generation projects specified to operate efficiently and with minimal pollution to the environment.

[0003] To gasify the coal for the IGCC, impure high pressure oxygen is used. In addition, nitrogen is generally required in a relatively pure state at quite high pressure in the combustion of the synthesis gas in the gas turbine to dilute the synthesis gas or hydrogen produced during the gasification process, so as to reduce the nitrous oxides (NOx) emission levels.

[0004] To produce oxygen for an IGCC plant, three well known techniques used in the context are:

- producing the oxygen in an independent ASU (air separation unit).
- taking air for the ASU from the gas turbine compressor.
- taking part of the air for the ASU from the gas turbine compressor and using a dedicated compressor to produce the rest.

[0005] The types of gasification or gas turbine would dictate the required quantity of nitrogen to be used in the IGCC complex. It can be seen from this characteristic that the air separation unit (ASU) for the IGCC is a combination of an oxygen plant and a nitrogen generator plant.

[0006] The air separation process frequently used for this type of application is the elevated pressure process. Although air separation units operating with this concept have good energy efficiency and reduced power consumption, it is not always possible to use this sort of ASU because the nitrogen/oxygen ratio is generally fixed at a value close to that found for air, ie close to 3.6. If the required ratio is higher than this value, for example about 5, then an elevated pressure plant would be required to use an excess air to generate the needed quantity of nitrogen and by doing so it will generate wastefully an excess of oxygen under pressure, which reduces the efficiency of the process. It can be seen that a different process cycle needs to be used in this situation to satisfy the requirement of nitrogen/oxygen ratio and at the same time yielding good cycle efficiency.

[0007] An object of the present invention is to provide an air separation unit with reduced energy consumption but which is capable of producing nitrogen and oxygen with a nitrogen/oxygen ratio of greater than 3.6, preferably greater than 4.

[0008] FR-A-2930328 describes an air separation process in which liquid oxygen is vaporized in the top

condenser of a low pressure column, which is heated using a double reboiler system.

[0009] According to an object of the invention, there is provided a process for the separation of air by cryogenic distillation wherein:

- i) purified air is cooled in a heat exchanger and sent to a first column of a column system operating at between 9 and 17 bars abs,
- ii) nitrogen enriched liquid from the first column is sent to a second column operating at a lower pressure than the first column,
- iii) oxygen enriched liquid from the first column or a liquid derived therefrom is sent to the second column,
- iv) oxygen rich liquid is removed from the bottom of the second column, pressurized, vaporized in the heat exchanger and removed as a pressurized gaseous oxygen product,
- v) nitrogen rich fluid is removed from at least one column of the column system, warmed in the heat exchanger and removed as a gaseous nitrogen product, the ratio between the gaseous nitrogen product and the pressurized gaseous oxygen product being greater than 3.6, preferably greater than 4,
- vi) oxygen rich liquid is removed from the bottom of the second column, expanded and vaporized in a top condenser of the second column to produce a waste stream and
- vii) nitrogen rich gas from the top of the second column is condensed in the top condenser and sent back to the second column and
- viii) nitrogen rich gas from the top of the first column is condensed in a bottom condenser of the second column and sent back at least in part to the first column.

[0010] According to further optional features:

- at least part of the feed air is cooled in the heat exchanger, removed from an intermediate point of the heat exchanger, compressed in a cold compressor, sent back to the heat exchanger, liquefied outside any column of the column system and sent to a column of the column system.
- the vaporization pressure of the oxygen rich liquid in the heat exchanger is greater than 30 bars abs.
- the vaporization pressure of the oxygen rich liquid in the heat exchanger is greater than 50 bars abs.
- the second column contains only a single vaporizer in the lower part of the column.
- all the oxygen rich liquid removed at the bottom of the second column is sent either to the top condenser or to the heat exchanger.
- the ratio between the gaseous nitrogen product and the pressurized gaseous oxygen product is greater than 4.
- the ratio between the gaseous nitrogen product and

the pressurized gaseous oxygen product is greater than 4.5.

