



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁴ : C07C 1/04, B01J 23/76, 23/78 B01J 29/24, 29/34	A1	(11) International Publication Number: WO 86/ 07350 (43) International Publication Date: 18 December 1986 (18.12.86)
(21) International Application Number: PCT/GB86/00342 (22) International Filing Date: 12 June 1986 (12.06.86) (31) Priority Application Number: 8515222 (32) Priority Date: 15 June 1985 (15.06.85) (33) Priority Country: GB (71) Applicant (for all designated States except US): THE BRITISH PETROLEUM COMPANY P.L.C. [GB/GB]; Britannic House, Moor Lane, London EC2Y 9BU (GB). (72) Inventors; and (75) Inventors/Applicants (for US only) : MCATEER, Colin, Hugh [GB/GB]; NAY, Barry [GB/GB]; 11 Thurlton Court, Horsell, Woking, Surrey GU21 4AU (GB). (74) Agent: FAWCETT, Richard, Fennelly; BP International Limited, Patents Division, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN (GB).		(81) Designated States: AU, JP, NO, US. Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: SYNGAS CONVERSION CATALYST, ITS PRODUCTION AND USES THEREOF (57) Abstract Hydrocarbons having a carbon number greater than one are produced by contacting synthetis gas at elevated temperature and atmospheric or superatmospheric pressure with a catalyst having a composition represented by the formula: $\text{Co}_a\text{A}_b\text{La}_c\text{CeO}_x$ wherein A is an alkali metal, a is greater than zero and up to 25% w/w, b is in the range from zero to 5% w/w, c is in the range from zero to 15% w/w, x is a number such that the valence requirements of the other elements for oxygen is satisfied, and the remainder of the composition, subject to the requirement for x, is cerium.		

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SYNGAS CONVERSION CATALYST, ITS PRODUCTION AND USES THEREOF

The present invention relates to the use of a novel catalyst in the conversion of gaseous mixtures comprising principally carbon monoxide and hydrogen (synthesis gas) into hydrocarbons of carbon number greater than one, in particular into aliphatic hydrocarbons in the gasoline boiling range.

The conversion of synthesis gas into hydrocarbons by the Fischer-Tropsch process has been known for many years but the process has only achieved commercial significance in countries such as South Africa where unique economic factors prevail. The growing importance of alternative energy sources such as coal and natural gas has focussed renewed interest in the Fischer-Tropsch process as one of the more attractive direct and environmentally acceptable routes to high quality transportation fuels.

Many metals, for example cobalt, nickel, iron, molybdenum, tungsten, thorium, ruthenium, rhenium and platinum are known to be catalytically active, either alone or in combination, in the conversion of synthesis gas into hydrocarbons and oxygenated derivatives thereof. Of the aforesaid metals, cobalt, nickel and iron have been studied most extensively. Generally, the metals are used in combination with a support material, of which the most common are alumina, silica and carbon.

The use of cobalt as a catalytically active metal in combination with a support has been described in, for example, EP-A-127220, EP-A-142887, GB-A-2146350, GB-A-2130113 and GB-A-2125062. EP-A-127220, for example, discloses the use of

a catalyst comprising (i) 3-60 pbw cobalt, (ii) 0.1-100 pbw zirconium, titanium, ruthenium or chromium per 100 pbw silica, alumina or silica-alumina, (iii) the catalyst having been prepared by kneading and/or impregnation.

5 Rare earth metals have also been used in a promotional capacity
as components of syngas conversion catalysts. Thus, for example,
J5 9179154A describes a syngas conversion catalyst obtained by
depositing a catalytic iron group metal, preferably cobalt or iron,
with manganese oxide, a platinum group metal, preferably ruthenium,
10 rhodium, palladium, platinum or iridium, and at least one of alkali
metal oxide, preferably potassium, sodium, lithium, cesium or
rubidium or an alkaline earth metal oxide, for example magnesium,
calcium, barium or strontium, or a rare earth metal oxide,
preferably lanthanum, cerium, praeosodymium or samarium, on a
15 catalyst carrier consisting of silica and/or alumina.

