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(71) Applicant *(for all designated States except US):* ISIS INNOVATION LIMITED [GB/GB]; 2 South Parks Road, Oxford OX1 3UB (GB).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)* **:** GREEN, Malcolm, Leslie, Hodder [GB/GB]; 25 Blandford Avenue, Oxford OX2 8EA (GB). CHEETHAM, Anthony, Kevin [GB/US]; 1695 E. Valley Road, Montecito, CA 936108 (US). VERNON, Patrick, Desmond, Fraser [GB/GB]; 74 Oxford Road, Littlemore, Oxford OX4 4PE (GB). ASHCROFT, Alexander, Thomas [GB/GB]; 89 Northumberland Avenue, Cleveleys, Blackpool, Lancs. FY5 2JZ (GB).

(74) Agent: PENNANT, Pyers; Stevens, Hewlett & Perkins, 1 Serjeants' Inn, Fleet Street, London EC4Y 1LL (GB).

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(54) Title: IMPROVED PROCESSES FOR THE CONVERSION OF METHANE TO SYNTHESIS GAS

(57) Abstract

A method of converting a reactant gas mixture of CO_2, O_2 and CH_4 comprises contacting the reactant gas at 750 - 850 °C with a solid catalyst, which is a d-block transition metal or oxide such as a group VIII metal on a metal oxide support such as alumina, and which selectively converts the reactant gas into a product gas mixture comprising H_2 and CO.

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Improved Processes for the Conversion of Methane to Synthesis Gas

In view of the dwindling supplies of fossil fuels and the relative abundance of methane, there is considerable interest in processes which have greater efficiency and selectivity for the conversion of methane to synthesis gas. There are several known reactions for the oxygenation of methane.

There are several known reactions for the oxygenation of methane.

$$
\begin{array}{lll}
CH_4 + O_2 & \rightarrow & CH_3OH \quad (1) \\
CH_4 + O_2 & \rightarrow & CO + H_2 \quad (2) \\
CH_4 + O_2 & \rightarrow & CH_2O + H_2O \quad (3) \\
CH_4 + O_2 & \rightarrow & C_2H_4 + C_2H_6 + CO_2 + CO + H_2O \, (4) \\
CH_4 + O_2 & \rightarrow & CO_2 + H_2O \quad (5)
\end{array}
$$

The partial oxidation of methane by dioxygen to synthesis gas, according to the stoicheiometry:

$$CH_4 + 1/2\, O_2 \longrightarrow CO + 2\, H_2 \qquad \text{Equation (2)}$$

is an exothermic reaction, for which the values for ΔH and ΔS at 298 K are[1] -36 $kJmol^{-1}$, and +170 $JK^{-1}mol^{-1}$, respectively, and for which $\Delta G = -215\ kJmol^{-1}$ at 1050 K.

There are also catalysts for the reforming of methane using carbon dioxide.

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad (6)$$

This reduction of carbon dioxide by methane is an endothermic reaction[1] ($\Delta H_{298} = +247\ kJmol^{-1}$). At high temperatures, its favourable entropy change ($\Delta S_{298} = +257\ JK^{-1}mol^{-1}$) makes it a favourable equilibrium, $\Delta G = -23\ kJmol^{-1}$ at 1050 K.

Different catalysts promote these reactions to different extents, but selectivity is normally poor. This patent application results from our discoveries of a class of catalysts that is capable of selectively reforming methane to carbon monoxide and hydrogen according to equation (6) and a class of catalysts capable of combining both the partial oxygenation reaction shown in equation 2 with the reforming reaction shown in (6).

The major commercial process for the utilization of methane (steam reforming) involves a nickel catalysed reaction of methane with steam.

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$

The products of this reaction are four gases which under catalytic conditions are in the equilibrium known as the water-gas shift reaction, namely

$$CO+H_2O \rightleftharpoons CO_2+H_2$$

The equilibrium concentrations depend on the temperature and pressure at which the catalytic reaction is carried out.

