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PROCESS AND CATALYST FOR THE SELECTIVE HYDROGENATION OF BUTINE DIOL TO BUTENE DIOL

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(56) Prior Art Documents
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EP 0312253

(57)

It has now been found, surprisingly, that copper- and zinc-doped palladium on aluminum oxide catalysts have significantly higher selectivity in the novel process than a catalyst containing only palladium and copper. This allows a significant increase in the butenediol yield. In particular, these Pd/Zn/Cu catalysts allow the total amount of the byproducts butynediol, butanediol and acetals in the novel process to be reduced to a level below that of the $Pd/Zn/Al_2O_3$ and $Pd/Zn/Cd/Al_2O_3$ catalysts of the prior art.

Claim

1. A process for the preparation of 2-butene-1,4-diol by hydrogenation of butynediol in the presence of a palladium catalyst, wherein a catalyst is used which, in addition to palladium, contains the elements zinc and copper or zinc and silver or zinc and copper and silver.

2. A process as claimed in claim 1, wherein a palladium supported catalyst having a palladium content of from 0.1 to 7% by weight, calculated as Pd and based on the total weight of the catalyst, is used.

.../2

7. A process as claimed in any of claims 1 to 6, wherein a palladium supported catalyst on a support of aluminum oxide, calcium carbonate, magnesium oxide, spinel, barium sulfate, titanium dioxide, zirconium dioxide or mixtures thereof is used.

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(54) Title: PROCESS AND CATALYST FOR THE SELECTIVE HYDROGENATION OF BUTINE DIOL TO BUTENE DIOL

(54) Bezeichnung: VERFAHREN UND KATALYSATOR ZUR SELEKTIVHYDRIERUNG VON BUTINDIOL ZU BUTENDIOL

(57) Abstract

A process is disclosed for the selective hydrogenation of butine-2-diol(1,4) to butene-2-diol(1,4) using a palladium catalyst to which copper and zinc or silver and zinc are added as doping agents. In the preferred embodiment, it has been possible, by optimizing the composition of the catalyst, to improve the activity and selectivity of the catalysts in question while also eliminating the need to handle toxic substances during the catalyst manufacturing process.

(57) Zusammenfassung

Die vorliegende Erfindung beschreibt ein Verfahren zur selektiven Hydrierung von Butin-2-diol(1,4) zu Buten-2-diol(1,4) mit Hilfe eines Palladiumkatalysators, der mit Kupfer und Zink bzw. Silber und Zink dotiert ist. Bei der bevorzugten Ausführungsform ist es gelungen, durch Optimierung der Katalysatorzusammensetzung die Aktivität und Selektivität der Katalysatoren zu steigern und gleichzeitig die Handhabung toxischer Stoffe bei der Katalysatorherstellung und -verwendung zu vermeiden.

BASF Aktiengesellschaft

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Process and catalyst for the selective hydrogenation of butynediol to butenediol

2-Butene-1,4-diol (referred to below as "butenediol") has been produced for some time on an industrial scale from 2-butyne-1,4-diol (referred to below as "butynediol"), which is produced on an industrial scale by the Reppe synthesis. Butenediol is required for some important crop-protection agents, pharmaceuticals and intermediates. It is of great importance that a very pure hydrogenation product is obtained, since product losses must be avoided and distillative removal of unhydrogenated butynediol and of butanediol formed by overhydrogenation is only possible in a complex procedure.

The catalytic hydrogenation of butynediol to butenediol is generally carried out batchwise using a suspension catalyst. In this process, hydrogen at 30-150°C and 1-20 bar is injected into a stirred reactor containing the butynediol solution and catalyst. The reaction is terminated when the stoichiometric amount of hydrogen has been taken up. Numerous proposals have been made regarding the catalysts, in particular palladium catalysts, and some have also been implemented in industry.

In order to achieve adequate selectivity, $Pd/BaSO_4$ catalysts with addition of quinoline (DE 1 115 238), Pd/Al_2O_3 catalysts with addition of carbon monoxide (DE 2 619 660) and Pd/Cu and Pd/Al_2O_3 catalysts with addition of copper acetate (GB 832 141) have been proposed.

However, soluble additives are inconvenient to handle and cause problems during work-up. Metering in of CO, as described in DE 2619 660, requires additional technical complexity and should therefore be avoided.

According to information in patents, good results have also been achieved with the following catalysts:

5% of $Pd/BaSO_4$ DE 2 605 241

5% of Pd/Al_2O_3 doped with lead acetate DE 2 818 260

5% of $Pd/BaSO_4$ with addition of copper nitrate DD 246 986

In spite of the use of high-percentage catalysts (5% of Pd), long hydrogenation times were necessary for these hydrogenations.