We have now found that cobalt in combination with ceria and optionally also lanthana, optionally promoted by an alkali metal, catalyses the conversion of syngas into higher (C_{4+}) hydrocarbons.

Accordingly, the present invention provides a process for the
20 production of hydrocarbons having a carbon number greater than one
by contacting the synthesis gas at elevated temperature and
atmospheric or superatmospheric pressure with a solid catalyst
characterised in that

the catalyst has a composition represented by the formula:

$$25 \quad \text{Co}_a \cdot \text{Al}_b \cdot \text{La}_c \cdot \text{CeO}_x \quad (\text{I})$$

wherein A is an alkali metal

a is greater than zero and up to 25% w/w.

b is in the range from zero to 5% w/w.

c is in the range from zero to 15% w/w.

30 x is a number such that the valence requirements of the other elements for oxygen is satisfied, and the remainder of the composition, subject to the requirement for x, is cerium.

the percentages w/w being based on the total weight of the
35 composition.

In the formula (I) A is an alkali metal, which largely for reasons of availability and cost, is preferably either sodium or potassium. Preferably the amount (b) of alkali metal is less than 2% w/w, even more preferably it is zero. The value of a in the
5 formula (I) is suitably less than 5% w/w, preferably less than 1% w/w. The value of c in the formula (I) is preferably greater than zero and preferably less than 10% w/w.

Cerium may be present in the composition either alone or admixed with lanthanum or lanthanum and other lanthanide rare earth
10 metal(s) oxides, such as for example those commonly found in commercially available technical grade ceria.

The catalyst having the formula (I) may be prepared by a variety of processes, for example by impregnation, by precipitation, by coprecipitation, by cogelation or by vapour deposition, or by any
15 other process. One method of preparing the catalyst of formula (I) involves impregnating a ceria support with a solution of a soluble cobalt compound. The solution may be an aqueous solution or a solution in an organic solvent of a suitable compound. Suitable compounds include cobalt complexes, for example cobalt (II)
20 acetylacetonate and cobalt (III) acetylacetonate, and cobalt salts such as a nitrate or a halide. In those catalysts incorporating an alkali metal, this may either be impregnated on to the rare earth metal oxide support simultaneously with the cobalt or may be added at a later stage in the preparation.

Alternatively, the cobalt may be precipitated on to the rare earth metal oxide support from a solution of a soluble compound thereof by treatment with a suitable precipitant, suitably by
25 (A) bringing together at a temperature below 100°C ceria, a solution of a soluble compound of cobalt and a precipitant
30 under conditions whereby cobalt is precipitated in the form of a heat decomposable compound, and
(B) recovering the mixture of the ceria and the precipitated cobalt compound obtained in step (A),

The amounts of the reagents employed should be such as to
35 satisfy the stoichiometric relationships in the formula (I).

In step (B) of the process of the invention the precipitate obtained in step (A) is recovered. This may suitably be accomplished by filtration but other methods for separating solids from liquids, for example centrifugation, may be employed. After recovery it is preferred to wash the precipitate, suitably with water, so as to remove unwanted residual soluble matter. It is also preferred to dry the precipitate, suitably at an elevated temperature below 200°C, for example about 150°C.

In a modification of the precipitation method hereinbefore described, a cerium compound or compounds convertible to ceria may be coprecipitated together with a cobalt compound.

For those catalysts containing lanthanum, the lanthanum may be incorporated at any stage in the preparative procedure.

Irrespective of whether the composition is prepared by impregnation, precipitation or coprecipitation or by any other method, it is preferred to carry out one or more additional steps before the composition is used as a catalyst. Thus it is preferred to roast the composition, suitably by heating it in, for example, a stream of gas such as nitrogen or air at a temperature suitably in the range from 250 to 600°C. It is also preferred to reductively activate the composition, suitably by contact at elevated temperature with a reducing gas, for example hydrogen, which may be diluted with nitrogen. Typically, the conditions employed during the reductive activation step may suitably be a pressure in the range from 1 to 100 bar and a temperature in the range from 150 to 500°C for a period of up to 24 hours or longer. Whilst it is preferred to effect the reductive activation step as a discrete step prior to use as a catalyst for the conversion of synthesis gas, it may be incorporated into the synthesis gas conversion process.

