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NOTICE OF ENTITLEMENT

We, EXXON CHEMICAL PATENTS INC. of 5200 Bayway Drive, Baytown, TX77520, United States of America being the applicant in respect of Application No. 43948/93 state the following:-

The Person nominated for the grant of the patent has entitlement from the actual inventors by assignment.

The person nominated for the grant of the patent has entitlement from the applicants of the application listed in the declaration under Article 8 of the PCT by assignment.

The basic application listed in the declaration made under Article 8 of the PCT is the first application made in a Convention country in respect of the invention.

By our Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS

RBaddeley .... 2 April, 1997 ....

Richard H. Baddeley

Registered Patent Attorney

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USE OF ZEOLITES IN THE CONVERSION OF OXYGENATES TO HYDROCARBONS

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(56) Prior Art Documents
US 4467133

(57) Claim

1. A process for producing light olefins which comprises contacting a starting material comprising an oxygenate, or a substituted paraffin which is a halide, a mercaptan, or a sulfide or an amine, with a microporous zeolite catalyst comprising ECR-1, a mazmorite or a synthetic paulingite-type zeolite, to produce the desired light olefin product.

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(54) Title: USE OF ZEOLITES IN THE CONVERSION OF OXYGENATES TO HYDROCARBONS

(57) Abstract

A process for converting an oxygenate feed to light olefins using a microporous zeolite catalyst such as ECR-1, mazmorites, and/or ECR-18 is provided. In a preferred embodiment, the process is conducted at 440 °C to 460 °C using a methanol:water (approximately 1:4 molar ratio) feed.

USE OF ZEOLITES IN THE CONVERSION OF OXYGENATES TO HYDROCARBONS

BACKGROUND OF THE INVENTION

This invention relates to a process for using microporous solid catalysts to convert oxygenates and substituted paraffins into olefinic hydrocarbons and, more particularly, relates to a process for converting alcohols into light olefins using ECR-1, mazmorite, or ECR-18 catalysts.

Light olefins have traditionally been produced through the process of steam or catalytic cracking. Because of the limited availability and high cost of petroleum sources, the cost of producing light olefins from such petroleum sources has been steadily increasing.

The search for alternative materials for light olefin production has led to the use of oxygenates such as alcohols, and more particularly to methanol, ethanol, and higher alcohols or their derivatives. These alcohols may be produced by fermentation or from synthesis gas. Synthesis gas can be produced from natural gas, petroleum liquids, carbonaceous materials, including coal, recycled plastics, municipal wastes, or any organic material. Thus, alcohol and alcohol derivatives may provide non-petroleum based routes for the production of olefin and other related hydrocarbons.

Molecular sieves such as the microporous crystalline zeolite catalysts are known to promote the conversion of oxygenates to hydrocarbon mixtures. Numerous patents describe this process for various types of zeolite catalysts: US-A-3,928,483, 4,025,575, (Chang et al.); 4,496,786 (Santilli et al.); 4,547,616 (Avidan et al.); 4,677,243 (Kaiser); 4,843,183 (Inui); 4,499,314 (Seddon et al.); and 4,447,669 (Harmon et al.). However, none of these patents teach the conversion of oxygenates to hydrocarbons using the type of zeolite catalysts described herein.

US-A-4,467,133 (Chang, et al.) discloses the conversion of alcohols and ethers to hydrocarbons, wherein the zeolite can be paulingite. However, inclusion of Paulingite is incidental, and not intended to suggest that paulingite can be used to convert oxygenate feeds to olefins or to hydrocarbons containing substantially only light olefins. Most of the zeolites listed by Chang, et al., are well known to have no hydrocarbon porosity (such as analcite, noselite, phillipsite, datolite, leucite, scapolite, and kaolin). From this list, only faujasite, L, gmelenite, and mordenite have pores greater than 6 angstroms, fitting the constraint index qualification of column 2 lines 43 to 53. From a catalytic perspective, Chang's list of zeolites has no significance. Rather, the list apparently refers to aluminosilicates in general, and contains no indication of the olefin forming effect of the zeolites which are employed in the instant invention.