DE 2 431 929 describes catalysts containing only 0.5% of Pd on Al_2O_3 with zinc, cadmium, bismuth and tellurium doping. The catalysts have good selectivity, but have the disadvantage of containing carcinogenic or toxic constituents.

A particular difficulty arises if crude butynediol is to be employed in the selective hydrogenation without prior purification. This material having a pH of about 5 contains methanol, formaldehyde, formic acid and propargyl alcohol. It also contains catalyst constituents, such as Cu and Bi, from the butynediol synthesis. The catalyst thus also needs to have substantial tolerance to these constituents of the starting material, although it is known that both added copper (cf. DD 246 986) and added bismuth (cf. DE 2 431 929) affect the hydrogenation.

In spite of the extensive prior art, there is a desire for a further improvement in the process for the selective hydrogenation of butanediol and in the catalyst which can be used for this purpose. The invention has the object of solving the following problems or part-problems - individually or in combination:

1. No toxic or carcinogenic substances, such as, for example, compounds of tellurium or cadmium, should be employed in the preparation of the catalyst.
2. The highest possible selectivity should be achieved in order to minimize product losses, in particular due to overhydrogenation and

acetal formation.

3. A high catalyst activity should be achieved in order to reduce the amount of catalyst employed, based on the amount of butynediol to be reacted.
4. Simple handling of the catalyst, in particular good filterability, should be achieved.
5. It should also be possible to carry out the selective hydrogenation using crude butynediol (in particular having a pH of 5).
6. It should also be possible to carry out the selective hydrogenation in the presence of one or more of the following contaminants: methanol, formaldehyde, formic acid, propargyl alcohol or Cu and/or Bi, which can originate, for example, from the butynediol synthesis.
7. Tolerance of the catalyst to constituents of the starting material.

These problems or part-problems of the invention are solved by means of processes and catalysts as defined in the claims. Preferred embodiments of the invention are shown in the subclaims and in the following description and the examples. In addition to palladium and zinc, the catalyst according to the invention also contains copper or silver, but expediently contains no cadmium. With respect to its active constituents, the catalyst preferably consists of these elements (Pd + Zn + [Cu and/or Ag]) and contains no other active constituents. The preferred catalyst is a supported palladium catalyst containing said active constituents. All amounts regarding metal oxides herein should be regarded as amounts based on the metal as the relevant oxide. The actual structure may differ from that stated.

In accordance with the invention, a process has been found for the preparation of 2-butene-1,4-diol by selective hydrogenation of butynediol in the presence of a palladium catalyst, wherein, in addition to palladium, the catalyst also contains the elements zinc and copper or zinc and silver

or zinc and copper and silver.

The supported catalyst which can be used according to the invention for the hydrogenation of butyne-1,4-diol to butene-1,4-diol generally contain from 0.1 to 7% by weight of palladium, preferably from 0.1 to 4% by weight of palladium, in each case calculated as Pd and based on the total weight of the catalyst, in their catalytically active material. As further catalytically active elements, the catalyst to be used according to the invention also contains, in addition to palladium, the elements zinc and copper or zinc and silver or zinc and copper and silver.

In addition to palladium in the abovementioned amounts, catalysts which can be used according to the invention and which comprise the catalytically active components palladium, zinc and copper in their catalytically active material contain the two other elements in amounts which correspond to a palladium:zinc atomic ratio of, generally, from 10:1 to 1:4 and a zinc:copper atomic ratio of, generally, 5:1 to 1:2.

In addition to palladium in the abovementioned amounts, catalysts which can be used according to the invention and which comprise the catalytically active components palladium, zinc and silver in their catalytically active material contain the elements zinc and silver in amounts which correspond to a palladium:zinc atomic ratio of, generally, from 10:1 to 1:4 and a zinc:silver atomic ratio of, generally, 5:1 to 1:2.

In addition to palladium in the abovementioned amounts, catalysts which can be used according to the invention and which comprise the catalytically active components palladium, zinc, copper and silver in their catalytically active material contain the elements zinc, copper and silver in amounts which correspond to a palladium:zinc atomic ratio of, generally, from 10:1 to 1:4, a zinc:copper atomic ratio of, generally, from 5:1 to 1:2 and a zinc:silver atomic ratio of, generally, 5:1 to 1:2.