As is well known in the art synthesis gas principally comprises carbon monoxide and hydrogen and possibly also minor amounts of carbon dioxide, nitrogen and other inert gases depending upon its origin and degree of purity. Methods of preparing synthesis gas are established in the art and usually involve the partial oxidation of a carbonaceous substance, e.g. coal. Alternatively, synthesis gas

may be prepared, for example by the catalytic steam reforming of methane. For the purpose of the present invention the carbon monoxide to hydrogen ratio may suitably be in the range from 2:1 to 1:6. Whilst the ratio of the carbon monoxide to hydrogen in the synthesis gas produced by the aforesaid processes may differ from these ranges, it may be altered appropriately by the addition of either carbon monoxide or hydrogen, or may be adjusted by the so-called shift reaction well known to those skilled in the art.

The elevated temperature may suitably be in the range from 190 to 400°C, preferably from 200 to 350°C. The pressure may suitably be in the range from 0 to 100 bar, preferably from 10 to 50 bar. The GHSV for continuous operation may suitably be in the range from 100 to 5000h⁻¹.

The process may be carried out batchwise or continuously in a fixed bed, fluidised bed or slurry phase reactor.

In a modification of the process of the present invention the catalyst of formula (I) may incorporate a suitable porometallotectosilicate. The porometallotectosilicate may suitably be an aluminosilicate zeolite, preferably an aluminosilicate zeolite having a high (that is greater than 10:1) silica to alumina ratio. Suitable aluminosilicate zeolites include, but are by no means restricted to, zeolite ZSM-5.

In a further modification, the process of the invention may include a further step in which the product, or at least a portion thereof, obtained by contacting synthesis gas with the catalyst of formula (I) is up-graded by, for example, oligomerisation of lower olefins present therein to higher hydrocarbons in the manner described in, for example, US-A-4544792, US-A-4520215 and US-A-4504693; hydrocracking in the manner described in, for example GB-A-2146350; cracking and isomerisation of heavy by-products in the manner described in, for example, US-A-4423265 and up-grading in the manner described in, for example AU-A-8321809 and GB-A-2021145.

The invention will now be further illustrated by the following Examples. In the Examples CO conversion is defined as moles of CO used/moles of CO fed x 100 and carbon selectivity as moles of CO

attributed to a particular product/moles of CO converted x 100.

A. CATALYST PREPARATION

Cobalt/ceria catalysts were made by impregnating dry powdered ceria with a solution containing a cobalt compound. Cobalt loadings
5 of 0.2, 0.3 and 0.5% w/w were tested.

Example 1 0.2% Co/CeO₂

0.75 g of [Co(III)(acac)₃] was dissolved in 35 cm³ of analar acetone. This solution was slowly added to 60 g of CeO₂ with continuous stirring until a uniform paste was formed. The paste was
10 dried over a steam bath, again with continuous stirring/kneading, until a uniform powder was obtained. The powder was stored in an oven at 150 °C overnight prior to pretreatment.

Example 2 0.3% Co/CeO₂

The same method as described in Example 1 was used with 1.15 g
15 of [Co(III)(acac)₃] being dissolved in 60 cm³ of analar acetone.

Example 3 0.3% Co/CeO₂

The same method as described in Example 2 was used except that 0.8 g of [Co(II)(acac)₂], dissolved in 55 cm³ of analar acetone, was impregnated onto 60 g of CeO₂.

Example 4 0.5% Co/CeO₂

The same method as described in Example 3 was used with 1.35 g
20 of [Co(II)(acac)₂] being dissolved in 150 cm³ of analar acetone.

Example 5 0.2% Co/CeO₂

[Co(acac)₃] (0.75 g, 2.1 mmol) was dissolved in analar acetone
25 (35 cm³). The solution was slowly added to a glass dish containing CeO₂ (60 g), with continuous stirring until a consistent paste was formed. A further portion of acetone (10 cm³) was used to ensure all the [Co(acac)₃] was washed onto the ceria. The paste was dried over a steam bath, with continuous stirring/kneading, until the
30 impregnated ceria became a powder. The powder was then dried in an air oven overnight at 150°C prior to pretreatment.

