



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<p>(21) International Application Number: PCT/GB85/00378 (22) International Filing Date: 23 August 1985 (23.08.85) (31) Priority Application Number: 8421646 (32) Priority Date: 25 August 1984 (25.08.84) (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) : FOSTER, Alan, Ivor [GB/GB]; 13 Albert Road, Ashford, Middlesex TW15 2LU (GB). JOYNER, Richard, William [GB/GB]; 28 Lightwater Meadow, Lightwater, Surrey GU18 5XL (GB). McCARROLL, John, James [GB/GB]; 1 Kilmore Drive, Camberley, Surrey GU15 1DT (GB). PARTINGTON, Stephen, Roy [GB/GB]; 7 Bagot Close, Ashtead, Surrey KT21 1NS (GB). SPIERS, Ranald, Gordon, Lyon [GB/US]; 104 West 70th</p>		<p>Street, Apartment 11G, New York, NY 10023 (US). TENNISON, Stephen, Robert [GB/GB]; 62 Farleigh Road, New Haw, Weybridge, Surrey KT15 3HR (GB). (74) Agent: RYAN, Edward, Terrence; BP International Limited, Patents Division, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN (GB). (81) Designated States: AU, BE (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, NL (European patent), NO, US. Published <i>With international search report.</i></p>
<p>(54) Title: FISCHER-TROPSCH CATALYST</p> <p>(57) Abstract</p> <p>A Fischer-Tropsch catalyst comprises cobalt or iron on a support which is carbon having a BET surface area of at least 100 m²/g, ratio of BET to basal plane surface area not greater than 4:1 and a ratio of basal plane surface area to edge surface area of at least 10:1.</p>		

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FISCHER-TROPSCH CATALYST

The present invention relates to catalysts suitable for use in the Fischer-Tropsch process, and to a Fischer-Tropsch process carried out using the catalysts.

In the well-known Fischer-Tropsch reaction a mixture of carbon monoxide and hydrogen (usually referred to as "syngas") is reacted to give relatively low molecular weight hydrocarbons, a substantial proportion of which are liquid at normal temperature and pressure.

The Fischer-Tropsch process is disclosed in numerous references for example US 4 088 671. This discloses that the catalysts usually used are supported Co and Fe catalysts. US 4 088 671 is concerned with a Co catalyst modified by the addition of Ru. Various catalyst supports are mentioned including activated carbon, coke, and charcoal. Although carbon is sometimes included in lists of supports which can be used for Fischer-Tropsch catalysts, it is recognised by skilled persons that carbon is in general not a satisfactory support for Fischer-Tropsch catalysts. In practice although carbon may sometimes be mentioned as a support, the experiments are carried out with oxide supports, as in US 4 088 671.

GB 1 565 074 discloses a catalyst for ammonia synthesis on a graphitised carbon support of defined BET/basal plane and basal plane/edge surface area ratios. There is nothing to suggest that this support would offer any advantages in the different Fischer-Tropsch reaction.

We have now found that by appropriate selection of the support a substantial increase in activity can be obtained by comparison

with a Fischer-Tropsch catalyst on an oxide support.

According to the present invention a Fischer-Tropsch catalyst comprising cobalt or iron on a support is characterised in that the support is a carbon having a BET surface area of at least 100 m²/g, a ratio of BET to basal plane surface area not greater than 4:1, and a ratio of basal plane surface area to edge surface area of at least 10:1.

Carbons may be characterised by their BET, basal plane, and edge surface areas. The BET surface area is the surface area determined by nitrogen adsorption using the method of Brunauer Emmett and Teller J. Am Chem. Soc. 60,309 (1938). The basal plane surface area is the surface area determined from the heat of adsorption on the carbon of *n*-dotriacontane from *n*-heptane by the method described in Proc.Roy.Soc. A314 pages 473-498, with particular reference to page 489. The edge surface area is the surface area determined from the heat of adsorption on the carbon of *n*-butanol from *n*-heptane as disclosed in the Proc.Roy.Soc. article mentioned above with particular reference to page 495.