According to one aspect of the present invention there is provided a process for producing olefins which comprises: contacting an oxygenate starting material (as herein defined) with a microporous zeolite catalyst comprising ECR-1, a mazmorite or a synthetic paulingite-type zeolite, to produce the desired olefin product.

Another aspect of the invention provides the use of ECR-1, a mazmorite or a synthetic paulingite-type zeolite such as ECR-18, for converting an oxygenate starting material (as herein defined) to an olefin.

In a preferred embodiment the oxygenate starting material, also termed "feed" herein, is converted to a hydrocarbon mixture containing light olefins, i.e., enriched in light olefins compared with the starting material. Preferably the product mixture contains substantially only light olefins.

As used herein, the term "oxygenate starting material" is intended to mean not only what might be considered "true" oxygenates, e.g., alcohols, ethers, carbonyl compounds (aldehydes, ketones, carboxylic acids and the like); but also those compounds which behave in a similar fashion to "true" oxygenates in the presence of the specified zeolites, such as substituted paraffins, e.g., halides, mercaptans, sulfides, amines.

In a preferred embodiment, methanol is employed as an oxygenate feed for conversion to hydrocarbons rich in light olefins by contacting this feed with ECR-1, mazmorites, and/or paulingite-type zeolites such as ECR-18. Other oxygenate feeds may be for example, but are not limited to, dimethyl ether, ethanol, isopropanol, n-propanol or mixtures thereof. Further, a diluent may be part of the feed and may comprise water, nitrogen (N_2), hydrogen (H_2), or other hydrocarbons, including but not limited to paraffins, olefins and aromatics.

DETAILED DESCRIPTION OF THE INVENTION

The present invention employs ECR-1, mazmorite and/or synthetic paulingite-type (such as ECR-18) microporous zeolite catalysts to convert oxygenate feeds to hydrocarbons. Zeolites are microporous, crystalline-hydrated aluminosilicates of Group I and II elements interconnected through shared oxygen atoms. The rigid three-dimensional framework of silica and alumina creates a tetrahedral-shaped block which forms the primary building unit of the zeolites. Because the oxygen atoms in zeolites are shared between tetrahedra, the framework possesses a net negative charge. The net negative charge is balanced by exchangeable cations in the crystalline structure, leading to the representation:

$$M_{x/n}\,[(AlO_2)_x\,(SiO_2)_y] \bullet zH_2O$$

where M is the cation, n is the cation charge, and z represents the water of hydration. The silica-to-alumina ratio is governed by the amounts of alumina "x" and silica "y" comprising the zeolite. When M is a proton, the zeolite acquires the characteristics of a Broensted acid.

The zeolites generally have ordered, porous crystalline structures containing a small number of cavities that are interconnected by a number of still smaller channels. The cavities and channels are uniform in size within a certain type of zeolitic material. The dimensions of the pores or cavities allow for adsorption of molecules of certain dimensions while excluding molecules of larger dimensions. The crystal structure of zeolites provides a selective, constrained access to and egress from the intracrystalline free space. This phenomenon, also called "shape-selective catalysis," derives from zeolite geometry.

An important component of zeolite geometry derives from the proportions of silicon and aluminum atoms comprising the tetrahedra. The molar ratio of silica-to-alumina may be determined by conventional analysis such as wet chemical analysis (e.g., atomic absorption spectrometry or inductively coupled plasma emission spectroscopy) or by the stoichiometry of silica and alumina used in zeolite synthesis. This ratio is meant to represent, as closely as possible, the silica-to-alumina ratio in the rigid anionic framework of the zeolite crystal. Aluminum in the binder or in cationic or other form within the porous channels is not considered in calculating the silica-to-alumina ratio.