Example 6 1.4% Co/10% La₂O₃/CeO₂

Co(NO₃)₃·6H₂O (3.5 g, 12.0 mmol) was dissolved in analar acetone (15 mmol) and added to a solution a La(NO₃)₃·6H₂O (13.3 g, 30.7
35 mmol) dissolved in analar acetone (15 mmol).

The solution was slowly added to CeO_2 powder (50 g, ex J.M) with careful stirring/kneading until a consistent paste was obtained. The paste was dried on the steam bath until a dry powder was obtained, which was then dried overnight in an air oven at 150°C.

The material dried into a solid block and no pressing was necessary.

Example 7 2.1% Co/10% $\text{La}_2\text{O}_3/\text{CeO}_2$

This catalyst was prepared in an identical manner to the catalyst of Example 5, the amounts of materials employed being altered in accordance with the above stoichiometry.

Comparison Test 1 0.3% Fe/ CeO_2

Example 1 was repeated except that 1.12g of $[\text{Fe(III)(acac)}_3]$ was dissolved in 60 cm^3 of analar acetone instead of 0.75 g of $[\text{Co(III)(acac)}_3]$ being dissolved in 35 cm^3 of analar acetone.

Comparison Test 2

Example 1 was repeated except that 0.80 g of $[\text{Ni(II)(acac)}_2]$ was dissolved in 60 cm^3 of analar acetone instead of 0.75 g of $[\text{Co(III)(acac)}_3]$ being dissolved in 35 cm^3 of analar acetone.

B. CATALYST PRETREATMENT

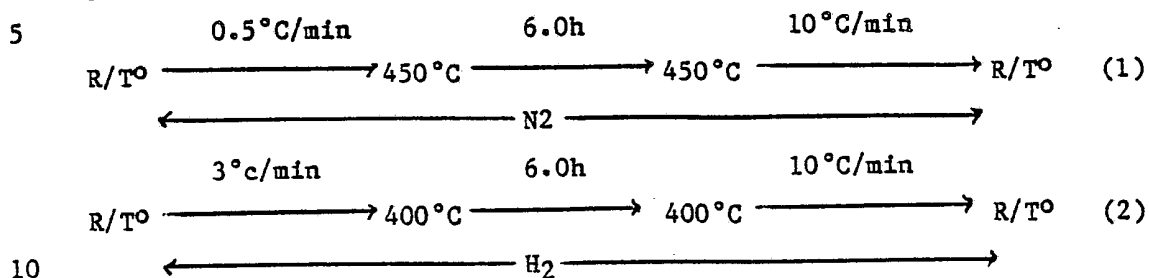
The Co/ CeO_2 powders obtained in Examples 1 to 4 and Comparison Tests 1 and 2 were treated individually as follows:-

The powder was heated in an atmosphere of nitrogen at a rate of 0.5°C/min to 450°C at which temperature it was held for 6 hours before being allowed to cool again to room temperature, the whole operation being conducted in the nitrogen atmosphere. In a hydrogen atmosphere, the powder was heated at a rate of 2°C/minute to 125°C, maintained at this temperature for 2 hours, heated again at 2°C/minute to 225°C, held at this temperature for 2 hours, heated again at 2°C/minute to 320°C, held at this temperature for 6 hours and finally allowed to cool to room temperature, all in the hydrogen atmosphere.

The treated catalyst was then pressed to 4 tons and the resulting pellets crushed and sieved to BSS 8-20 mesh. The catalyst was then loaded into a reactor and reduced in a slow stream of

hydrogen as follows:- heating at 2°C/minute to 150°C, then at 1°C/minute to 225°C and holding at this temperature for 14 hours.