The carbon supports are known, for example from GB 1 565 074. However the catalysts of the present invention behave in a completely different manner from the catalysts of GB 1 565 074. Thus the catalysts of GB 1 565 074 have their activity increased by the presence of alkali metals, and the presence of chloride ion is stated to be undesirable.

The catalysts of the present invention have their activity destroyed by the presence of excess alkali metals.

In a preferred embodiment of the present invention the catalyst additionally comprises a platinum or palladium, preferably platinum itself.

The platinum group metal is conveniently deposited by impregnation with an aqueous solution of a compound of a platinum group which is reducible to give the metal.

The platinum group metal may for example be deposited on the carbon support before the cobalt or iron. It may be preferred to carry out a reduction step to leave the metal before the deposition

of the cobalt or iron, particularly if the compound used to deposit the platinum group metal leaves components which interfere with reduction of the iron or cobalt.

5 The quantity of platinum group metal on the catalyst may for example be in the range 0.2 to 10% by weight of total catalyst, preferably 0.5 to 5% by weight.

Clearly if the objective is to make a Fischer-Tropsch catalyst materials which destroy the activity of the catalyst (eg alkali metals as indicated above) must be excluded. Whether given
10 materials adversely effect the activity may be determined by simple comparative tests.

The quantity of iron or cobalt deposited on the catalyst may be in the range 5 to 100% wt based on weight of carbon.

15 The catalyst may be prepared by impregnation with an aqueous solution of a salt of cobalt or iron. Examples of suitable salts are nitrates.

The preferred carbons for use in the present invention have a BET surface area of at least 200 m²/g, most preferable at least 300 m²/g. The BET surface area is preferably not greater than 1000
20 m²/g, more preferably not greater than 750 m²/g.

The ratio of BET to basal plane surface area is preferably not greater than 2.5:1. It is particularly preferred to use carbons with ratios of BET to basal plane surface area of not greater than 1.5:1.

25 It is preferred to use carbons with ratios of basal plane surface area to edge surface area of at least 100:1. It is not believed that there is an upper limit on the ratio, although in practice it will not usually exceed 200:1.

30 The preferred carbon support may be prepared by heat treating a carbon-containing starting material. The starting material may be an oleophilic graphite e.g. prepared as disclosed in GB 1 168 785 or may be a carbon black.

35 However oleophilic graphites contain carbon in the form of very fine particles in flake form and are therefore not very suitable materials for use as catalyst supports. We prefer to avoid their

use. Similar considerations apply to carbon blacks which also have a very fine particle size.

The preferred materials are activated carbons derived from vegetable materials e.g. coconut charcoal, or from peat or coal or from carbonizable polymers. The materials subjected to the heat treatment preferably have particle sizes not less than those indicated above as being preferred for the carbon support.

The preferred starting materials have the following characteristics: BET surface area of at least 100, more preferably at least 500 m²/g.

The preferred heat treatment procedure for preparing carbon supports having the defined characteristics, comprise successively (1) heating the carbon in an inert atmosphere at a temperature of from 900°C to 3300°C, (2) oxidizing the carbon at a temperature between 300°C and 1200°C, (3) heating in an inert atmosphere at a temperature of between 900°C and 3000°C.

The oxidation step is preferably carried out at temperatures between 300° and 600°C when oxygen (eg as air) is used as the oxidising agent.

The duration of the heating in inert gas is not critical. The time needed to heat the carbon to the required maximum temperature is sufficient to produce the required changes in the carbon.

The oxidation step must clearly not be carried out under conditions such that the carbon combusts completely. It is preferably carried out using a gaseous oxidizing agent fed at a controlled rate to avoid over oxidation. Examples of gaseous oxidising agents are steam, carbon dioxide, and gases containing molecular oxygen eg air. The oxidation is preferably carried out to give a carbon weight loss of at least 10% wt based on weight of carbon subjected to the oxidation step, more preferably at least 15% wt.

The weight loss is preferably not greater than 40 % wt of the carbon subjected to the oxidation step, more preferably not greater than 25 % wt of the carbon.

The rate of supply of oxidizing agent is preferably such that the desired weight loss takes place over at least 2 hours, more preferably

at least 4 hours.