The catalytic and adsorptive properties of the zeolite may also be varied by changing the ions within the catalyst. Conventional ion exchange techniques may be used to change the cations. There are a large number of both natural and synthetic zeolitic structures. The enormity of zeolite structural permutations can be understood by considering the book Atlas of Zeolite Structures by W. M. Meier and D. H. Olson.

ECR-1 is a 12-ring synthetic zeolite. It may be formed by using bis (2-hydroxyethyl) dimethylammonium or bis (2-hydroxypropyl) dimethylammonium as an organic template. ECR-1 is described more fully in US-A-4,657,748. ECR-1 has a silica-to-alumina (Si/Al_2) molar ratio of about 5-20, and usually about 7, comparable to naturally occurring mazzite. ECR-1 has a recurrent twin structure comprising component sheets structurally characteristic of naturally occurring mordenite (which normally has a silica-to-alumina molar ratio of greater than 10) and mazzite. Thus ECR-1 represents a complex synthetic zeolite having structural similarities to both these existing natural zeolites.

Mazmorites are materials similar and related to ECR-1 and are described in US-A-4,892,721. The mazmorites are complex intergrown synthetic permutations of ECR-1.

Paulingite is a very rare mineral classified as a member of the faujasite group. Synthetic paulingite-type zeolites may be used according to the invention, for example ECR-18 which is structurally similar to the natural mineral paulingite. ECR-18 may be produced using a tetraethylammonium template. It is described in more detail in US-A-4,661,332 and 5,013,536. Like ECR-1, ECR-18 is a complex synthetic zeolite having structural similarities to naturally occurring zeolites. The pore size and adsorptive capacities of these synthetic ECR zeolites are nevertheless different from the natural zeolites.

In accordance with the process of the present invention, an oxygenate feed is catalytically converted to hydrocarbons containing aliphatic moieties such as, but not limited to, methane, ethane, ethylene, propane, propylene and other higher aliphatics and aromatics, by contacting the oxygenate feed with a preselected zeolite catalyst. The oxygenate feed comprises hydrocarbons containing aliphatic moieties such as, but not limited to, alcohols, halides, mercaptans, sulfides, amines, ethers and carbonyl compounds or mixtures thereof. The aliphatic moiety preferably contains from 1 to 10 carbon atoms, and more preferably 1 to 4 carbon atoms. Representative oxygenate starting materials include, but are not limited to methanol, isopropanol, n-propanol, ethanol, fuel alcohols, dimethyl ether, diethyl ether, methyl mercaptan, methyl sulfide, methyl amine, ethyl mercaptan, ethylchloride, formaldehyde, dimethylketone, acetic acid, n-alkylamines, n-alkylhalides, and n-alkylsulfides preferably having alkyl groups of 1 to 10 carbon atoms or mixtures thereof. In a preferred embodiment, methanol is used as the oxygenate feed.

The total charge of starting material to the reaction zone may contain additional compounds such as diluents. Thus the process may be generally conducted in the presence of one or more diluents which may be present in the oxygenate starting material in an amount between about 1 and about 99 molar percent, based on the total number of moles of all feed and diluent components fed to the reaction zone (or catalyst). Diluents include, but are not limited to, helium, argon, nitrogen, carbon monoxide, carbon dioxide, hydrogen, water, paraffins, hydrocarbons (such as methane and the like), aromatic compounds, or mixtures thereof. Use of an aqueous diluent as part of the feed imparts as a non-limiting example a hydrocarbon fraction particularly rich in light olefins. In a particularly preferred embodiment of the invention, the starting material comprises an oxygenate/water feed, preferably having a molar ratio of starting material:water of from 1:3 to 1:5, more preferably having an approximate 1:4 molar ratio. Most preferably a methanol:water feed is used, especially one having an approximate 1:4 molar ratio. Even though the process described herein may employ a diluent, computable quantities of the starting material (i.e., composition and weight hourly space velocity (WHSV) are to be computed as an essentially diluent-free feed unless otherwise stated.