The two gases, carbon monoxide and hydrogen, can be combined under catalytic conditions to give useful chemicals such as methanol or , via Fischer-Tropsch catalysis, higher hydrocarbons or aldehydes and alcohols. In consequence, the steam reforming process is an important industrial source of carbon monoxide and hydrogen, but the technology of steam conversion requires considerable capital investment, and is relatively inefficient since water and carbon dioxide are unwanted by-products of the reaction.

Therefore there is considerable industrial interest in the combined reforming-partial oxidation of methane to give carbon monoxide and hydrogen as the substantially major products.

British Patent Application No. 9018781.6 describes the catalysts for the partial oxidation of methane by oxygen to synthesis gas under relatively mild conditions of 650-900^{o}c and pressures of 10-600 KPa without the use of steam. The catalysts include d-block transition metals on a refractory support and d-block transition metal oxides including mixed metal oxides.

Thus, this invention is concerned with essentially two processes. Process 1 is the reaction of CO_2 with methane giving synthesis gas according to Equation 6. Process 2 is the reaction of oxygen and carbon dioxide mixtures with methane also giving synthesis gas.

$$(a)CO_2+(b)O_2+(c)CH_4 \rightarrow (x)CO+(y)H_2$$

A potential application of reaction 6, which is endothermic, is to use energy such as solar energy to drive the reaction to form the synthesis gas, which could then be stored and transported. The reverse reaction, namely the reduction of CO to methane, for which there are well-known catalysts, is highly exothermic thus heat stored by the first reaction can be released by the reverse methanation.

Another aspect of the invention concerns the potential application for usage of CO_2, which has environmental implications towards the general problem of the greenhouse effect.

This invention is concerned with the definition of the conditions and catalysts which will give rise to the conversion of the methane and CO_2, O_2 to synthesis gas with greatly improved selectivity and conversions. Accordingly, the present invention provides a method of converting a reactant gas mixture comprising CO_2, O_2 and CH_4 into a product gas mixture comprising H_2 and CO which method comprises bringing the reactant gas mixture at a temperature of from 600-1000°C into contact with a solid catalyst of the following formula:

$M_xM'_yO_z$ or M_xO_z or M'_yO_z or M′ on a suitable support

where M is at least one metal selected from Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, B, Al, Sc, Y, Ln, Ga, In, Tl, Bi, U, Th and Pb.

Ln is selected from La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y.

M′ is at least one metal selected from Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Th and U.

Each of the ratios x/z and y/z and (x + y)/z is independently from 0.1 to 8, preferably from 0.5 to 0.75

Alternatively, the metal oxide systems may be catalyst precursors, from which the active catalyst is formed by heating under non-oxidizing conditions. For example, the catalyst precursor may decompose to yield the metal on the oxide support.

All the metal oxide systems may be crystalline, monophasic or polyphasic, they may be amorphous, they may be stoichiometric or non-stoichiometric; they may have defect structures. They may be solid solutions. The values of x, y and z may be integral or non-integral. In the mixed metal oxides, the ratio of x to y is not critical and may for example be from 0.001 to 1000.

Catalyst preparation is normally straightforward: the metal oxides, or precursors thereof such as carbonates or nitrates or any thermally decomposable salts, can be precipitated onto a refractory solid which may itself be massive or particulate. Or one metal oxide or precursor may be precipitated onto the other.

Preferred catalyst precursors are those having M' highly dispersed on an inert metal oxide support and in a form readily reducible to the elemental state.

The combined partial pressures of the reactant gases should preferably lie in the range 0.01MPa - 10MPa, preferably at 0.1 MPa.

The reaction 6 is endothermic, $H = +247$ kJ and it is required to heat the reactant gases at temperatures in the range 600-1000°C. The ratio of CO_2 to methane may vary from 0.1 - 10. A preferred temperature range is from 750 to 850°C.

One advantage of using as a feed-stock gas a mixture of CO_2, O_2 and methane is to obtain an effectively thermal neutral reaction, and this can be achieved when the ratio of CO to O_2 is approximately 1:6. Many natural sources of methane contain carbon dioxide.