The catalysts which can be used according to the invention are

supported catalysts. Preferred supports are materials of low acidity or basic supports. Examples of advantageous support materials are aluminum oxides, calcium carbonate, magnesium oxide, spinel ($MgAl_2O_4$), barium sulfate, titanium dioxides and zirconium dioxide. The catalysts which can be used according to the invention can also be prepared using mixtures of these support materials. A particularly preferred support material is aluminum oxide, in particular δ-aluminum oxide, which can be prepared as described in Ullmanns Encyklopädie der technischen Chemie, 4th Edn., Volume 7, pp. 298-299, Verlag Chemie, Weinheim, 1974. A particularly suitable δ-aluminum oxide support material has been found to be δ-aluminum oxide having a BET surface area of 100 to 130 m^2/g (measured by the method of C.N. Satterfield. Heterogeneous Catalysis in Practice, pp. 102-105, New York 1980) and having a particle size of from 100 to 200 μm, which has particularly good settling and filtration properties and results, when used as support material, in only low acetal and polymer formation. In general, however, the support materials used have a BET surface area of 5 to 200 m^2/g, a porosity of 0.1 to 1 ml/g, determined by water absorption, and a mean particle size of from 20 to 150 μm with a maximum particle size of up to 300 μm.

Particularly advantageous catalysts have proven to be those prepared by impregnating the support material with a solution of the catalytically active catalyst components. The impregnation of the support can be carried out simultaneously by impregnation with a mixed solution of water-soluble salts of the catalytically active components, preferably with a solution of their nitrates or acetates, or by sequential impregnation with solutions of in each case one of these salts, the impregnated support expediently being dried after the individual impregnation steps. The impregnation can be accomplished by treating the support material with a supernatant solution of these salts, particularly advantageously by adding a mixed solution to the support in a rotating drum, it being advantageous

to use an amount of solution which corresponds to the pore volume of the support. After drying and, if desired, calcination, in general at from 300 to 600°C, preferably at from 400 to 550°C, the catalyst can be employed in the novel process. The catalysts can be activated before use in the novel process, for example by treatment with hydrogen or other reducing agents, such as hydrazine, but this is generally unnecessary since these catalysts can advantageously be reduced and activated in situ in the reaction mixture.

It has now been found, surprisingly, that copper- and zinc-doped palladium on aluminum oxide catalysts have significantly higher selectivity in the novel process than a catalyst containing only palladium and copper. This allows a significant increase in the butenediol yield. In particular, these Pd/Zn/Cu catalysts allow the total amount of the byproducts butynediol, butanediol and acetals in the novel process to be reduced to a level below that of the $Pd/Zn/Al_2O_3$ and $Pd/Zn/Cd/Al_2O_3$ catalysts of the prior art.

Other very selective catalysts in the novel process have proven to be silver- and zinc-doped palladium on aluminum oxide catalysts. The use of basic supports, such as calcium carbonate or magnesium oxide, allows a further increase in the yield to be achieved in the novel process, the amount of acetal byproducts formed being further reduced.

These catalysts achieve the objects of the novel process. In particular, the use of these catalysts allows particularly high space-time yields to be achieved and the formation of byproducts to be minimized. In addition, they are easy to handle with respect to environmental protection and workplace safety.

The selective hydrogenation of butynediol to butenediol can be carried out by means of the catalysts to be used in accordance with the invention by hydrogenation techniques which are conventional per se. The catalysts are preferably employed in suspended form in the reaction mixture. The

hydrogenation can be carried out at atmospheric pressure or under superatmospheric pressure. In general, a pressure of from 1 to 20 bar, preferably from 1 to 10 bar, and a temperature of, generally, from 20 to 150°C, preferably from 50 to 120°C, are used.

The starting material used can be pure butynediol or solutions thereof in a suitable solvent, for example water, but the novel process is preferably carried out using crude butynediol solution as produced, for example, in the butynediol preparation by the Reppe method. This crude butynediol generally contains about 50% by weight of water, from 1.5 to 2.5% by weight of impurities from the Reppe synthesis. Although these impurities tend to form byproducts and tar-like residues during hydrogenation, this formation of byproducts and residues can be minimized with the aid of the catalysts to be used in accordance with the invention.

The hydrogen can be fed to the hydrogenation reactor, preferably a stirred reactor with gas dispersion stirrer, in a stoichiometric or excess amount, preferably a stoichiometric amount, with respect to the butynediol.

For work-up, the reaction mixture is generally distilled, expediently after prior removal of the catalyst, for example by filtration or centrifugation.

It is expedient here first to remove water and an initial cut containing predominantly allyl alcohol. This is expediently followed by removal of the butenediol together with the byproducts butanediol, butynediol and acetals from the high-boiling residue by distillation, after which the butenediol can be isolated in a final purification distillation step.

The novel process can be carried out either batchwise, for example in stirred autoclaves, or continuously, for example in stirred reactor cascades. The process is preferably carried out batchwise.