The feedstock flow rate affects olefin production. Increasing the feedstock flow rate (expressed as weight hourly space velocity, or WHSV) enhances the formation of olefin production relative to paraffin production. However, the enhanced olefin production relative to paraffin production is offset by a diminished conversion of oxygenate to hydrocarbons.

The process of the invention is conducted such that the oxygenate feed is contacted in a reaction zone with the zeolite catalyst at effective process conditions to produce olefinic hydrocarbons, i.e., an effective temperature, pressure, WHSV and, optionally, an effective amount of diluent, correlated to produce hydrocarbons rich in olefins. Preferably the process is conducted in the vapor phase. Alternatively, the process may be conducted in a liquid phase.

When the process is carried out in the liquid phase the process necessarily involves the separation of products formed in a liquid reaction media and can result in different conversions and selectivities of feedstock-to-product with respect to the relative ratios of the light olefin products as compared to that formed by the vapor phase process.

The process is effectively carried out over a wide range of pressures, including autogenous pressures. At pressures between about 0.001 atmospheres (0.76 torr) and about 1000 atmospheres (760,000 torr), the formation of light olefin products will be effected although the optimum amount of product will not necessarily form at all pressures. The preferred pressure is between about 0.01 atmospheres (7.6 torr) and about 100 atmospheres (76,000 torr). The pressures referred to herein for the process are exclusive of the inert diluent, if any, that is present, and refer to the partial pressure of the feedstock as it relates to oxygenate starting material and/or mixtures thereof. Pressures outside the stated range are not excluded from the scope of this invention, although such do not fall within certain desirable embodiments of the invention. At the lower and upper end of the pressure range, and beyond, the selectivities, conversions and/or rates to light olefin products may not occur at the optimum, although light olefin such as ethylene may still be formed.

The process is effected for a period of time sufficient to produce the desired light olefin products. In general, the residence time employed to produce the desired product can vary from seconds to a number of hours. It will be readily appreciated that the residence time will be determined to a significant extent by the reaction temperature, the molecular sieve selected, the WHSV, the phase (liquid or vapor) and process design characteristics selected.

The temperature which may be employed in the process may vary over a wide range depending, at least in part, on the selected molecular sieve catalyst. In general, the process can be conducted at an effective temperature of for example from 200°C (392°F) to 700°C (1292°F). Temperatures outside the stated range are not excluded, although they do not fall within certain desirable embodiments of the present invention. At the lower end of the temperature range, and thus, generally at a lower rate of reaction, the formation of the desired light olefin products may become markedly slow. At the upper end of the temperature range and beyond, the process may not form an optimum amount of light olefin products. Notwithstanding these factors, the reaction will still occur and the feedstock, at least in part, can be converted to the desired light olefin products at temperatures outside the range between about 200°C (392°F) and about 700°C (1292°F).

The processes employing ECR-1, Mazmorite, a synthetic paulingite-type zeolite such as ECR-18, or mixtures of any two or more thereof, for conversion of an oxygenate feed to hydrocarbons are preferably conducted at temperatures of from 350°C to 550°C, more preferably 400°C to 500°C, and most preferably 440°C to 460°C. The WHSV of these processes is preferably from 0.01 $hr.^{-1}$ to 100 $hr.^{-1}$, more preferably 0.1 $hr.^{-1}$ to 10 $hr.^{-1}$, and most preferably 0.8 $hr.^{-1}$ to 1.2 $hr.^{-1}$. At 0.8 $hr.^{-1}$ to 1.2 $hr.^{-1}$ WHSV, approximately 95% to 100% conversion of oxygenate feed to light olefin hydrocarbons occurs.

