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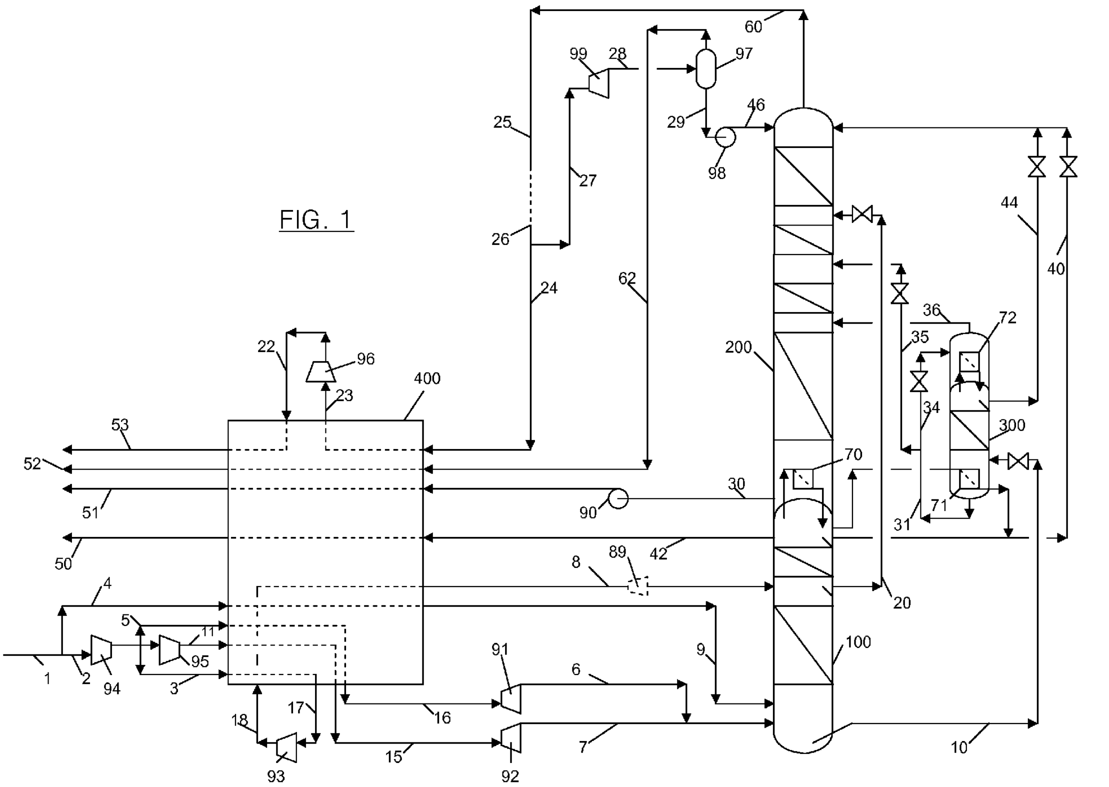
(54) **Process and apparatus for the separation of air by cryogenic distillation**

(57) In a process for the separation of air by cryogenic distillation in a triple column (100, 200, 300), the ratio between the amount of nitrogen rich gas produced and the amount of oxygen rich gas produced, is less than 3 or even less than 2.5 and a second nitrogen rich gas removed from the column system is expanded in a turboexpander (99) having an inlet temperature lower than the ambient temperature, the turboexpander being driven by a cold compressor (96).

FIG. 1



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Description

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

[0002] The Integrated Gasifier 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 ie with a low pressure operating at at least 2 bars abs, preferably at least 3 bars abs.

[0007] 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 it is necessary to reach this high efficiency that the nitrogen/oxygen ratio is very close to that found for air, ie close to 3.6. If the required ratio is lower than this value, for example about 2.5, the power consumption of such a plant is higher that in the case of a conventional "low pressure" process because part of the elevated pressure nitrogen product is not fully utilized and either must be vented or depressurized.

[0008] It is known from EP-A-0518491 to take nitrogen from a low pressure column and expand it at a low temperature to produce liquid nitrogen. If liquid nitrogen is not required then this approach cannot be used.

[0009] 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 3.6 or less, preferably less than 2.9.

[0010] Since nitrogen or oxygen can be extracted from one or several columns of the process, the nitrogen/oxygen ratio is defined as the total of nitrogen flow divided by the total of oxygen flow.