[0011] According to a further object of the invention, there is provided an apparatus for the separation of air by cryogenic distillation comprising a column system having a first column of a column system operating at between 9 and 17 bars abs and at least a second column operating at a pressure lower than that of the first column, the second column having a top condenser and a bottom vaporizer, a heat exchanger for cooling purified air, a conduit for sending nitrogen enriched liquid from the first column to the second column, a conduit and possibly separation means for sending oxygen enriched liquid from the first column or a liquid derived therefrom to the second column, a pump for pressurizing oxygen rich liquid removed from the bottom of the second column, a conduit for sending pressurized oxygen rich liquid to be vaporized in the heat exchanger, a conduit for removing vaporized pressurized oxygen rich liquid as a pressurized gaseous oxygen product, a conduit for removing nitrogen rich fluid from at least one column of the column system and for sending the nitrogen rich fluid to be warmed in the heat exchanger and removed as a gaseous nitrogen product, the ratio between the gaseous nitrogen product and the pressurized gaseous oxygen product being greater than 3.6, preferably greater than 4, a conduit for removing oxygen rich liquid from the bottom of the second column, means for expanding the oxygen rich liquid and a conduit for sending the expanded oxygen rich liquid to be vaporized in the top condenser of the second column to produce a waste stream, a conduit for sending nitrogen rich gas condensed in the top condenser to the second column, a conduit for sending nitrogen rich gas from the top of the first column to be condensed in the bottom condenser of the second column and a conduit for sending the condensed nitrogen rich gas from the bottom vaporizer at least in part to the first column.

[0012] Other optional features include:

- the apparatus comprises a compressor, a conduit for removing at least part of the feed air from an intermediate point of the heat exchanger and sending it to the compressor and a conduit for sending the air compressed in the compressor back to the heat exchanger.
- the second column contains only a single condenser in the lower part of the column.
- the apparatus comprises means for dividing the oxygen rich liquid into only two parts, one part being sent to the top condenser and the other to the heat exchanger.
- the apparatus comprises means for dividing the oxygen rich liquid into only three parts, one part being sent to the top condenser, another to the heat exchanger and another serving as a liquid oxygen product.

[0013] The invention will be described with respect to figure 1 which shows a process according to the invention.

[0014] All pressures in this document are absolute pressures.

[0015] An oxygen enriched fluid contains at least 30% mol. oxygen and an oxygen rich fluid contains at least 80% mol oxygen.

[0016] A nitrogen enriched fluid contains at least 85% nitrogen and a nitrogen rich fluid contains at least 90% mol. nitrogen.

[0017] Figure 1 shows a double column having a first column 100 operating at between 12 and 17 bars abs and a second column 200 operating at between 4.2 and 6.3 bars abs. The reboiler 70 at the bottom of the second column is warmed using nitrogen rich gas from the top of the first column in order to vaporize the bottom liquid of the second column 200.

[0018] Air is cooled using a brazed aluminum plate fin heat exchanger 400.

[0019] In the case where the ratio of nitrogen/oxygen is required to be above 3.6, or above 4, or above 4.5, surplus oxygen is produced.

[0020] As shown in the figure, 1000 Nm³/h of air 1 at 15.8 bars are produced by a main compressor and the air is purified by a front end purification unit (not shown). The purified air 1 is divided into two parts 2, 4. Part 2 (502 Nm³/h) is compressed to 44 bars in a booster 94 and divided into three fractions 3, 5, 11. Fraction 3 is cooled in the heat exchanger to an intermediate temperature T1 of the heat exchanger, removed as stream 17, compressed to 69 bars in cold compressor 93, sent back to the heat exchanger as stream 18 at an intermediate temperature T2 and cooled up to the cold end of the heat exchanger 400. The cold compressed air is removed as stream 8 from the heat exchanger and is then expanded in a dense fluid expander 89 or a valve and sent to the first column 100 and possibly to the second column 200. Fraction 5 of the air is cooled in the heat exchanger at the outlet pressure of booster 94 to a temperature T3 colder than T1, removed as stream 16 and expanded in a turbine 91 to form expanded stream 6 before being sent to the first column 100 in gaseous form. Fraction 11 is boosted in a booster 95, cooled in the heat exchanger 400, removed as stream 15 to a temperature T4 colder than T1 and sent to turbine 92 to produce expanded stream 7 and thence to first column 100.

[0021] Part 4 of the air from the main compressor is cooled at the pressure of the first column in heat exchanger 100 and introduced as stream 9 into the first column 100 in gaseous form.

[0022] Turbine 91 is preferably coupled to compressor 93 and turbine 92 is preferably coupled to compressor 95.

[0023] Oxygen enriched liquid 10 from the bottom of the first column 100 is expanded in valve and sent to a third column 300 operating at a pressure between the pressure of the first column and the pressure of the second column 200. The oxygen enriched liquid is separated

in the third column forming a bottom liquid further enriched in oxygen 31. Part of this liquid is sent as stream 34 to the top condenser 72 of the third column 300 after expansion in a valve. The vaporized liquid 36 is then sent to the second column 200. The rest 35 is expanded in a valve and sent to the second column 200.