Where an inert atmosphere is required it may be supplied by nitrogen or an inert (Group 0) gas.

The catalysts of the present invention may be used for the Fischer-Tropsch conversion of synthesis gas to hydrocarbons which are liquid at normal temperatures and pressures.

The temperature may for example be in the range 150 to 300°C, preferably 200 to 250°C. The pressure may for example be in the range 1 to 50 bar absolute (0.1 to 5 MPa). The molar ratio of hydrogen to carbon monoxide may for example be in the range 3:1 to 1:1, more preferably about 2:1. The gas hourly space velocity may be 100 to 10,000, preferably 500 to 3000.

The invention will now be illustrated by reference to the following Examples.

15

Example 1

This Example shows the preparation of a cobalt Fischer-Tropsch catalyst supported on a graphitised carbon.

The carbon used as support was prepared from a commercially available extrudate activated carbon sold by Degussa under the designation Katepon BKIV. The carbon was in the form of extrudates of 4mm diameter and had typical BET, basal plane, and edge surface areas of 939,182 and 32 m²/g respectively. The activated carbon was heat treated as follows. The carbon was heated from room temperature in a stream of helium to 1700°C over a period of about 1 hour. When the temperature reached 1700°C the carbon was allowed to cool in the stream of helium to 25°C. The carbon was then heated in air in a muffle furnace at approximately 520°C for a time known from experience to give a weight loss of 20 %wt. The carbon was then heated in helium to between 1800°C and 1850°C as in the helium heating step mentioned above. The carbon was allowed to cool to room temperature in a helium atmosphere.

Typical values found for carbon treated in this manner were:

BET surface area	710-749 m ² /g
Basal plane surface area	416-666 m ² /g
Edge surface area	3.6-3.8 m ² /g

35



The support was ground and sieved to 16-30 mesh (0.5-1.0 mm) and washed by refluxing in (1) dilute (10% w/w) hydrochloric acid and (2) distilled water to remove sulphur and impurity transition metals before use.

5 The carbon was then impregnated with an aqueous solution of cobalt nitrate (analytical reagent grade). The quantity of cobalt nitrate used was such that 10g of carbon support were treated with 2g of cobalt (giving a nominal metal loading of 16.7% w/w based on weight of catalyst). The quantity of water used was the minimum
10 used necessary to ensure even wetting of the carbon support (a few drops of methanol may be added to assist in wetting of the support).

The impregnation of the carbon was conducted in a rotary evaporator at 50-80°C under a vacuum of 200-800 m bar (20 kPa-80 kPa). The impregnated carbon was dried overnight in a
15 vacuum oven at 120°C, 200-300 m bar (20 kPa-80 kPa).

The catalyst was tested (using a 2.2 ml sample) in a once-through microreactor equipped with an on-line gas chromatography apparatus to analyse for CO, CO₂, and C₁-C₁₀ organic products. The catalyst was reduced before use by treating
20 for 2-8 hours with a stream of hydrogen (25-100 ml/min) at 400-450°C and 8 bar (0.8 MPa) gauge. Synthesis gas at a molar ratio of H₂:CO of 2:1 was then admitted. The conditions used and the results obtained are given in Table 1.

Definition of Terms used in the Results

25 The CO conversion is defined as the percentage of the carbon monoxide fed to the reactor that was converted to analysed products. It may be represented as:

$$30 \quad 100 - \left[\frac{\text{molar \% CO in product}}{\text{SUM(molar \% carbon-containing material x carbon number)}} \times 100 \right] \%$$

The selectivity to organic products is defined as the percentage of the total carbon monoxide converted to C₁-C₁₀ organic products rather than to CO₂. It may be represented as:

$$35 \quad \frac{\text{SUM(molar \% organic products x carbon number)} \times 100\%}{\text{SUM(molar \% organic products x carbon number)} + \text{molar \% CO}_2}$$

The alpha factor represents the relative quantities of the organic products and is defined by P. Biloen and W.M.H. Sachtler in "Advances in Catalysis", Volume 30, pp 165 et seq, published by the Academic Press Inc 1981. In the present application the factor is
5 calculated for products with carbon numbers from C₃-C₁₀.