[0011] According to an object of the invention, there is provided a process for the separation of air by cryogenic distillation in which air is purified, cooled in a heat exchanger and separated in a column system including at least a first column, a second column and a third column, the first column operating at a higher pressure than the second column, the second column operating at at least 2 bars abs, preferably at at least 4 bars abs, the third column operating at a pressure intermediate to the pressures of first and second columns and the top of the first column being thermally linked to the bottom of the second column via a first reboiler-condenser, oxygen enriched liquid is removed from the first column and sent to the third column, oxygen enriched liquid from the bottom of the third column is sent to the second column, nitrogen enriched liquid from the top of the third column is sent to the second column, nitrogen enriched liquid is removed from the first column and sent to the second column, oxygen rich liquid is removed from the second column, pressurized and vaporized in the heat exchanger to form an oxygen rich gas, nitrogen rich fluid is removed from the column system and warmed in the heat exchanger to form a first nitrogen rich gas, wherein the product ratio, being the ratio between the amount of nitrogen rich gas produced and the amount of oxygen rich gas produced, is less than 3.6 or even less than 2.5 and a second nitrogen rich gas removed from the second column is expanded in a turboexpander having an inlet/outlet pressure ratio of at least 2, or even at least 3, said turboexpander having an inlet temperature lower than the ambient temperature.

[0012] According to further optional aspects of the invention

- a nitrogen rich gas removed from the column system or an air stream is compressed in a compressor driven by the turboexpander and having an inlet temperature less than -20°C.
- the nitrogen rich gas is removed from the second column and divided in two, one part being sent to the compressor and the other part being expanded in the turboexpander.
- the nitrogen rich gas is expanded in the turboexpander without having been warmed.
- the product ratio is less than 2.
- the turboexpander has an inlet temperature of at most -50°C, preferably of at most -100°C.
- during the second period, the outlet pressure of the turboexpander is substantially equal to the pressure of the second column.
- gas from the phase separator is sent to the heat exchanger.
- the compressor is driven by the turboexpander.

- nitrogen enriched liquid is sent to a phase separator from the outlet of the turboexpander and gas is removed from the phase separator.
- liquid from the phase separator is sent back to the column system to be separated.

[0013] According to a further aspect of the invention, there is provided an apparatus for the separation of air by cryogenic distillation comprising column system including at least a first column, a second column and a third column, the first column operating at a higher pressure than the second column" the third column operating at a pressure between that of the first column and that of the second column, the second column operating at least 2 bars abs and the top of the first column being thermally linked to the bottom of the second column via a first reboiler-condenser, a heat exchanger, a compressor, a turboexpander, purification means for purifying air, means for sending purified air to the heat exchanger to be cooled, means for sending cooled purified air to the first column, a conduit for sending an oxygen enriched liquid from the first column to the third column, a conduit for sending oxygen enriched liquid from the bottom of the third column to the second column , a conduit for sending nitrogen enriched liquid from the top of the third column to the second column, a conduit for removing nitrogen enriched liquid from the first column and sending it to the second column, a conduit for removing oxygen rich liquid from the second column, to be pressurized and vaporized in the heat exchanger to form an oxygen rich gas, a conduit for removing nitrogen rich fluid from the column system to be warmed in the heat exchanger to form a first nitrogen rich gas, wherein the product ratio, being the ratio between the amount of nitrogen rich gas produced and the amount of oxygen rich gas produced, is less than 3.6, less than 3 or even less than 2.5 and a conduit for removing a second nitrogen rich gas and sending it to the turboexpander having an inlet temperature lower than the ambient temperature and upstream of the heat exchanger, a phase separator, a conduit for sending nitrogen enriched liquid to the phase separator from the outlet of the turboexpander and a conduit for removing nitrogen enriched gas from the phase separator,

[0014] According to further optional features, the apparatus may comprise:

- means for sending nitrogen enriched gas to the compressor, the nitrogen enriched gas being removed either directly from the column system or after warming in the heat exchanger, the compressor being coupled to the turboexpander.
- pressurizing means for pressurizing the nitrogen enriched liquid and a conduit for sending the pressurized nitrogen enriched liquid to the column system.

[0015] The invention will be described in greater detail with reference to Figure 1 which represents a process according to the invention.

[0016] In Figure 1, a cryogenic air separation process using a standard double column equipped with an intermediate column 300, having a first column 100 operating at between 12 and 17 bars abs and a second column 200 operating at between 4 and 6 bars abs, the first column operating at a higher pressure than the second column and being placed below the second column. The top of the first column 11 is thermally linked to the bottom of the second column 15 by means of a vaporizer-condenser 70. The intermediate column 300 operates at a pressure between the pressures of columns 100 and 200.