[0024] An intermediate liquid stream 20 is removed from the first column 100, expanded and sent to the second column 200.

[0025] Nitrogen enriched liquid 40 from the top of the first column is expanded in a valve and sent to the top of the second column 200.

[0026] Nitrogen enriched gas from the top of the first column is used to heat bottom reboiler 71 of the third column 300. The liquid produced is sent in part back to the top of the first column 100 and in part as part of stream 40 to the top of the second column.

[0027] Nitrogen enriched liquid 44 from the top of the third column 300 is expanded and sent to the top of the second column 200.

[0028] Oxygen rich liquid 30 containing at least 80% oxygen is removed from the bottom of the second column 200, pressurized in pump 90 and sent as liquid to the heat exchanger 400 where it vaporizes to form 217 Nm³/h of pressurized oxygen rich gas 51 containing 95% oxygen at 67 bars.

[0029] Nitrogen rich gas 60 from the top of the second column 200 is warmed in heat exchanger and removed as 713 Nm³/h of gas 52 at 5 bars abs.

[0030] Nitrogen rich gas 42 containing at least 85% nitrogen is removed from the top of the first column 100, warmed in exchanger 400 and removed as 70 Nm³/h of nitrogen rich gas 50 at 15 bars abs. The ratio between nitrogen rich gas (50 and 51) and the oxygen rich gas (51) is in the region of 3.6.

[0031] To produce a higher nitrogen/oxygen ratio, the solution according to the invention is to vaporize part of the oxygen from the bottom of the second column 100 in a top condenser 73 of the second column 200. Part 26 of oxygen rich liquid 30 is taken at the pressure of the second column 200, divided from stream 30, expanded to just above atmospheric pressure in a valve and sent to the top condenser 73 wherein it is vaporized to form a waste gas 25, warmed in heat exchanger 400 to form waste stream 53.

[0032] Nitrogen rich gas from the top of the second column 200 is condensed in the top condenser 73.

[0033] A nitrogen rich gaseous stream 60 is removed from the top of the second column, warmed in heat exchanger 400 to form stream 52.

[0034] The figure shows a triple column but the invention applies equally to a double column process in which the oxygen enriched liquid 10 is sent directly from the first to the second column.

Claims

1. Process for the separation of air by cryogenic distillation wherein:

- i) purified air is cooled in a heat exchanger (400) and sent to a first column (100) of a column system operating at between 9 and 17 bars abs,
- ii) nitrogen enriched liquid (20, 40) from the first column is sent to a second column (200) operating at a lower pressure than the first column,
- iii) oxygen enriched liquid (10) from the first column or a liquid derived therefrom is sent to the second column,
- iv) oxygen rich liquid (30) is removed from the bottom of the second column, pressurized, vaporized in the heat exchanger and removed as a pressurized gaseous oxygen product (51),
- v) nitrogen rich fluid (42, 60) is removed from at least one column of the column system, warmed in the heat exchanger and removed as a gaseous nitrogen product (50, 52), the ratio between the gaseous nitrogen product and the pressurized gaseous oxygen product being greater than 3.6, preferably greater than 4,
- vi) oxygen rich liquid (26) is removed from the bottom of the second column, expanded and vaporized in a top condenser (73) of the second column to produce a waste stream (25, 53),
- vii) nitrogen rich gas from the top of the second column is condensed in the top condenser and sent back to the second column and
- viii) nitrogen rich gas from the top of the first column is condensed in a bottom vaporizer (70) of the second column and sent back at least in part to the first column.