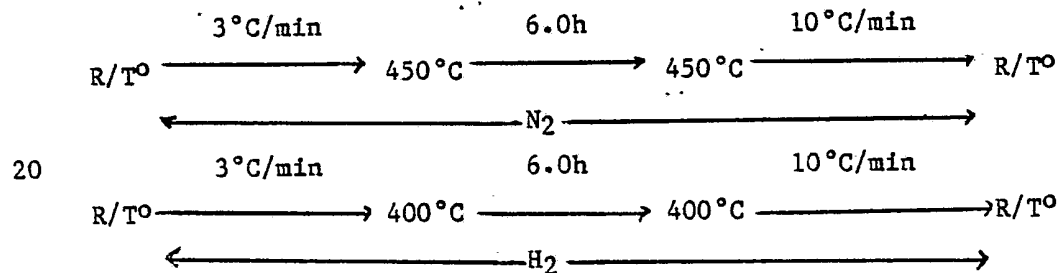
The cobalt/ceria powder of Example 5 was pretreated (after pressing to 1 ton) in the manner of the following scheme:



The catalyst was pressed to 4 tons and then sieved to pass 8-20 mesh BSS.

The catalyst was then loaded into a reactor and reduced in a slow stream of hydrogen at 320°C.

15 The catalysts of Examples 6 and 7 were pretreated (without pressing) in the manner of the following scheme:



The catalysts were sieved to 18-25 mesh BSS and loaded into the reactor.

25 The catalysts were reduced in the plant at 400°C/H₂.

C. CATALYST TESTING

Examples 8 to 11 and Comparison Tests 3 and 4

At the end of the catalyst pretreatment of B above, syngas was introduced into the reactor containing in turn the pretreated catalysts of Examples 1 to 4 and Comparison Tests 1 and 2 with the pressure adjusted to 20 bar. The conditions were adjusted to those shown in the Table.

The results of testing the pretreated catalysts of Examples 1 to 4 and Comparison Tests 1 and 2 are shown as Examples 8 to 11 and Comparison Tests 3 and 4 respectively in Table 1.

Example 12

At the end of the catalyst pretreatment of B above, syngas was introduced into the reactor containing the pretreated catalyst of Example 5 under the conditions shown in Table 2.

5 Examples 13 and 14

At the end of the catalyst pretreatment of B above, syngas was introduced into the reactor containing in turn the pretreated catalysts of Examples 6 and 7 under the conditions shown in Table 3.

10 The results of testing the pretreated catalysts of Examples 6 and 7 are shown as Examples 13 and 14 in Table 3.

The results of testing the pretreated catalyst of Example 5 is shown as Example 12 in Table 2.

15 With reference to Table 1, the results shown for Examples 9 and 10 demonstrate that there is no significant difference in catalyst performance between a catalyst having a Co (II) precursor and one having a Co (III) precursor.

At identical low loadings (0.3%), the supported iron and nickel catalysts are inferior in all respects to the supported cobalt catalysts.

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TABLE 1
Ceria-Supported Catalysts Prepared by Impregnation

$H_2:CO = 2:1$ Molar Ratio

Pressure = 20 bar

$GHSV(h^{-1}) = 2500$

Example	Catalyst	T/°C	%CO Converted	Carbon Molar Selectivity %*					C_3^+ Productivity kg/m ³ cat/h
				CO ₂	CH ₄	C ₂	C ₃ ⁺	C ₅ ⁺	
8	Ex 1	282	41	6.2	18.3	4.5	67.9	49.9	132
9	Ex 2	279	36	5.3	21.6	4.7	65.4	47.6	130
10	Ex 3	280	39	5.6	21.6	4.6	65.3	47.3	135
11	Ex 4	242	31	7.0	37.7	5.6	43.9	30.7	76
Comp Test 3	Comp Test 1	400	14	44.4	28.5	13.5	13.5	0	17
Comp Test 4	Comp Test 2	400	about 3	61.0	23.5	8.1	7.7	0	2

* Oxygenates not included

TABLE 2

CO:H₂ ratio = 1:2 molar
 GHSV = 2500 h⁻¹
 Temp = 285°C
 Pressure = 30 bar

Ex	Catalyst	% CO conv.	Carbon Molar Selectivity					C ₃ ⁺ and C ₅ ⁺ Productivity Kg _m ³ cat/h	
			CO ₂	CH ₄	C ₂	C ₃ ⁺	C ₅ ⁺	C ₃ ⁺	C ₅ ⁺
12	Ex. 5	49	3.38	17.3	2.8	73.7	59.2	188	151

