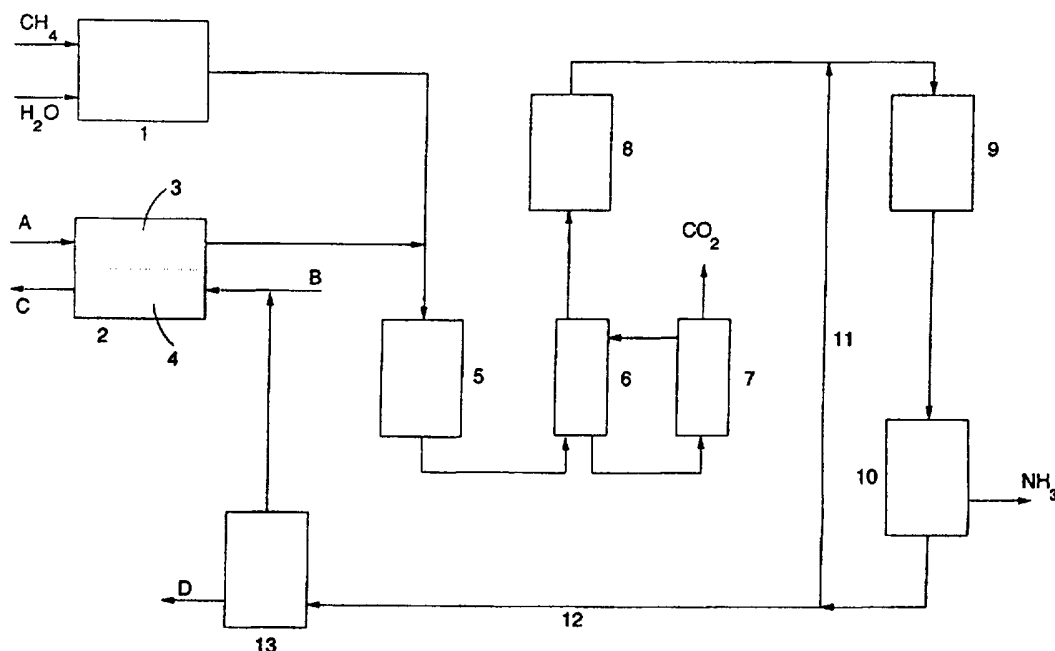




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/NL97/00127 <b>(22) International Filing Date:</b> 12 March 1997 (12.03.97) <b>(30) Priority Data:</b> 1002582                      12 March 1996 (12.03.96)                      NL <b>(71) Applicant (for all designated States except US):</b> TECHNISCHE UNIVERSITEIT DELFT [NL/NL]; Julianalaan 134, NL-2628 BL Delft (NL). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> DIKEMA, Gerhard, Pieter, Jan [NL/NL]; Eemwijkstraat 20, NL-2271 RE Voorburg (NL). <b>(74) Agent:</b> ALTENBURG, Bernardus, Stephanus, Franciscus; Octrooibureau Los en Stigter B.V., Weteringschans 96, NL-1017 XS Amsterdam (NL).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>In English translation (filed in Dutch).</i>

**(54) Title:** METHOD FOR THE MANUFACTURE OF AMMONIA**(57) Abstract**

The invention relates to a method for the production of ammonia, wherein a hydrogen-comprising discharge flow is utilized for the depletion of oxygen in air. Subsequently the oxygen-depleted air is - as nitrogen-comprising flow - brought into contact with water gas, which is the hydrogen - comprising flow. Oxygen depletion is carried out with the aid of a fuel cell installation (2). The method according to the invention is energy-saving.

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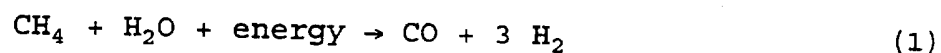
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## Method for the manufacture of ammonia

The present invention relates to a method for the production of ammonia, wherein a nitrogen-comprising flow is brought together with a hydrogen-comprising flow and nitrogen and hydrogen are catalytically reacted.

5        Such a method is generally known in the field. For the preparation of the hydrogen-comprising flow, so-called water gas is produced by reacting a carbon source, such as methane, with water at an elevated temperature and pressure.

10



The water gas is the hydrogen-comprising flow. The nitrogen-comprising flow is applied in the form of air which, however, first has to be stripped to a considerable extent of oxygen. This is done by deliberately retaining  $\text{CH}_4$  in the water gas, known as the methane slip, in the amount necessary to remove all oxygen from the supplied air by selective, catalytic oxidation under increased pressure.