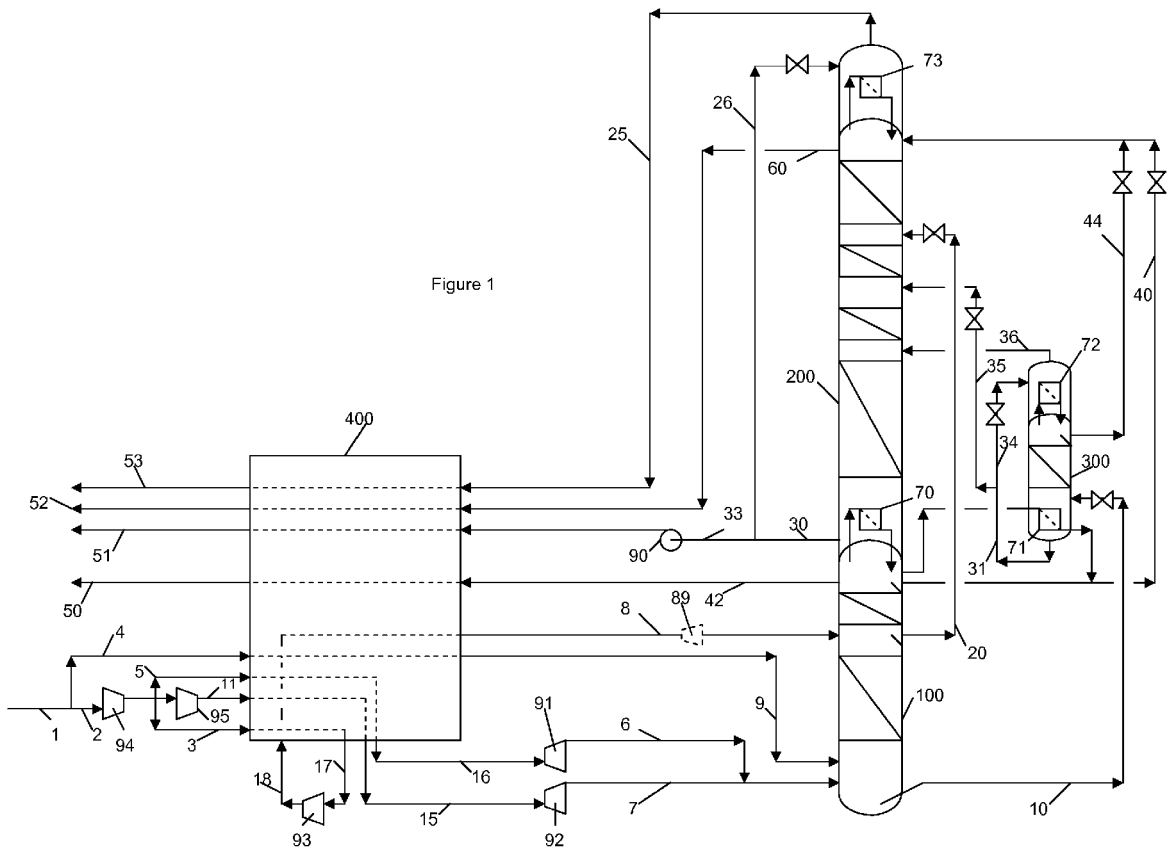
2. Process according to claim 1 wherein at least part of the feed air is cooled in the heat exchanger (400), removed from an intermediate point of the heat exchanger, compressed in a cold compressor (93), sent back to the heat exchanger, liquefied outside any column of the column system and sent to a column of the column system.

3. Process according to any preceding claim wherein the vaporization pressure of the oxygen rich liquid (33) in the heat exchanger is greater than 30 bars abs.

4. Process according to Claim 3 wherein the vaporization pressure of the oxygen rich liquid (33) in the heat exchanger is greater than 50 bars abs.

5. Process according to any preceding claim wherein the second column contains only a single vaporizer (70) in the lower part of the column.