The gas hourly space velocity (GHSV) is defined as the ml/hour of CO/H₂ feedstock (at NTP) per ml of catalyst.

Example 2

A catalyst was prepared as in Example 1 but containing 5g of Co
10 per 10g of support (nominal metal loading 33.3% w/w). This catalyst was tested at two different space velocities and the results obtained are given in Tables 1 and 2.

Comparative Test A

This is a comparative test not according to the invention.

15 A sample of oxide-supported Fischer-Tropsch catalyst (the conventional type) was tested using the apparatus used in Example 1. The catalyst contained cobalt, magnesium oxide, and zirconium oxide. It was prepared on a 50-100 mesh silica support according to the general method described by J R Anderson in
20 "Structure of Metallic Catalysts", page 455, published by Academic Press, 1975. It contains 22.7% w/w CO, 1.2% w/w MgO and 2.16% w/w ZrO₂. It was reduced before use as in Example 1.

The activity and selectivity of this catalyst under the conditions used for the previous examples are given in Tables 3 and
25 4.

Comparison of the results with Tables 1 and 2 (a catalyst according to the invention) shows that the oxide-based catalyst possessed an activity (expressed as CO conversion) comparable with the catalyst of Example 1 and considerably poorer than the catalyst
30 of Example 2 at comparable temperatures. When the relative densities of the catalyst as loaded into the reactor are taken into consideration (0.40g/ml for the catalyst of the Example 1, 0.53g/ml for the catalyst of Example 2 and 0.77g/ml for the catalyst of Comparative Test A), it is apparent that the catalysts of the
35 invention possess considerable higher activity per unit mass of metal present in the reactor.

Table 1

Catalyst (% w/w Co)	Example 1 - 16.7% w/w Co	Example 2 - 33.3% w/w Co
Temperature (°C)	222	202
CO Conversion (%)	59	39
Selectivity to organic products (%)	93	97
" " carbon dioxide (%)	7	3
Alpha Factor	0.63	0.69

(a) GHSV:- 500 h⁻¹
 H₂:CO:- 2:1
 Pressure:- 8 Bar Gauge (0.9 MPa absolute)

Table 2

Catalyst (% w/w Co)	Example 2 - 33.3% w/w Co
Temperature (°C)	205
CO Conversion (%)	31
Selectivity to Organic Products (%)	98
" " Carbon Dioxide (%)	2
Alpha Factor	0.81

(b) GHSV:- 1000 h⁻¹
 H₂:CO:- 2:1
 Pressure:- 8 Bar Gauge (0.9 MPa absolute)

Table 3
Comparative Tests

5	Temperature	(°C)	222	241
	CO Conversion	(%)	60	99
	Selectivity to organic products	(%)	88	84
	" " carbon dioxide	(%)	12	16
	Alpha Factor		0.87	0.72

10 (a) GHSV:- 500 h⁻¹
 H₂:CO:- 2:1
 Pressure:- 8 Bar gauge (0.9 MPa absolute)

Table 4
Comparative Tests

15	Temperature	(°C)	195	256	270
	CO Conversion	(%)	0	59	81
	Selectivity to organic products	(%)	-	90	50
	" " carbon dioxide	(%)	-	10	50
20	Alpha Factor		-	0.77	0.57

(b) GHSV:- 1000 h⁻¹
 H₂:CO:- 2:1
 Pressure:- 8 Bar gauge (0.9 MPa absolute)

25 Example 3

A sample of graphitised carbon support (as used in Example 1) was impregnated with chloroplatinic acid from aqueous solution. The technique of impregnation and drying was similar to that described for cobalt impregnation in Example 1. The quantity of
 30 chloroplatinic acid used was such that 10g of carbon support were treated with 0.2g of platinum (giving a nominal metal loading of 1.9% w/w).