20    Sub-sequently a CO-shift reaction is carried out, in which CO is converted into  $\text{CO}_2$  which is removed, yielding a mixture (synthesis gas) which is rich in nitrogen and hydrogen in a for the production of ammonia stoichiometric ratio. After the conversion of remaining CO traces into methane

25    (methanization), the mixture is further compressed and reacted at 450-600°C, yielding ammonia. The measure of conversion is limited. Non-reacted nitrogen and hydrogen are fed back. The accumulation of non-reactants such as inert gasses and methane requires these to be discharged in the

30    form of a hydrogen-comprising discharge flow or to remove them from the synthesis gas by means of further treatment. The energy content of this hydrogen-comprising discharge flow is utilized by, for instance, combustion.

It is the object of the present invention to improve the method according to the preamble. A particular object is to improve the energy efficiency. An additional object

35

is to provide a method by which the capacity of an existing plant for the production of synthesis gas can be expanded, or how, when building a new plant of a certain capacity, a smaller installation can be made to suffice.

5 To this end the method according to the invention is characterized in that the nitrogen-comprising flow is obtained by means of a fuel cell installation having a cathode and an anode, by feeding air to the cathode and a fuel-containing flow to the anode, resulting at the cathode  
10 in oxygen-depleted air and at the anode in a fuel-depleted flow, after which the oxygen-depleted air as the nitrogen-comprising flow is combined with the hydrogen-comprising flow and the oxygen present in the oxygen-depleted air is used for the catalytic conversion of a hydrocarbon present  
15 in the hydrogen-comprising flow.

As a result of oxygen-depleted air being fed to the hydrogen-comprising flow, the amount of hydrocarbon (usually methane) in the water gas required for the removal of oxygen may be reduced. This means that reaction (1) can  
20 be carried out at elevated temperature. Because the amount of methane in the water gas is decreased, a gas mixture is provided having less volume, a lower concentration of CO and CO<sub>2</sub>, and a higher concentration of H<sub>2</sub> and N<sub>2</sub>. Energy is saved through the fact that for the removal of oxygen by  
25 selective oxidation of methane and later for the ammonia production less air or rather, according to the invention, oxygen-depleted air has to be brought up to an increased pressure and temperature.

US 4,578,214 discloses a method for the production  
30 of ammonia using a fuel cell. Herein a flow coming from a secondary reformer is subjected to a catalytic shift reaction yielding a hydrogen-comprising flow. According to the method known from this US patent specification, oxygen depletion of air takes place with the aid of a fuel cell,  
35 while the fuel is supplied by an offshoot of the hydrogen-comprising flow. The oxygen-depleted air is subsequently fed to a unit for the complete removal of oxygen, yielding a nitrogen-comprising flow from which oxygen is substantially completely removed. The part of the hydrogen-com-

prising flow which is not fed to the fuel cell, is fed to a pressure swing adsorption unit for the removal of carbon dioxide, carbon monoxide, water and methane. Hereby, however, part of the hydrogen and an even larger part of the nitrogen are also discharged from the hydrogen-comprising flow. To further the recovery of hydrogen and to compensate the loss of nitrogen, the pressure swing adsorption unit is washed with the substantially completely oxygen-depleted nitrogen flow. Although the opposite is intended, the known method requires relatively much energy. With the present invention an oxygen-depleted nitrogen flow coming from a fuel cell and (without further separation or conversion of oxygen) is fed to the secondary reformer.

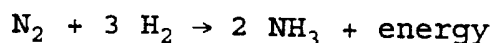
According to a preferred embodiment of the method in accordance with the invention, as fuel-containing flow a second hydrogen-comprising flow, in particular a hydrogen-comprising process flow from the ammonia production, is applied.

Such an application makes the method more economic. According to a particularly advantageous embodiment hydrogen-comprising discharge gas is used as the hydrogen-comprising process flow of the ammonia production.

This discharge gas having a high energy content is used for the generation of high-grade electric energy, while the remaining energy content of the resulting hydrogen-depleted flow being released at the anode of the fuel cell installation can be used by combustion.

Other goals and advantages of the invention are described and elucidated with reference to the drawing which is a schematic representation of an embodiment of the method according to the invention.

Methane and excess steam are reacted in a reformer 1 yielding a mixture of CO and H<sub>2</sub> with in addition small amounts of CO<sub>2</sub>, so-called water gas. This conversion usually takes place at 20-30 bar and 800°C. This water gas provides the hydrogen required for the production of ammonia in accordance with the reaction equation:



(2)

This reaction is carried out at a temperature of 475-600°C and greatly increased pressure (100-200 bar) in the presence of a catalyst. Compression requires much energy.