The mole ratio of the reactant gases CO_2 and O_2 to CH_4 should be:CO_2 (a): O_2 (b): CH_4 (c=2b + a), at ideal stoichiometry.

In a further aspect of the invention the reaction is carried out with an excess of CO_2 such that the ratio of a/c-2b > 1. Under these conditions of excess CO_2, the reaction 2CO   C + CO_2 is suppressed this allows the use of cheaper catalysts such as nickel. This is demonstrated in the data in Experiment 15 using a nickel catalyst. The excess CO_2 is largely converted (by the hydrogen generated) to CO by the reverse water gas shift reaction

$$CO_2 + H_2 \longrightarrow CO + H_2O$$

This gives excellent overall CO yields.

The reaction vessel containing the catalytic reaction should be made of an inert material for example inert oxides, such as quartz (SiO_2) or alumina, and containers such as steel are ineffective if they cause deposition of carbon.

We presently believe that the catalysts serve to achieve essentially thermodynamic equilibrium between all possible products according to the following equations:

$$\begin{aligned} CH_4 + 2O_2 &\rightleftharpoons CO_2 + 2H_2O \\ CH_4 + H_2O &\rightleftharpoons CO + 3H_2 \\ CH_4 + CO_2 &\rightleftharpoons 2CO + H_2 \end{aligned}$$

The selectivity shown towards the major and desired products, namely CO and H_2 reflect the thermodynamic equilibrium under the prevailing conditions. Computer simulations, based on minimizing the total free energy of all possible product combinations excluding carbon, (limited by stoichiometry, of course) predict very similar results to those we obtain, and we are thus confident that thermodynamic equilibrium is attained under our reaction conditions.

The present invention is further illustrated by the following examples in which the reaction 6, $CO_2 + CH_4 \longrightarrow 2CO + 2H_2$, has been catalysed by a number of catalysts, as indicated in the data in experiments 1-8.

Experiments 1-6 show that man different transition metals can act as catalysts.

Experiments 1, 7, 8 show how the reaction conditions affect the products.

All the experiments were carried out using 50mg of solid, powdered catalyst, lightly packed between <20mg of silica wool (MULTILAB) in a straight silica reaction tube of i.d. ca. 4mm. The reaction tube (300mm) was placed in the vertical tube furnace of a LABCON microreactor and connected to a supply of the gas reaction mixture. The reactant gases, methane (supplied by Union Carbide, Gas and Equipment Ltd.), carbon dioxide (supplied by British Oxygen Company), dioxygen (supplied by Air Products) and dinitrogen (supplied by Air Products) were dried over molecular sieves and passed over the catalyst at a rate of 1-50 ml/min (GHSV of $0.12 - 7 \times 10^4$ $hour^{-1}$). The temperature of the reaction tube was raised from ambient to the required temperature (typically 1050K, unless otherwise stated) over a period of 2 hours. The reaction products were monitored using an on-line Hewlett-Packard 5890A gas chromatography apparatus. Separation of all gases was obtained using Helium carrier gas through Porapak Q and 5A molecular sieve packed columns, and were detected using a Thermal Conductivity Detector, calibrated on site. In all cases, O_2 conversion was >99.5%, and C, H, O, N mass balances were better than 96%.

Particulars for the catalytic reduction of CO_2 by CH_4. Mixtures of methane and carbon dioxide were passed over heterogeneous catalyst systems which were selected in the light of our previous experience with catalysts for the partial oxidation of methane. The conditions of the experiments and the products of the reactions are given in the Tables 1-8. These show that several of the catalysts under study are highly effective for the conversion of methane to synthesis gas operating under mild conditions of pressure, at 1050K, and with large gas hourly space velocities.

Particulars for the catalytic conversion of mixtures of CO_2, O_2 and CH_4 to synthesis gas.