6. Process according to any preceding claim wherein all the oxygen rich liquid (30) removed at the bottom of the second column is sent either to the top condenser (73) or to the heat exchanger (400).
7. Process according to any preceding claims wherein the ratio between the gaseous nitrogen product (50, 52) and the pressurized gaseous oxygen product (51) is greater than 4.
8. Process according to any preceding claims wherein the ratio between the gaseous nitrogen product (50, 52) and the pressurized gaseous oxygen product (51) is greater than 4.5.
9. Apparatus for the separation of air by cryogenic distillation comprising a column system having a first column (100) of a column system operating at between 9 and 17 bars abs and at least a second column (200) operating at a pressure lower than that of the first column, the second column having a top condenser (73) and a bottom vaporizer (70), a heat exchanger (400) for cooling purified air, a conduit for sending nitrogen enriched liquid from the first column to the second column, a conduit and possibly separation means for sending oxygen enriched liquid from the first column or a liquid derived therefrom to the second column, a pump (90) for pressurizing oxygen rich liquid removed from the bottom of the second column, a conduit for sending pressurized oxygen rich liquid to be vaporized in the heat exchanger, a conduit for removing vaporized pressurized oxygen rich liquid as a pressurized gaseous oxygen product, a conduit for removing nitrogen rich fluid from at least one column of the column system and for sending the nitrogen rich fluid to be warmed in the heat exchanger and removed as a gaseous nitrogen product, the ratio between the gaseous nitrogen product and the pressurized gaseous oxygen product being greater than 3.6, preferably greater than 4, a conduit for removing oxygen rich liquid from the bottom of the second column, means for expanding the oxygen rich liquid and a conduit for sending the expanded oxygen rich liquid to be vaporized in the top condenser of the second column to produce a waste stream, a conduit for sending nitrogen rich gas condensed in the top condenser to the second column, a conduit for sending nitrogen rich gas from the top of the first column to be condensed in the bottom condenser of the second column and a conduit for sending the condensed nitrogen rich gas from the bottom vaporizer at least in part to the first column.
10. Apparatus according to claim 9 comprising a compressor (93), a conduit for removing at least part of the feed air from an intermediate point of the heat exchanger (400) and sending it to the compressor
- and a conduit for sending the air compressed in the compressor back to the heat exchanger.
11. Apparatus according to Claim 9 or 10 wherein the second column (200) contains only a single vaporizer (70) in the lower part of the column.
12. Apparatus according to Claim 9, 10 or 11 comprising means for dividing the oxygen rich liquid into only two parts, one part being sent to the top condenser (73) and the other to the heat exchanger (400).
13. Apparatus according to Claim 9, 10 or 11 comprising means for dividing the oxygen rich liquid into only three parts, one part being sent to the top condenser (73), another to the heat exchanger (400) and another serving as a liquid oxygen product.





EUROPEAN SEARCH REPORT

Application Number
EP 12 30 5506

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 6 116 052 A (HA BAO [US] ET AL) 12 September 2000 (2000-09-12)	1,3-9, 11-13	INV. F25J3/04
Y	* column 4, lines 63-65; figure 4 * * column 6, line 64 - column 7, line 9 *	2,10	
Y	US 5 901 576 A (AGRAWAL RAKESH [US] ET AL) 11 May 1999 (1999-05-11) * figure 6 *	2,10	
Y	US 6 196 023 B1 (CORDUAN HORST [DE] ET AL) 6 March 2001 (2001-03-06) * column 1, line 61 - column 2, line 4 * * column 5, lines 58-62; figure 6 * * column 7, lines 5-8 *	1-13	
Y	EP 0 955 509 A1 (LINDE AG [DE]) 10 November 1999 (1999-11-10) * paragraphs [0008], [0012], [0029]; figure 2 *	1-13	
Y	FR 2 864 213 A1 (AIR LIQUIDE [FR]) 24 June 2005 (2005-06-24) * page 4, lines 3-10; figure * * page 5, lines 1-10 *	2,10	
A	EP 0 924 486 A2 (BOC GROUP PLC [GB]) 23 June 1999 (1999-06-23) * figures 1,3 *	1,9	F25J
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 16 October 2012	Examiner Göritz, Dirk
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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EPO FORM 1503 03 82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 12 30 5506

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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16-10-2012

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 6116052	A	12-09-2000	CA 2303664 A1	09-10-2000
			EP 1043556 A1	11-10-2000
			JP 2000310481 A	07-11-2000
			US 6116052 A	12-09-2000

US 5901576	A	11-05-1999	CA 2259060 A1	22-07-1999
			CN 1233740 A	03-11-1999
			EP 0932002 A2	28-07-1999
			JP 11257845 A	24-09-1999
			US 5901576 A	11-05-1999
			ZA 9900397 A	20-07-2000

US 6196023	B1	06-03-2001	CA 2277838 A1	07-05-1998
			CN 1235666 A	17-11-1999
			DE 19735154 A1	07-05-1998
			DE 59702301 D1	05-10-2000
			DK 948730 T3	16-10-2000
			EP 0948730 A1	13-10-1999
			ES 2150291 T3	16-11-2000
			JP 2001509246 A	10-07-2001
			KR 20000052974 A	25-08-2000
			PT 948730 E	29-12-2000
			US 6196023 B1	06-03-2001
			WO 9819122 A1	07-05-1998

EP 0955509	A1	10-11-1999	EP 0955509 A1	10-11-1999
			JP 4450886 B2	14-04-2010
			JP 11351738 A	24-12-1999
			US 6196022 B1	06-03-2001

FR 2864213	A1	24-06-2005	NONE	

EP 0924486	A2	23-06-1999	EP 0924486 A2	23-06-1999
			TW 469152 B	21-12-2001
			US 6141989 A	07-11-2000

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- FR 2930328 A [0008]