5 In practice, the flow used to obtain nitrogen is air. The use of pure nitrogen is known in itself. However, the production of nitrogen from air by means of gas separation requires much energy and is expensive. An important advantage of the method according to the present invention  
10 is that by feeding to the secondary reformer, a further separation, in particular a further separation or conversion of oxygen from (oxygen-depleted) air is avoided.

By using the method according to the present invention, air A is oxygen-depleted by supplying the same to a  
15 fuel cell 2, which has a cathode at a cathode side 3 and an anode at an anode side 4. A fuel-containing flow B is supplied to the anode. Such operation of the fuel cell 2 efficiently provides high-grade electric energy. The heat released in the fuel cell 2 may optionally be utilized in  
20 the production process. Any kind of fuel cell having sufficient capacity may be used as fuel cell 2 for the oxygen depletion of air A. Naturally those fuel cells are preferred which generate electricity with the most efficiency, optimally oxygen-deplete the air A and exhibit the least  
25 sensitivity to possible impurities present in the supplied air A and fuel flow B. An example of a suitable fuel cell 2 is the phosphoric acid fuel cell (PAFC) which is capable of removing more than 50% of oxygen from air A.

Outside the field of ammonia production the application  
30 tion of fuel cells for the removal of oxygen from air is known from US 5,330,857 and 4,767,606.

The type of fuel to be supplied depends on the kind of fuel cell used. Often hydrogen is suitable. In the production of ammonia there are various hydrogen-comprising  
35 gas flows that can be used as fuel for the fuel cell 2, for instance water gas. Some kinds of fuel cells, such as the molten carbonate fuel cell (MCFC), are also able to use CO as fuel, therefore they will be preferred when using CO-

containing gas flows. The so-called "direct-reforming" fuel cells, such as DIR-MCFC, are able to use methane as fuel.

As will be explained later, during the production of ammonia a hydrogen-comprising discharge gas is formed, and according to a very favourable embodiment this hydrogen-comprising discharge gas is supplied to the anode of the fuel cell 2.

In relation to the starting amount of methane, the method according to the invention results in a larger amount of synthesis gas, so that it is possible to increase the production capacity of existing installations for the production of nitrogen-hydrogen mixtures which are required for the production of ammonia, by providing them with a fuel cell device 2 for the production of oxygen-depleted air. If 50% of the oxygen present in air is removed, the maximal capacity increase is 8.8%. A removal of 67% results in a capacity increase of maximally 12%. Newly to be built installations having a particular capacity may be dimensioned smaller, which lowers costs. If the installation for the production of ammonia cannot accommodate the capacity increase, the up-stream installation for the production of nitrogen-hydrogen mixture can be operated with a reduced energy consumption.

The volume of oxygen-depleted air is smaller than that of the air used in accordance with the invention, therefore less energy is required for its compression. Compression is necessary for the removal of the remaining oxygen through selective oxidation of methane.

A primary reformer 1 running on steam is unable to convert all the methane. However, further removal of methane which is present in the water gas is necessary in order to limit the amount of gas discharged from the ammonia production. In practice this is done by means of selective oxidation in a secondary reformer 5, whereby the oxygen of the air is completely used up. This leaves the required nitrogen, which nitrogen together with hydrogen will be converted into ammonia. The operation conditions of the primary reformer 1 are chosen such that after the

methane present in the water gas has been converted with oxygen from the air, a for the production of ammonia stoichiometric ratio of hydrogen and nitrogen (3:1) is obtained.

5           The prior art fuel cells are not able to use all the oxygen from the supplied air. By using the method according to the invention, more methane can be converted in the first reformer 1 and the remaining methane in the secondary reformer 5 is removed with the aid of a still oxygen-com-  
10           prising nitrogen flow coming from the fuel cell. Consequently, the nitrogen and hydrogen mixture called synthesis gas, which results from the selective oxidation of methane, contains less CO and CO<sub>2</sub>. Carbon monoxide is catalytically converted into carbon dioxide (CO-shift, not  
15           shown) according to the prior art, which is removed in the usual manner in an absorption column 6. For this purpose a suitable absorbent liquid such as Selexol® may be used, which is continuously regenerated in a second desorption and regeneration column 7. Because the concentration of CO  
20           and CO<sub>2</sub> in the synthesis gas according to the invention is lower, it can be more easily regenerated. The capacity of the absorption column described below may be smaller and the operation of column 7 costs less energy. Traces of carbon dioxide which could interfere with the conversion of  
25           nitrogen and hydrogen into ammonia, are removed by converting them into methane in a methanizer 8.