[0017] When the process is in operation, an air stream 1 of 1000 Nm^3/h at 15.8 bars (ie compressed to the operating pressure of the first column 100) is divided into two parts. One part 4 is cooled in heat exchanger 400 and sent in gaseous form to the first column 100. The other part 2 (400 Nm^3/h) is boosted to a higher pressure of 44 bars abs by booster compressor 94 and sent to the heat exchanger 400. One part 3 of the boosted air at 44 bars abs is cooled to an intermediate temperature of the heat exchanger 400, removed from the heat exchanger, compressed in cold compressor 93, cooled and expanded and sent as a liquid stream to column 100. Another part 5 of the boosted air cooled to an intermediate temperature of the heat exchanger 400, expanded in turboexpander 91 as stream 16 and sent to column 100 in gaseous form. The other part 12 is further boosted in booster 95, cooled in the heat exchanger 400, to an intermediate temperature thereof, expanded in turboexpander 92 as stream 15 and sent to the first column 100 after expansion in gaseous form.

[0018] The inlet temperature of the cold compressor 93 is warmer than the inlet temperature of turboexpanders 91, 92.

[0019] Oxygen enriched liquid 10 from the bottom of the first column 100 is expanded in a 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.

[0020] An intermediate liquid stream 20 is removed from the first column 100, expanded and sent to the second column 200.

[0021] 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.

[0022] 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.

[0023] Nitrogen enriched liquid 44 from the top of the third column 300 is expanded and sent to the top of the second column 200.

[0024] The column system produces a high pressure gaseous oxygen stream 51 by removing liquid oxygen 30 containing at least 80% mol oxygen (in this example 210 Nm^3/h oxygen at 95% mol oxygen) from the bottom of second column 200, pressurizing it via pump 90 and vaporizing the pumped liquid in exchanger 400. This produces a stream at 67 bars abs.

[0025] The column system produces a gaseous nitrogen stream 50 at 15.35 bars abs by removing gaseous nitrogen 42 from the top of column 100 and warming it in exchanger 400.

[0026] Nitrogen rich gas 60 from the top of the second column 200 is warmed in a heat exchanger (not shown) to yield stream 26, a portion 27 is expanded in turboexpander 99 to low pressure close to atmospheric pressure to yield stream 28, which can be partially liquefied, then sent to phase separator 97. The remaining portion 24 of stream 26 is warmed in exchanger 400,to an intermediate temperature and sent as stream 23 to a cold compressor 96, which compresses the nitrogen rich gas to higher pressure as stream 22. The compressed nitrogen rich gas is removed as nitrogen product 53 at about 5 bars abs. The vapor stream 62 from separator 97 is warmed in exchanger 400 and exits the process as a waste or vented low pressure nitrogen 52. The liquid fraction 29 (if it exists) can be pumped by pump 98 and sent to the top of column 200 as additional reflux. The energy generated by expander 99 can be used to drive the compressor 96.

[0027] Stream 51 may be sent to a gasifier.

[0028] The ratio between the amount of nitrogen rich gas produced (total of 50 and 53) and the amount of oxygen rich gas 51 produced (known as the "product ratio"), is less than 3, less than 2.5, or even less than 2, The combination of the turboexpander 99 for expansion of the excess nitrogen and the cold nitrogen compressor allows the produced nitrogen pressure to be increased. This can reduce the number of nitrogen compressor stages required if the product nitrogen is to be compressed to a higher pressure. By adjusting the expanded flow in expander 99 the flow and pressure of the nitrogen product portion 53 can be adapted to satisfy the required nitrogen/oxygen ratio. The process efficiency can be maintained by recovering the energy of the expander 99 to drive the compressor 96 to increase the product pressure of stream 53.

[0029] Either the cold nitrogen compressor 96 or the cold air compressor 93 must be present, but not necessarily both.

[0030] The invention could in theory also be applied to a double column without any intermediate pressure column, however to produce low purity oxygen at around 95% purity, the low pressure column would need to operate at around 2 to 2.5 bars. In this case, the nitrogen expander ratio would be very low (from 1.5 to 1.9) and so power recovery would not be optimal.

[0031] The present invention is consequently reduced to the triple column case where the low pressure column operates at at least 4 bars abs, so as to have a nitrogen expansion ratio which is higher than in the double column case and therefore more suitable for power recovery.