Mixtures of CO_2, O_2 (or air) and CH_4 have been passed over selected heterogeneous catalysts. The conditions and products of the reactions are given in Tables 9-15. The data show that several of the catalysts studied are highly efficient for the conversion to synthesis gas. Extended catalyst life-time studies are in progress but, as indicated in Table 1 most catalysts should be expected to show no deterioration in activity after 80 hours, and possibly much longer.

Experiment 1: Results obtained over 50 mg 1% Ir/Al_2O_3, GHSV = 2 x 10^4 hour $^{-1}$, 1050 K, 0.1 MPa.

Catalyst prepared via an incipient wetness technique from $IrCl_3$, subsequently reduced under flowing hydrogen at 800°C for 24 hours.

CO_2/CH_4	% CH_4 converted	% CO_2 converted	% yield H_2	%yield CO
3.84	100	41	70	54
2.96	99	50	76	62
1.99	97	62	83	74
1.00	88	91	87	89*
0.60	58	96	57	71
0.49	47	98	47	64
0.35	34	100	34	51

* This experiment ran for 80 hours with no observed loss of activity or selectivity.

Experiment 2: Results obtained over 50 mg 1% Rh/Al_2O_3, GHSV = 1.7 x 10^4 hour^{-1}, 1050 K, 0.1 MPa.

Catalyst prepared via an incipient wetness technique from $RhCl_3$, subsequently reduced under flowing hydrogen at 800°C for 24 hours.

CO_2/CH_4	% CH_4 converted	% CO_2 converted	% yield H_2	%yield CO
1.10	88	86	87	88
1.00	86	88	85	87

Experiment 3: Results obtained over 50 mg 1% Ru/Al_2O_3, GHSV = 1.9 x 10^4 hour^{-1}, 1050 K, 0.1 MPa.

Catalyst prepared via an incipient wetness technique from an organometallic $CpRu(PMe)_3(B_4H_9)$, subsequently reduced under flowing hydrogen at 800°C for 24 hours.

CO_2/CH_4	% CH_4 converted	%CO_2 converted	% yield H_2	%yield CO
1.05	67	71	62	69
0.92	58	73	53	65

Experiment 4: Results obtained over 50 mg 1% Pd/Al_2O_3, GHSV = 1.9 x 10^4 hour $^{-1}$, 1050 K, 0.1 MPa.

Catalyst prepared via an incipient wetness technique from $PdCl_2$, subsequently reduced under flowing hydrogen at 800°C for 24 hours.

CO_2/CH_4	% CH_4 converted	%CO_2 converted	% yield H_2	%yield CO
0.95	70	77	69	74
0.98	71	75	69	73

Experiment 5: Results obtained over 50 mg Ni/Al_2O_3, GHSV = 2 x 10^4 hour^{-1}, 1050 K, 0.1 MPa.

Catalyst ex-British Gas Plc., CRG ´F´, 1/8" pellets, lightly crushed before use in the microreactor.

CO_2/CH_4	% CH_4 converted	%CO_2 converted	% yield H_2	%yield CO
0.98	88	81	88	85

Experiment 6: Results obtained over 50 mg 1% Pt/Al_2O_3, GHSV = 2 x 10^4 hour^{-1}, 1050 K, 0.1 MPa.

Catalyst prepared via an incipient wetness technique from $PtCl_2$, subsequently reduced under flowing hydrogen at 800°C for 24 hours.

CO_2/CH_4	% CH_4 converted	%CO_2 converted	% yield H_2	%yield CO
0.81	22.3	41.3	16.9	30.8
0.95	23.8	42.6	15.6	33.0
At GHSV 5 x 10^3 hour^{-1}				
0.97	71.9	84.6	66.9	78.2

Catalysts 1% Pd/Al_2O_3 and Ni/Al_2O_3 formed large amounts of carbon, gradually losing their activity and becoming totally clogged up with coke within a few hours.

<u>Experiment 7</u>: Results obtained over 50 mg **1% Ir/Al_2O_3**, GHSV = 2 x 10^4 hour^{-1}, CO_2/CH_4 = 1.00, 0.1 MPa.