The dried catalyst was reduced in a stream of flowing hydrogen at atmospheric pressure, 200°C for 5 hours. It was then purged with
 35 nitrogen and re-impregnated with cobalt nitrate as described in Example 1. The quantities used were such that 10g of the platinum/carbon catalyst were treated with 2g of cobalt (nominal metal loading of the finished catalyst 16.7% w/w cobalt and 1.7% w/w platinum).

The catalyst was then reduced and tested as in Example 1, the results being shown in Table 5.

Table 5

5	Temperature	(°C)	203	221	230
	CO Conversion	(%)	39	75	99
	Selectivity to Organic Products	(%)	99	95	83
	" " Carbon Dioxide	(%)	1	5	17
10	Alpha Factor		0.98	0.81	0.71

GHSV:- 500 h⁻¹

H₂:CO:- 2:1

Pressure:- 6 Bar Gauge (0.7 MPa absolute)

The benefits of the platinum addition to the cobalt catalyst are clearly demonstrated by comparison with Table 6. This shows typical performance data obtained under similar test conditions from a 16.7% w/w cobalt catalyst prepared by the technique used in Example 1.

Table 6

20	Temperature	(°C)	199	212	231	246
	CO Conversion	(%)	15	38	76	99
	Selectivity to Organic Products	(%)	100	99	94	79
25	Selectivity to Carbon dioxide	(%)	0	1	6	21
	Alpha Factor		0.94	0.91	0.79	0.62

GHSV:- 500 h⁻¹

30 H₂:CO:- 2:1

Pressure:- 6 Bar Gauge (0.7 MPa absolute)

It may be seen by comparison of Tables 5 and 6 that the effect of platinum addition to the cobalt catalyst is to increase the CO conversion achieved at a particular temperature, with other aspects of catalyst performance largely unchanged.

Example 4

A catalyst containing 16.7% w/w iron and 0.8% w/w platinum was prepared from ferric nitrate using the technique described for Example 3. The performance data for this catalyst is presented in Table 7.

Table 7

Temperature	(°C)	200	216	226	237	251
CO Conversion	(%)	10	20	37	58	91
Selectivity to Organic Products	(%)	81	68	62	64	53
Selectivity to Carbon dioxide	(%)	19	32	38	36	47
Alpha Factor		0.74	0.65	0.61	0.58	0.58

GHSV:- 500 h⁻¹

H₂:CO:- 2:1

Pressure:- 6 Bar Gauge (0.7 MPa absolute)

The benefit of the platinum addition may be seen by comparison with a similar catalyst in which the platinum was omitted.

Table 8

Temperature	(°C)	226	249	264
CO Conversion	(%)	11	40	70
Selectivity to Organic Products	(%)	71	65	59
" " Carbon Dioxide	(%)	29	35	41
Alpha Factor		0.63	0.58	0.56

GHSV:- 500 h⁻¹

H₂:CO:- 2:1

Pressure:- 6 Bar Gauge (0.7 MPa absolute)

Comparison of Tables 7 and 8 shows that, as in the case of Example 3, the effect of platinum addition is primarily to increase the catalyst activity (CO conversion achieved at a particular temperature).

Comparative Test B

This is a comparative experiment not according to the invention.

A catalyst was prepared as in Example 3 containing 16.7% wt/wt cobalt and 1.7% wt/wt platinum. However the carbon used as support was not a carbon having the surface area characteristics required for the present invention. It was instead a commercial available activated carbon supplied by BDH Chemicals Ltd, Poole, England, and had the following surface area characteristics.

	Basal plane surface area:	128 m ² g ⁻¹
	BET surface area:	1020 m ² g ⁻¹
	Edge surface area:	30 m ² g ⁻¹
10	BET/based plane:	8
	Basel plane/edge:	4.3

The catalyst was tested as in Example 3 at a gas hourly space velocity of 500 hr⁻¹, an H₂:CO molar ratio of 2:1 a pressure of 6 bar gauge (0.7 MPa absolute), and at various temperatures.