The following examples illustrate the invention:

Example 1

A synthetic ECR-1 zeolite catalyst was produced as described in US-A-4,657,748. The ECR-1 described in this example had a silica-to-alumina molar ratio of 7:1, determined by chemical analysis. ECR-1 was calcined at 510°C (950°F) to remove the template and the calcined material was ion-exchanged with an ammonium-nitrate solution (85°C, 185°F; 12 hrs.). Generally, the ion exchange was repeated two or three times, with a calcination at 510°C (950°F) between each ion exchange step. The catalytic conversion of oxygenate to hydrocarbons was conducted at 450°C (842° F) and at a WHSV of 1.0 $hr.^{-1}$. The feed consisted of a mixture of methanol:water (approximately 1:4 molar ratio).

The catalytic conversion of methanol to hydrocarbons was carried out in a fixed bed (1/2", 1.27 cm diameter), stainless steel reactor having three spaced zones and equipped with a 1/8" (0.32 cm) coiled preheater. In addition, the reactor was equipped with a 1/8" (0.32 cm) thermocouple well running axially through the reactor. The reactor was inserted into and heated in an Applied Test Systems 3 zone tube furnace (12", 30.5 cm long; 1 1/4", 3.18 cm I.D.). The first reactor zone is used as a preheater zone; the catalyst bed is heated in the second reactor zone. The third zone operates as a quench zone maintained at a temperature of about 200°C (392°F) to about 300°C (572°F).

Generally, 2 grams (0.07 ounces) catalyst (-14/+20 mesh) were mixed with 2.5 grams (0.09 ounces) of quartz (-20/+60 mesh); the first and third zones of the reactor were filled with quartz chips (-10/+20 mesh). To improve the heat transfer between the second reactor zone (containing the catalyst bed) and the furnace heating coils, the second reactor zone was equipped with a cylindrical (~4", 10.2 cm long; 1 1/4", 3.18 cm O.D.) aluminum or stainless steel block. This block contained a central hole for a thermocouple well in order to be able to measure the block temperature.

Gas flows (nitrogen or hydrogen) were controlled by mass flow controllers, while liquid feed rates were controlled by a Beckmann 114M pump or a Sage 341B syringe pump.

The product emerging from the bottom of the reactor was analyzed on line for (i) carbon monoxide; carbon dioxide; water; dimethyl ether; methanol; C_1-C_3 hydrocarbons, including ethylene (C_2=), propylene (C_3=), and other products (such as C_4 and higher hydrocarbons) with a Porepack Q (capillary column gas chromatography) column using a thermal conductivity detector and (ii) C_1-A_{10} hydrocarbons with a DB-1 (capillary column gas chromatography) column using a flame ionization detector. Product distribution was:

Hydrocarbon	Hydrocarbon distribution (Wt%, Excluding H_2O)
CH_4	33
$C_2=$	27
$C_3=$	11
$C_2 + C_3$	24
Other	5

Example 2

A synthetic paulingite-type zeolite catalyst (ECR-18) was produced as described in US-A-5,013,536. The ECR-18 described in this example had a silica-to-alumina molar ratio of 6.4 as determined by wet chemical analysis. ECR-18 was calcined at 510°C (950° F) and the calcined material was ion-exchanged with an ammonium-nitrate solution (85°C, 185°F; 12 hrs.). Generally, the ion exchange was repeated two or three times, with a calcination at 510°C (950°F) between each ion exchange step. The catalytic conversion of oxygenate to hydrocarbons was conducted at 450°C (842° F) and at a WHSV of 1.0 $hr.^{-1}$, in the same equipment, using the same catalyst loadings, the same reaction conditions, and the same measurement techniques as described for Example 1. Again, the feed consisted of a mixture of methanol:water (approximately 1:4 molar ratio).

Product distribution:

Hydrocarbon	Hydrocarbon distribution (Wt%, Excluding H_2O)
CH_4	7
$C_2=$	38
$C_3=$	30
$C_2 + C_3$	7
Other	18

CLAIMS:

1. A process for producing light olefins which comprises contacting a starting material comprising an oxygenate, or a substituted paraffin which is a halide, a mercaptan, or a sulfide or an amine, with a microporous zeolite catalyst comprising ECR-1, a mazmorite or a synthetic paulingite-type zeolite, to produce the desired light olefin product.