Temp K	% CH_4 converted	%CO_2 converted	% yield H_2	%yield CO
900	20	30	14	26
950	34	44	28	40
1000	59	68	54	64
1050	88	91	87	89

<u>Experiment 8</u>: Results obtained over 50 mg **1% Rh/Al_2O_3**, 1050 K, CO_2/CH_4 = 1.00, 0.1 MPa.

GHSV hour^{-1}	% CH_4 converted	%CO_2 converted	% yield H_2	%yield CO
5 x 10^3	88	91	87	89
1 x 10^4	88	91	87	89
1.7 x 10^4	86	88	85	87
2.4 x 10^4	85	87	83	86
5.6 x 10^4	68	74	68	71

Experiment 9: Results obtained passing $CH_4/CO_2/O_2$ mixtures over 50 mg 1% Ir/Al_2O_3, GHSV = 2 x 10^4 $hour^{-1}$, 1050 K, 0.1 MPa.

O_2 conversions ≥ 99.7%

Feed Composition			% CH_4	%CO_2	% yield	%yield
% CH_4	% CO_2	% O_2	converted	converted	H_2	CO
64.4	3.5	32.1	92	9	89	86
59.4	20.0	20.6	87	83	81	86
58.3	23.7	18.0	84	83	81	84
58.0	28.0	14.0	83	90	79	85
49.8	48.8	1.4	91	87	91	89

Experiment 10: Results obtained passing $CH_4/CO_2/O_2$ mixtures over 50 mg 1% Pd/Al_2O_3, GHSV = 2 x 10^4 $hour^{-1}$, 1050 K, 0.1 MPa.

O_2 conversions ≥ 99.7%

Feed Composition			% CH_4	%CO_2	% yield	%yield
% CH_4	% CO_2	% O_2	converted	converted	H_2	CO
58.1	28.5	13.4	60	56	53	59

Experiment 11: Results obtained passing $CH_4/CO_2/O_2$ mixtures over 50 mg 1% Ru/Al_2O_3, GHSV = 2 x 10^4 $hour^{-1}$, 1050 K, 0.1 MPa.

O_2 conversions ≥ 99.7%

Feed Composition			% CH_4	%CO_2	% yield	%yield
% CH_4	% CO_2	% O_2	converted	converted	H_2	CO
57.3	29.5	13.2	70	74	63	71
56.8	29.3	14.0	72	73	64	72

Experiment 12: Results obtained passing $CH_4/CO_2/O_2$ mixtures over 50 mg 1% Rh/Al_2O_3, GHSV = 2×10^4 hour^{-1}, 1050 K, 0.1 MPa.

O_2 conversions ≥ 99.7%

Feed Composition			% CH_4	%CO_2	% yield	%yield
% CH_4	% CO_2	% O_2	converted	converted	H_2	CO
56.5	29.0	14.5	85	88	79	86
57.2	29.5	13.3	82	89	77	85*
56.2	28.5	15.3	88	90	83	89**

* GHSV = 4×10^4 hour^{-1}

** GHSV = 1.5×10^4 hour^{-1}

Experiment 13: Results obtained passing $CH_4/CO_2/O_2$ mixtures over 50 mg Ni/Al_2O_3(CRG'F'), GHSV = 2×10^4 hour^{-1}, 1050 K, 0.1 MPa.

O_2 conversions ≥ 99.7%

Feed Composition			% CH_4	%CO_2	% yield	%yield
% CH_4	% CO_2	% O_2	converted	converted	H_2	CO
56.7	28.1	15.0	89	83	87	87
56.4	29.2	14.4	85	87	79	85

Experiment 14: Results obtained passing $CH_4/CO_2/O_2$ mixtures over 50 mg 1% Pt/Al_2O_3, GHSV = 2×10^4 $hour^{-1}$, 1050 K, 0.1 MPa. O_2 conversions ≥ 99.7%