Examples

The % by weight data in the examples are based on the entire catalyst as 100% by weight.

Catalyst A (Comparative example)

5 kg of δ-Al_2O_3 having a particle size of 100-200 μm were introduced into a rotating drum and sprayed with a mixed solution of palladium nitrate and copper nitrate. The amount of solution was calculated so that the pores of the support were filled; about 2500 ml of solution were required for 5 kg of the support. When all the solution had been taken up, the catalyst was dried at 120°C and calcined at 500°C. Its composition was:

0.5% by weight of Pd

0.25% by weight of CuO

Remainder Al_2O_3

Catalyst B (Comparative example)

The procedure was as in the preparation of catalyst A, but a mixed solution of palladium nitrate and zinc nitrate was used for the impregnation. The catalyst composition was:

0.5% by weight of Pd

0.25% by weight of ZnO

Remainder Al_2O_3.

Catalyst C (Comparative example)

The procedure was as in the preparation of catalyst A, but a mixed solution of palladium nitrate, cadmium nitrate and zinc nitrate was used for the impregnation. The catalyst composition was:

0.5% by weight of Pd

0.11% by weight of CdO

0.12% by weight of ZnO

Remainder Al_2O_3.

Catalyst D

The procedure was as in the preparation of catalyst A, but a mixed solution of palladium nitrate, copper nitrate and zinc nitrate was used for the impregnation. The catalyst composition was:

0.5% by weight of Pd

0.12% by weight of CuO

0.12% by weight of ZnO

Remainder Al_2O_3.

Catalyst E

The procedure was as in the preparation of catalyst A, but a mixed solution of palladium nitrate, silver nitrate and zinc nitrate was used for the impregnation. The catalyst composition was:

0.5% by weight of Pd

0.11% by weight of Ag_2O

0.12% by weight of ZnO

Remainder Al_2O_3.

Catalyst F

The procedure was as in the preparation of catalyst D, but pulverulent, precipitated calcium carbonate was impregnated. The amount of solution required was about 2500 ml for 5 kg of support. The catalyst composition was:

0.5% by weight of Pd

0.11% by weight of CuO

0.11% by weight of ZnO

Remainder $CaCO_3$

Catalyst G

The procedure was as in the preparation of catalyst D, but precipitated magnesium oxide which had been converted to a particle size of 100-300 μm by compaction and screening was impregnated. The catalyst composition was:

0.5% by weight of Pd

0.10% by weight of CuO

0.10% by weight of ZnO

Remainder MgO.

Table 1 Catalyst testing (small autoclave)

Catalyst	Active components	Support	Hydrogenation time min.
A Comparison	Pd/Cu	Al_2O_3	87
B Comparison	Pd/Zn	Al_2O_3	62
C Comparison	Pd/Zn/Cd	Al_2O_3	86
D Invention	Pd/Zn/Cu	Al_2O_3	48
E Invention	Pd/Zn/Ag	Al_2O_3	69
F Invention	Pd/Zn/Cu	$CaCO_3$	59
G Invention	Pd/Zn/Cu	MgO	114

Catalyst	Byproducts in the hydrogenation product			
	Butanediol	"Acetal" area %	Butynediol area %	Total area %
A Comparison	1.30	0.3	1.60	3.2
B Comparison	3.1	0.7	0.1	3.9
C ~~Invention~~ Comparison	1.6	0.35	1.3	3.25
D Invention	1.3	0.3	0.8	2.4

E Invention	2.0	0.5	0.1	2.6
F Invention	0.9	0.14	0.1	1.14
G Invention	2.1	0.2	0	2.3

Catalyst testing

The hydrogenation experiments were carried out at 100°C and 18 bar in a small autoclave fitted with a magnetic lifting stirrer. The starting material used was 125 ml of crude butynediol solution to which 150 mg of catalyst had been added. The hydrogen consumption was monitored through the drop in pressure in the autoclave; the hydrogen it consumed was replaced periodically. Due to the difficulty in recognizing the end point in the selective hydrogenation to butenediol, somewhat higher byproduct values were generally found than in the production plant, which allows better recognition of the end point.

The hydrogenation product was analyzed by gas chromatography; the results are given in area percent. The first cut amounts were independent of the catalyst and given by the quality of the crude butynediol.

The data for the hydrogenation product are shown in Table I. The residue amounts were only measured for catalysts B, C and D and were, in each case based on 100 g of hydrogenation product:

17.5 g for catalyst B

10.8 g for catalyst C

12.9 g for catalyst D.

The results are means from five experiments.