          The mixture of nitrogen and hydrogen thus purified is fed to reactor 9. As mentioned above, the reaction yield is low, so that, after separation of the ammonia that has  
30           been formed, non-reacted nitrogen and hydrogen have to be fed back via pipe 11 to reactor 9. This causes an accumulation of non-reactants, such as inert gasses. Therefore they have to be discharged as a hydrogen-comprising discharge gas via pipe 12. According to a very favourable embodiment  
35           of the method according to the invention this hydrogen-comprising discharge gas is utilized as the fuel flow B. In this manner this discharge gas, whose energy content according to the prior art can only be converted into low-grade heat energy, is utilized for the generation of high-grade

electric energy while at the same time process air is depleted of oxygen. This advantage is partly due to the fact that the amount of hydrogen in discharge gas complements the amount of oxygen to be depleted from air A. As  
5 the fuel cells according to the state of the art do not convert all the fuel supplied, the fuel-depleted gas flow is still combustible. It is also possible to recover the remaining hydrogen by means of the pressure swing absorption technique. Although the PSA technique could also be  
10 used to directly extract hydrogen from the hydrogen-comprising discharge flow, part of this hydrogen will only become available under low pressure. Both the PSA technique and raising the pressure demands energy, while according to the invention hydrogen is used to generate high-grade  
15 energy. Separation over a membrane yields hydrogen which is under low pressure. To compress it again requires much energy. According to the invention the hydrogen can indeed be separated over a membrane and yet be used for the generation of high-performance energy.

20 Depending on the sensitivity of the fuel cell installation 2 to contaminants, such as residual  $\text{NH}_3$ , the hydrogen-comprising discharge gas will be purified, for instance by means of a membrane separation unit 13, a pressure swing absorption unit or simply by washing with water.  
25 The hydrogen-depleted flow D can advantageously be utilized as starting material for the recovery of inert gasses. According to an alternative embodiment, the starting material used for the recovery of inert gasses is the hydrogen-depleted flow C released at the cathode. This is  
30 possible if interfering contaminants are removed from the fuel flow B which is to be fed to the anode.

CLAIMS

1. A method for the production of ammonia, wherein a  
5 nitrogen-comprising flow is brought together with a hydrogen-comprising flow and nitrogen and hydrogen are catalytically reacted, **characterized** in that the nitrogen-comprising flow is obtained by means of a fuel cell installation  
(2) having a cathode and an anode, by feeding air (A) to  
10 the cathode and a fuel-containing flow (B) to the anode, resulting at the cathode in oxygen-depleted air and at the anode in a fuel-depleted flow (C), after which the oxygen-depleted air as the nitrogen-comprising flow is combined with the hydrogen-comprising flow and the oxygen present in the oxygen-depleted air is used for the catalytic  
15 conversion of a hydrocarbon present in the hydrogen-comprising flow.

2. A method according to claim 1, **characterized** in that the fuel flow (B) is a second hydrogen-comprising  
20 flow.

3. A method according to claim 2, **characterized** in that as the second hydrogen-comprising flow (B) a hydrogen-comprising process flow from the ammonia production is applied.

25 4. A method according to claim 3, **characterized** in that the hydrogen-comprising process flow from the ammonia production is subjected to a purification treatment prior to being fed to the anode.