Feed Composition			% CH_4 converted	%CO_2 converted	% yield H_2	%yield CO
% CH_4	% CO_2	% O_2				
58.2	27.9	13.9	37.5	28.0	25.7	34.5

Experiment 15: Results obtained passing $CH_4/CO_2/O_2$ mixtures over 50 mg Ni/Al_2O_3(CRG´F´), GHSV = 2×10^4 $hour^{-1}$, 1050 K, 0.1 MPa. O_2 conversions ≥ 99.7%

Feed Composition			% CH_4 converted	%CO_2 converted	% yield H_2	%yield CO
% CH_4	% CO_2	% O_2				
15.0	74.7	10.3	99.8	19.2	33.4	32.7
17.2	72.0	10.8	100.0	23.4	25.9	38.2
25.0	65.8	9.2	99.2	40.9	58.3	57.0
34.0	58.1	7.9	97.0	56.3	74.1	52.4
33.0	58.3	8.7	98.0	53.3	73.7	69.4

References

1. All data taken from "Handbook of Chemistry and Physics" 61st ed. (CRC Press, 1980-1981).

2. J. T. Richardson and S. A. Paripatyader, Appl. Catal., 1990, 61, 293.

CLAIMS

1. A method of converting a reactant gas mixture comprising CO_2, O_2 and CH_4 into a product gas mixture comprising H_2 and CO which method comprises bringing the reactant gas mixture at a temperature of from 600-1000°C into contact with a solid catalyst of the following formula:

$M_xM'_yO_z$ or M_xO_z or M'_yO_z or
M' on a suitable support

where M is at least one metal selected from Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, B, Al, Sc, Y, Ln, Ga, In, Tl, Bi, U, Th and Pb.

Ln is selected from La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y.

M' is at least one metal selected from Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Th and U,

each of the ratios x/z and y/z and (x + y)/z being independently from 0.1 to 8.

2. A method according to claim 1, wherein each of the ratios x/z and y/z and (x+y)/z is independently from 0.5 to 0.75.

3. A method according to claims 1 or 2 in which composition of the reactant gas mixture is selected so as to obtain a thermally neutral reaction.

4. A method according to claims 1 to 3, wherein the ratio of CO_2 to O_2 is approximately 1:6.

5. A method according to any of claims 1 to 4 in which the ratio of CO_2 and O_2 to CH_4 is $CO_2(a):O_2(b):CH_4$ (2b+a).

6. A method according to any of claims 1 to 4 in which the ratio of $CO_2(a)$ and $O_2(b)$ to $CH_4(c)$ is $a/c - 2b>1$.

7. A method according to any of claims 1 to 6, wherein the combined partial pressure of the reactant gases if from 0.01 MPa to 10MPa.

8. A method according to any of claims 1 to 7, wherein the combined partial pressure of the reactant gases is approximately 0.1MPa.

9. A method according to any of claims 1 to 8, wherein the reaction temperature is from 750 to 850°C.

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 91/02323

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C01B3/40; C01B3/38

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C01B

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
X	NITROGEN no. 187, September 1990, LONDON, GB pages 28 - 29; 'Transition metal catalysts show potential: Partial oxidation of methane to synthesis gas' see the whole document	1,2,9
P,Y	GB,A,2 239 406 (GAS RESEARCH INSTITUTE) 3 July 1991 cited in the application see page 3, line 30 - page 10, line 4 see page 12, line 9 - page 25, line 17 see claims	1,2,7-9
Y	EP,A,0 084 273 (THE STANDARD OIL COMPANY) 27 July 1983 see page 2, line 18 - page 8, line 20 see claims 1,2,5-9	1,2,7-9

° Special categories of cited documents : [10]

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 31 MARCH 1992	Date of Mailing of this International Search Report 09. 04. 92
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer VAN DER POEL W.

1

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. GB 9102323 SA 54828

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A-2239406	03-07-91	NL-A- 9001508	16-01-91
EP-A-0084273	27-07-83	JP-A- 58120501 US-A- 4690777	18-07-83 01-09-87

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