Hydrogenation results from a production plant

Catalysts B, C and D were subjected to long-term testing on an

industrial scale. Butynediol hydrogenation was carried out batchwise by the suspension method. 1 kg of catalyst was employed per m^3 of crude butynediol.

The byproduct content, given in area percent of the gas chromatographic analysis, was determined as follows:

Catalyst	Butanediol	"Acetal"	Butynediol	Total (an+ac+in)
B	1.34%	0.47%	0.35%	2.16%
C	0.94%	0.37%	0.53%	1.84%
D	0.83%	0.33%	0.29%	1.45%

These data confirm the advantages given by using the novel catalyst D.

BASF Aktiengesellschaft

NAE19930625PC G/br
April 19, 1996

We claim:

1. A process for the preparation of 2-butene-1,4-diol by hydrogenation of butynediol in the presence of a palladium catalyst, wherein a catalyst is used which, in addition to palladium, contains the elements zinc and copper or zinc and silver or zinc and copper and silver.

2. A process as claimed in claim 1, wherein a palladium supported catalyst having a palladium content of from 0.1 to 7% by weight, calculated as Pd and based on the total weight of the catalyst, is used.

3. A process as claimed in claim 1 or 2, wherein a palladium supported catalyst is used in which the atomic ratio between the catalytically active elements is
palladium:zinc 10:1 to 1:4 and
zinc:copper 5:1 to 1:2.

4. A process as claimed in claim 1 or 2, wherein a palladium supported catalyst is used in which the atomic ratio between the catalytically active elements is
palladium:zinc 10:1 to 1:4 and
zinc:silver 5:1 to 1:2.

5. A process as claimed in claim 1 or 2, wherein a palladium supported catalyst is used in which the atomic ratio between the catalytically active elements is
palladium:zinc 10:1 to 1:4
zinc:copper 5:1 to 1:2 and
zinc:silver 5:1 to 1:2.

6. A process as claimed in any of claims 1 to 5, wherein a palladium supported catalyst is used in which the catalytically active elements have been applied to a basic or low-acidity support material.

7. A process as claimed in any of claims 1 to 6, wherein a palladium supported catalyst on a support of aluminum oxide, calcium carbonate, magnesium oxide, spinel, barium sulfate, titanium dioxide, zirconium dioxide or mixtures thereof is used.

8. A process as claimed in any of claims 1 to 7, wherein a palladium supported catalyst on a support of δ-aluminum oxide is used.

9. A process as claimed in any of claims 1 to 8, wherein the reaction is carried out at from 20 to 150°C and from 1 to 20 bar.

10. A process as claimed in any of claims 1 to 9, wherein the starting material is a solution of crude butynediol from the Reppe synthesis.

11. A process for the preparation of 2-butene-1,4-diol by hydrogenation of butynediol in the presence of a palladium catalyst, substantially as described with reference to the examples relating to Catalysts D, E, F and G.

DATED this 19th day of December, 1997.
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Abstract

A process for the selective hydrogenation of 2-butyne-1,4-diol to 2-butene-1,4-diol uses a palladium catalyst which has been doped with copper and zinc or silver and zinc. In the preferred embodiment, the activity and selectivity of the catalysts have been increased and at the same time the handling of toxic substances during preparation and use of the catalysts has been avoided by optimizing the catalyst composition.

INTERNATIONAL SEARCH REPORT

Interm al Application No
PCT/EP 95/02592

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C29/17 B01J23/89 B01J23/66 C07C33/035

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 C07C B01J

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.
A	DATABASE WPI Week 8145 Derwent Publications Ltd., London, GB; AN 81-82217D & JP,A,56 120 687 (DAINIPPON INK & CHEMICALS) , 22 September 1981 see abstract ---	1
A	DD,A,246 986 (CHEMISCHE WERKE BUNA) 24 June 1987 cited in the application see the whole document ---	1
A	DE,A,24 31 929 (BASF) 22 January 1976 cited in the application see the whole document --- -/--	1

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"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.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 October 1995	-7. 11. 95

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016	English, R

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INTERNATIONAL SEARCH REPORT

Intern. al Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 180 108 (BASF) 7 May 1986 see the whole document	1
A	EP,A,0 184 150 (BASF) 11 June 1986 see the whole document	1
A	EP,A,0 011 439 (SHIN-ETSU CHEMICAL) 28 May 1980 see examples 1-3	1
X	DE,A,24 60 078 (MAGYAR TUDOMANYOS AKADEMIA) 3 July 1975 see example 13	11
X	EP,A,0 312 253 (KAO) 19 April 1989 see page 11 - page 15; claim 1	11

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern al Application No
PCT/EP 95/02592

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
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