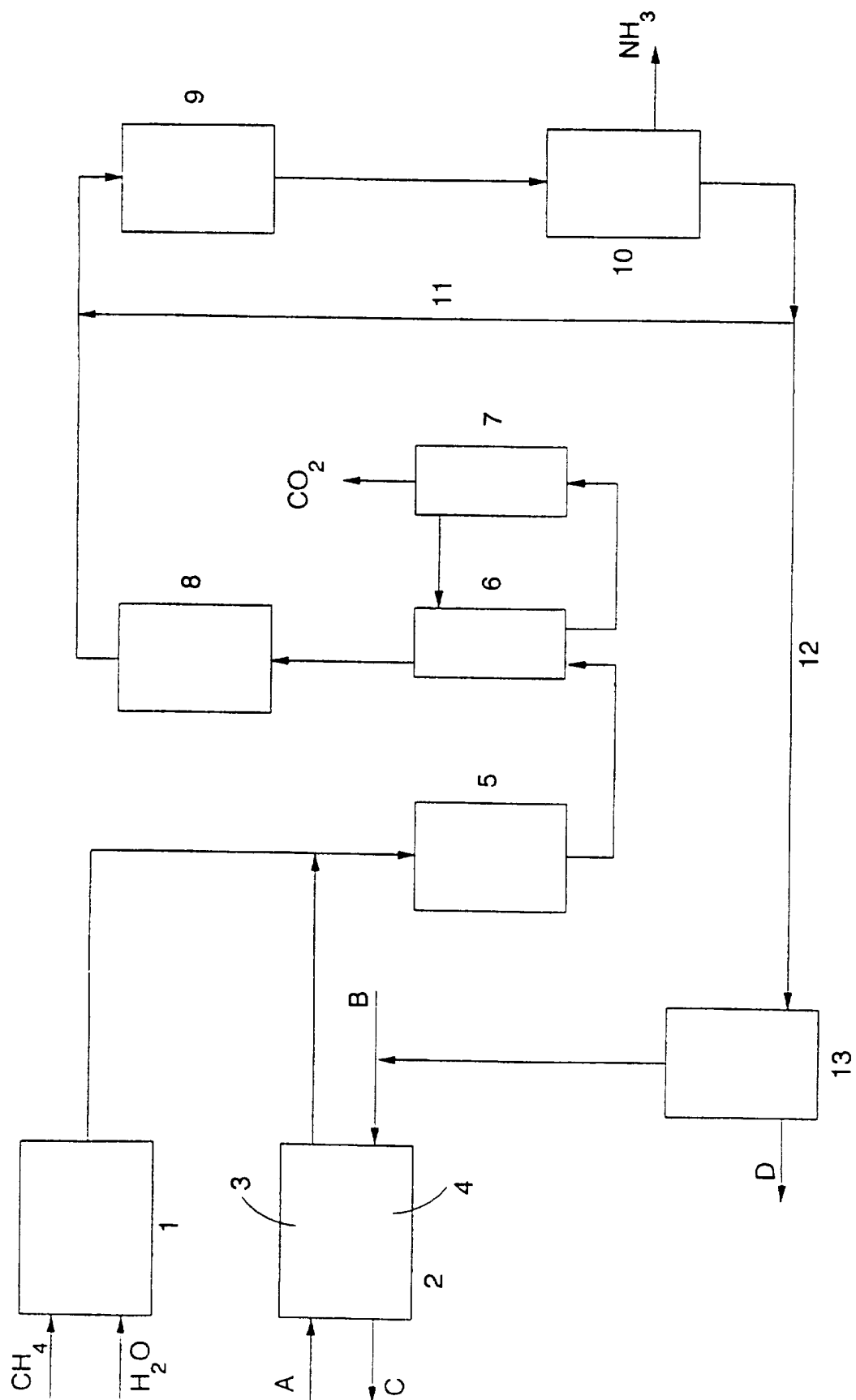
5. A method according to claim 3 or 4, **characterized**  
30 in that as the hydrogen-comprising process flow from the ammonia production hydrogen-comprising discharge gas is applied.

6. A method according to one of the preceding claims, **characterized** in that the hydrogen-depleted flow C released at the anode of the fuel cell installation (2) is  
35 used as the starting material for the recovery of inert gasses.

7. A method according to claim 4 or 5, **characterized** in that the purification treatment comprises the formation

of a second hydrogen-comprising flow and a flow containing the pollutants, and the flow containing the pollutants is utilized as starting material for the recovery of inert gasses.

1/1



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 97/00127

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 6 C01B3/02 C01C1/04 H01M8/06

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 6 C01B C01C

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)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 578 214 A (JUNGERHANS ROBERT R J) 25 March 1986 see the whole document ---	1-3
A	US 5 330 857 A (SEDERQUIST RICHARD A ET AL) 19 July 1994 cited in the application see column 2, line 23 - column 3, line 12 see claims ---	1
A	FR 2 496 078 A (DIDIER ENG) 18 June 1982 see page 3, line 3 - page 5, line 34 -----	1

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

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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NL - 2280 HV Rijswijk  
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Fax (+ 31-70) 340-3016

Authorized officer

Van der Poel, W

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 97/00127

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4578214 A	25-03-86	NONE	
US 5330857 A	19-07-94	NONE	
FR 2496078 A	18-06-82	DE 3047257 A BE 891464 A	08-07-82 31-03-82