Claims

1. Process for the separation of air by cryogenic distillation in which air is purified, cooled in a heat exchanger (400) and separated in a column system including at least a first column (100), a second column (200) and a third column (300), the first column operating at a higher pressure than the second column, the second column operating at at least 2 bars abs, preferably at at least 4 bars abs, the third column operating at a pressure intermediate to the pressures of first and second columns and the top of the first column being thermally linked to the bottom of the second column via a first reboiler-condenser (70), oxygen enriched liquid (10) is removed from the first column and sent to the third column, oxygen enriched liquid (31) from the bottom of the third column is sent to the second column, nitrogen enriched liquid (44) from the top of the third column is sent to the second column, nitrogen enriched liquid (20) is removed from the first column and sent to the second column, oxygen rich liquid (30) is removed from the second column, pressurized and vaporized in the heat exchanger to form an oxygen rich gas, nitrogen rich fluid (24) is removed from the column system and warmed in the heat exchanger to form a first nitrogen rich gas, wherein the product ratio, being the ratio between the amount of nitrogen rich gas produced (50, 52, 53) and the amount of oxygen rich gas (51) produced, is less than 3.6 or even less than 2.5 and a second nitrogen rich gas (27) removed from the second column is expanded in a turboexpander (99) having an inlet/outlet pressure ratio of at least 2, or even at least 3, said turboexpander having an inlet temperature lower than the ambient temperature.

2. Process according to Claim 1 wherein a nitrogen rich gas removed from the column system or an air stream is compressed in a compressor (96) driven by the turboexpander (99) and having an inlet temperature less than -20°C.

3. Process according to Claim 2 wherein the nitrogen rich gas (60) is removed from the second column and divided in two, one part (24) being sent to the compressor (96) and the other part (27) being expanded in the turboexpander (99).

4. Process according to any preceding claim wherein the nitrogen rich gas is expanded in the turboexpander (99) without having been warmed.

5. Process according to any preceding claim wherein the product ratio is less than 2.

6. Process according to any preceding claim wherein the turboexpander (99) has an inlet temperature of at most -50°C, preferably of at most -100°C.

7. Process according to any preceding claim wherein during the second period, the outlet pressure of the turboexpander (99) is substantially equal to the pressure of the second column.

8. Process according to any preceding claim wherein gas is sent from the turboexpander (99) to a phase separator (97) and gas from the phase separator (97) is sent to the heat exchanger.

9. Process according to any preceding claim wherein the compressor is driven by the turboexpander.

10. Process according to any preceding claim wherein nitrogen enriched liquid is sent to a phase separator (97) from the outlet of the turboexpander and gas (62) is removed from the phase separator.

11. Process according to Claim 10 wherein liquid (29, 46) from the phase separator (97) is sent back to the column system to be separated.

12. Apparatus for the separation of air by cryogenic distillation comprising column system including at least a first column (100), a second column (200) and a third column (300), the first column operating at a higher pressure than the second column" the third column operating at a pressure between that of the first column and that of the second column, the second column operating at least 2 bars abs and the top of the first column being thermally linked to the bottom of the second column via a first reboiler-condenser (70), a heat exchanger (400), a compressor (96), a turboexpander (99), purification means for purifying air, means for sending purified air to the heat exchanger to be cooled, means for sending cooled purified air to the first column, a conduit for sending an oxygen enriched liquid from the first column to the third column, a conduit for sending oxygen enriched liquid from the bottom of the third column to the second column , a conduit for sending nitrogen enriched liquid from the top of the third column to the second column, a conduit for removing nitrogen enriched liquid from the first column and sending it to the second column, a conduit for removing oxygen rich liquid from the second column, to be pressurized and vaporized in the heat exchanger to form an oxygen rich gas, a conduit for removing nitrogen rich fluid from the column system to be warmed in the heat exchanger to form a first nitrogen rich gas, wherein the product ratio, being the ratio between the amount of nitrogen rich gas produced and the amount of oxygen rich gas produced, is less than 3.6, less than 3 or even less than 2.5 and a conduit for removing a second nitrogen rich gas and sending it to the turboexpander having an inlet temperature lower than the ambient temperature and upstream of the heat exchanger, a phase separator, a conduit for sending nitrogen enriched liquid to the phase separator from the outlet of the turboexpander and a conduit for removing nitrogen enriched gas from the phase separator.

13. Apparatus according to Claim 13 comprising means for sending nitrogen enriched gas to the compressor (96), the nitrogen enriched gas being removed either directly from the column system or after warming in the heat exchanger, the compressor being coupled to the turboexpander (99).

14. Apparatus according to Claim 13 or 14 comprising pressurizing means (98) for pressurizing the nitrogen enriched liquid from the phase separator (97) and a conduit for sending the pressurized nitrogen enriched liquid to the column system.