Oxygenates = 2.9% selectivity

TABLE 3

CO:H₂ ratio = 1:2 molar
 GHSV = 2500 h⁻¹
 Pressure = 30 bar

Ex		HOS	T°C	CO % conv	Carbon Molar Selectivity %					Productivity	
					CO ₂	CH ₄	C ₂	C ₃ ⁺	C ₅ ⁺	C ₃ ⁺	C ₅ ⁺
13	6	188	275	51	21.4	10.8	4.4	59.3	47.1	157	125
14	7	70	270	55	18.0	10.6	4.4	63.8	52.5	183	150

* Oxygenates not included.

Claims:

1. A process for the production of hydrocarbons having a carbon number greater than one by contacting the synthesis gas at elevated temperature and atmospheric or superatmospheric pressure with a solid catalyst

5 characterised in that

the catalyst has a composition represented by the formula:



wherein A is an alkali metal

- 10 a is greater than zero and up to 25% w/w,
 b is in the range from zero to 5% w/w,
 c is in the range from zero to 15% w/w,
 x is a number such that the valence requirements of the other elements for oxygen is satisfied, and the remainder of the composition, subject to the requirement for x, is
15 cerium,

the percentages w/w being based on the total weight of the composition.

2. A process according to claim 1 wherein b in the formula (I) is greater than zero and the alkali metal (A) is either sodium or
20 potassium.

3. A process according to claim 1 wherein the value of b in the formula (I) is zero.

4. A process according to any one of the preceding claims wherein the value of (a) in the formula (I) is less than 5% w/w.

25 5. A process according to any one of the preceding claims wherein

the value of c in the formula (I) is greater than zero.

6. A process according to any one of the preceding claims wherein the catalyst incorporates a porotectometallosilicate.

7. A process according to claim 6 wherein the
5 porotectometallosilicate is an aluminosilicate having a silica to alumina ratio greater than 10:1.

8. A process according to any one of the preceding claims wherein before use the catalyst having a composition according to formula (I) is reductively activated.

10 9. A process according to any one of the preceding claims wherein the elevated temperature is in the range from 190 to 400°C and the pressure is in the range from 0 to 100 bar.

10. A process according to any one of the preceding claims including a further step whereby the product, or at least a portion
15 thereof, obtained by contacting synthesis gas with the catalyst composition of formula (I) is up-graded.

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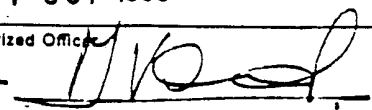
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INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 86/00342

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC ⁴ C 07 C 1/04; B 01 J 23/76; B 01 J 23/78; B 01 J 29/24; IPC: B 01 J 29/34		
II. FIELDS SEARCHED		
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Classification System	Classification Symbols	
IPC ⁴	C 07 C 1/00; B 01 J 23/00; B 01 J 29/00	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *		
III. DOCUMENTS CONSIDERED TO BE RELEVANT *		
Category *	Citation of Document, ¹¹ with Indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	DE, A, 3316320 (RESEARCH ASSOCIATION FOR PETROLEUM ALTERNATIVES DEVELOPMENT) 10 November 1983, see claims 1,3,4,19 --	1-7,9
Y	US, A, 4399234 (BEUTHER ET AL.) 16 August 1983, see column 2, lines 42-63 --	1-7,9
Y	DE, A, 2750007 (SHELL INTERNATIONAL RESEARCH) 18 May 1978, see claims 1,16,18 --	1-7,9
Y	US, A, 4374819 (PALILLA ET AL.) 22 February 1983, see column 2, line 58 - column 3, line 16; column 6, lines 34-46 --	1-7,9
A	DE, B, 2739466 (TOKYO GAS CO. LTD) 9 March 1978, see claim 1 --	1
A	GB, A, 1458247 (TEXACO DEVELOPMENT CORP.) 8 December 1976, see claims 1,2 -----	1,10
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"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</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"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.</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
25th August 1986	07 OCT 1986	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	M. VAN MOL 	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/GB 86/00342 (SA 13616)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 15/09/86

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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US-A- 4399234	16/08/83	None	
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