15 The results are shown in Table 9.

Table 9

	Temperature	(°C)	203	230	220
	CO Conversion	(%)	7.6	16.1	11.0
20	Selectivity to Organics	(%)	87.4	92.7	90.4
	Selectivity to CO ₂	(%)	12.6	7.3	9.6
	Alpha Factor		0.54	0.56	0.55

GHSV:- 500 h⁻¹
 25 H₂:CO:- 2:1
 Pressure:- 6 Bar Gauge (0.7 MPa absolute)

A Comparison of Table 9 shows the very much greater conversion and higher alpha factor obtained using the catalysts according to the invention.

30 A comparison of Table 9 with Tables 3 and 4 shows that the performance of the catalyst supported on active carbon is very much inferior to that obtained using a conventional oxide support. No skilled person studying the results obtained with activated carbon would believe that carbon was a satisfactory support for
 35 Fischer-Tropsch catalysts.

Claims:

1. A Fischer-Tropsch catalyst comprising cobalt or iron on a support characterised in that the support is a carbon having a BET surface area of at least $100 \text{ m}^2/\text{g}$, a ratio of BET to basal plane surface area not greater than 4:1, and a ratio of basal plane surface area to edge surface area of at least 10:1.
5
2. A process according to claim 1 wherein the carbon has a BET surface area of at least $200 \text{ m}^2/\text{g}$.
3. A process according to either one of claims 1 or 2 wherein the carbon has a ratio of basal plane to surface area to edge surface area of at least 100:1.
10
4. A process according to any one of the preceding claims wherein the ratio of BET to basal plane surface area is not greater than 2.5:1.
5. A process according to claim 4 wherein the ratio is not greater than 1.5:1.
15
6. A process according to any one of the preceding claims wherein the catalyst also contains platinum.
7. A process according to any one of the preceding claims wherein the quantity of platinum is in the range 0.2% to 10% by weight of the total catalyst.
20
8. A process according to any one of the preceding claims wherein the catalyst has a content of cobalt or iron in the range 5 to 100% wt, based on weight of carbon.
9. A process for the production of hydrocarbons which comprises bringing a mixture of carbon monoxide and hydrogen into contact with a catalyst according to any one of the preceding claims at a temperature in the range 150 to 300°C and a pressure in the range 0.1 to 5 MPa.
25



10. A process according to claim wherein the molar ratio of hydrogen to carbon monoxide is in the range 3:1 to 1:1.

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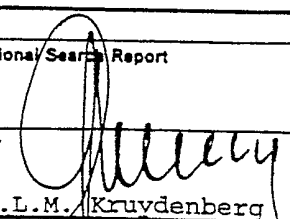
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INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 85/00378

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		
IPC ⁴ : C 07 C 1/04; B 01 J 35/10; B 01 J 23/74; B 01 J 23/89		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁴	C 07 C; B 01 J	
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 ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	GB, A1, 565074 (BRITISH PETROLEUM) 16 April 1980, see claims 1,2; page 3, lines 7,8; examples	1,6,7
X	(cited in the application) --	2-5,8
P,Y	EP, A, 0128302 (ALLIED CORPORATION) 19 December 1984, see claims 1,8	1
X	--	8-10
X	FR, A, 947385 (STANDARD OIL) 10 January 1944, see page 1, lines 51 to 57 --	10
A	US, A, 4088671 (GULF RESEARCH & DEVELOPMENT CO.) 9 May 1978 (cited in the application) --	
Y	EP, A, 0016851 (THE DOW CHEMICAL) 15 October 1980, see claim 1 --	6,7
P,Y	US, A, 4478954 (STANDARD OIL) 23 October 1984, see claim 1 -----	1
<p>¹⁰ Special categories of cited documents:</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> <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>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
4th December 1985	26 DEC. 1985	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	 G.L.M. Kruidenberg	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/GB 85/00378 (SA 10465)

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 18/12/85

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A- 565074		None	
EP-A- 0128302	19/12/84	US-A- 4468474 AU-A- 2763084 JP-A- 59222229 US-A- 4554291	28/08/84 22/11/84 13/12/84 19/11/85
FR-A- 947385		US-A- 2512608	
US-A- 4088671	09/05/78	None	
EP-A- 0016851	15/10/80	None	
US-A- 4478954	23/10/84	US-A- 4513096	23/04/85

For more details about this annex :
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