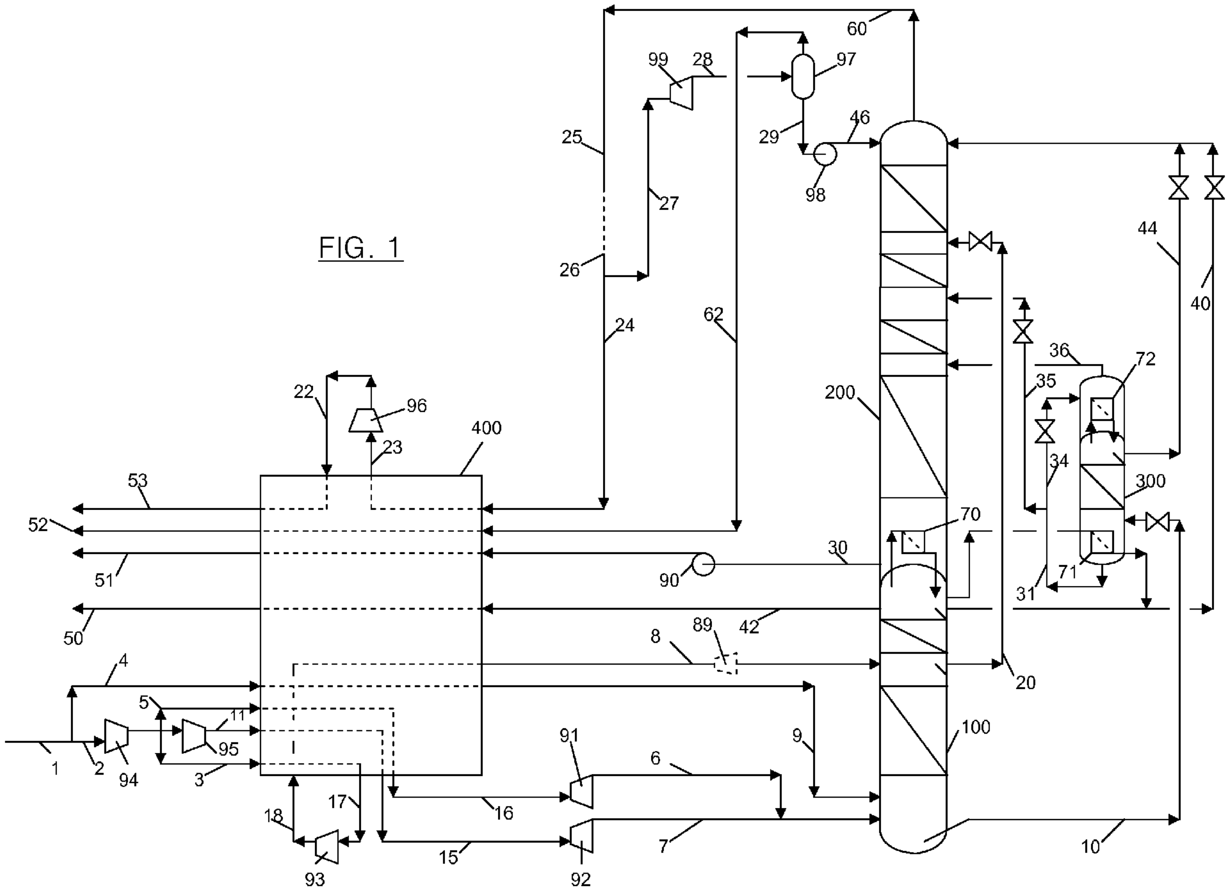
FIG. 1
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EUROPEAN SEARCH REPORT

Application Number
EP 12 30 6527

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 Y	FR 2 819 046 A1 (AIR LIQUIDE [FR]) 5 July 2002 (2002-07-05) * page 2, lines 14-20; figure 2 * * page 3, lines 4-10 * * page 5, lines 9-12 * * page 5, line 34 - page 6, line 7 * -----	1-6,9 7,8, 10-14	INV. F25J3/04
X Y	US 6 286 336 B1 (PROSSER NEIL MARK [US]) 11 September 2001 (2001-09-11) * column 4, lines 40-42 * * column 5, line 19 - column 6, line 26; claims 6,8,9,17; figures 2,3 * -----	1-6,9 7,8, 10-14	
Y	FR 2 686 405 A1 (AIR LIQUIDE [FR]) 23 July 1993 (1993-07-23) * page 4, line 11 - page 5, line 8; figure 2 * -----	8,10-14	
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TECHNICAL FIELDS SEARCHED (IPC)

F25J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	19 June 2013	Göritz, Dirk

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EPO FORM 1503 03.82 (P04C01)

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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