2. A process according to Claim 1, wherein the light olefin product comprises a hydrocarbon mixture containing substantially only light olefins.

3. A process according to Claim 1 or 2, wherein the light olefin comprises ethylene or propylene.

4. A process according to any preceding claim, wherein the synthetic paulingite-type zeolite comprises ECR-18.

5. A process according to any preceding claim, wherein the oxygenate starting material comprises an alcohol, an ether or a carbonyl compound.

6. A process according to Claim 5, wherein the oxygenate starting material comprises methanol, dimethyl ether, diethyl ether, isopropanol, n-propanol, ethanol, or a mixture of any two or more thereof.

7. A process according to any preceding claim, wherein the starting material additionally includes a diluent.

8. A process according to Claim 7, wherein the diluent comprises helium, argon, nitrogen, carbon monoxide, carbon dioxide, hydrogen, water, a hydrocarbon (preferably paraffinic or aromatic), or a mixture of any two or more thereof.

9. A process according to Claim 8, wherein the diluent is water and the molar ratio of starting material to water is from 1:3 to 1:5, preferably approximately 1:4.

10. A process according to any preceding claim, wherein the catalyst and starting material are contacted at a temperature of from 350°C (662° F) to 550°C (1022°F), preferably from 400°C (752°F) to 500°C (932° F), more preferably from 440°C (824°F) to 460°C (860°F).

11. A process according to any preceding claim, when performed at a weight hourly space velocity (WHSV) of from 0.01 hr. $^{-1}$ to 100 hr. $^{-1}$, preferably from 0.8 hr. $^{-1}$ to 10 hr. $^{-1}$, more preferably from 0.8 hr. $^{-1}$ to 1.2 hr. $^{-1}$.

12. A process according to any preceding claim when performed at a pressure of from 0.001 atmospheres (0.76 torr), to 1000 atmospheres (760,000 torr), preferably from 0.01 atmospheres (7.6 torr) to 100 atmospheres (76,000 torr).

13. A process according to Claim 1, comprising: contacting a methanol/water starting material (preferably in approximately 1/4 molar ratio) with ECR-1 or a synthetic paulingite-type zeolite comprising ECR-18, at a temperature of from 440°C to 460°C, a WHSV of 0.8 hr. $^{-1}$ to 1.2 hr. $^{-1}$ and a pressure of between 0.01 atmospheres (7.6 torr) and 100 atmospheres (76,000 torr) to produce a light olefin enriched hydrocarbon mixture.

14. The use of ECR-1, a mazmorite or a synthetic paulingite-type zeolite such as ECR-18, for converting a starting material comprising an oxygenate, or a substituted paraffin which is a halide, a mercaptan, a sulfide or an amine, to a light olefin.

13. A process according to claim 1 comprising: contacting a methanol/water starting material (preferably in approximately 1:4 molar ratio) with ECR-1 or a synthetic paulingite-type zeolite comprising ECR-18, at a temperature of from 440°C to 460°C, a WHSV of 0.8 hr.$^{-1}$ to 1.2 hr.$^{-1}$ and a pressure of between 0.01 atmospheres (7.6 torr) and 100 atmospheres (76,000 torr) to produce the light olefin enriched hydrocarbon mixture.

DATED this 2nd day of April, 1997

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INTERNATIONAL SEARCH REPORT

International Application No PCT/US 93/05053

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 C07C11/02; C07C1/20; C07C1/26; C07C1/32

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C07C

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]
A	US,A,4 467 133 (CHANG ET AL) 21 August 1984 cited in the application -----	

° Special categories of cited documents : [10]

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

"E" earlier document but published on or after the international filing date

"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)

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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

"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

IV. CERTIFICATION

Date of the Actual Completion of the International Search 25 AUGUST 1993	Date of Mailing of this International Search Report -3. 09. 93
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer J. VAN GEYT

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9305053
SA 75271

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
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4467133	21-08-84	None	

EPO FORM P0479

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82