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54 Process for the production of hydrocarbon oil distillates.

57 Distillates are produced from asphaltenes-containing hydrocarbon mixtures by a process comprising subjecting the hydrocarbon mixtures (101) to a catalytic hydrotreatment (106), and subjecting the distillation residue (102) of the hydroconverted product to a combination of solvent deasphalting (107) thermal cracking (108).

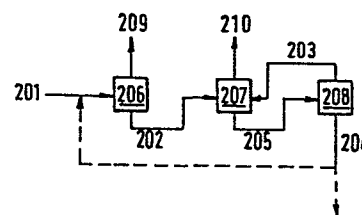
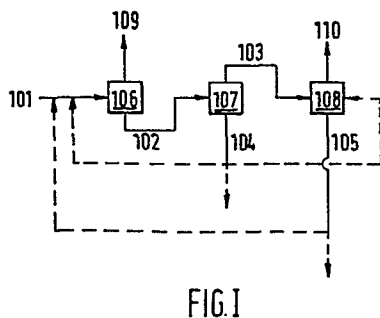
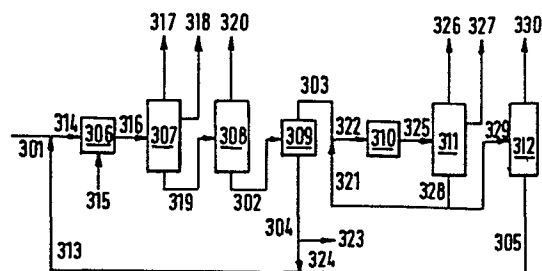


FIG II

FIG. III



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PROCESS FOR THE PRODUCTION OF HYDROCARBON
OIL DISTILLATES

The invention relates to a process for the production of hydrocarbon oil distillates from asphaltenes-containing hydrocarbon mixtures.

In the atmospheric distillation of crude mineral oil for the preparation of light hydrocarbon oil distillates, such as gasoline, kerosene and gas oil, an asphaltenes-containing residue is formed as a by-product. In the beginning these atmospheric residues (which in addition to asphaltenes, usually contain a considerable percentage of sulphur and metals) were used as fuel oil.

In view of the growing demand for light hydrocarbon oil distillates and the shrinking reserves of crude mineral oil, various treatments have already been proposed which aimed at converting atmospheric residues into light hydrocarbon oil distillates. For instance, the atmospheric residue may be subjected to thermal cracking. Further, the atmospheric residue may be separated by vacuum distillation into a vacuum distillate and a vacuum residue, the vacuum distillate may be subjected to thermal cracking or to catalytic cracking in the presence or in the absence of hydrogen and the vacuum residue to thermal cracking. Finally, the vacuum residue may be separated by solvent deasphalting into a deasphalted oil and an asphaltic bitumen, the deasphalted oil may be subjected to thermal cracking or to catalytic cracking in the presence or in the absence of hydrogen, and the asphaltic bitumen to thermal cracking.

Thermal cracking (TC) refers to a process wherein a heavy feedstock is converted into a product which contains less than 20% w C₄⁻ hydrocarbons and from which one or more distillate fractions may be separated as the desired light product and a heavy fraction as a by-product. TC has proved in actual practice to be a suitable treatment for the production of hydrocarbon oil distillates from a variety of asphaltenes-containing hydrocarbon mixtures.

It has now been investigated whether combining the TC treatment with pretreatment of the heavy feedstock and/or aftertreatment of the heavy fraction separated from the product of thermal cracking, and using at least part of the aftertreated heavy fraction as feed for the TC treatment, might yield a better result than employing nothing but the TC. In the assessment of the results the yield of light product is most important. The qualities of the light and heavy product are also of importance. In this context the quality of the light product is taken to be its suitability for processing into a valuable light fuel oil. This suitability will be greater according as the light product has, among other things, lower sulphur and olefin contents. In this context the quality of the heavy product is taken to be its suitability for use as a fuel oil component. This suitability will be greater according as the heavy product has among other things, lower metal and sulphur contents and lower viscosity and density. As pretreatments for the feed of the TC treatment and as aftertreatments for the heavy fraction of the TC product the following treatments were investigated: solvent deasphalting (DA) in which an asphaltenes-containing feed is converted into a product from which a deasphalted oil fraction and an asphaltic bitumen fraction are separated, and catalytic hydrotreatment (HT) in which an asphaltenes-containing feed is converted into a product having a reduced asphaltenes content from which can be separated one or more distillate fractions as the desired light product and a heavy fraction.

During the investigation a comparison was made between the results which can be obtained when equal quantities of an asphaltenes-containing hydrocarbon mixture are used as the starting material in the preparation of a hydrocarbon oil distillate having a given boiling range and a heavy by-product by using

- a) nothing but TC,
- b) TC combined with DA,
- c) TC combined with HT and
- d) TC combined with both DA and HT,

the conditions of the various treatments being as similar as possible. In view of the quantity and quality of the hydrocarbon oil distillate and the quality of the heavy by-product to be obtained in each of the procedures, the various procedures may be
 5 arranged as follows:

Quantity of hydrocarbon oil distillate	d	>c	>b	>a
Quality of hydrocarbon oil distillate	c	>d	>a	>b
Quality of heavy by-product	c	>d	>a	>b

Taking into account the considerable difference in yield of
 10 hydrocarbon oil distillate obtained using procedures c) and d) and the no more than slight differences between the qualities of the hydrocarbon oil distillates and the heavy by-products obtained using procedures c) and d), a procedure in which a combination of a TC treatment, a DA treatment and a HT is used is much preferred.

15 As regards the order in which the three treatments are carried out and also the feeds used for each of the three treatments, a number of embodiments may be considered. In all the embodiments the deasphalted oil fraction which is separated from the product of the DA treatment is used as the feed or a feed
 20 component for the TC treatment. Each of the embodiments may be placed in one of the following three classes:

I First, the asphaltenes-containing feed is subjected to a HT, from the product thus formed a heavy fraction is separated and subjected to a combination of a DA treatment and a TC
 25 treatment.

II First, the asphaltenes-containing feed is subjected to a DA treatment, from the product thus obtained a deasphalted oil fraction and an asphaltic bitumen fraction are separated and these are both subjected to a combination of a TC treatment
 30 and a HT.

III First, the asphaltenes-containing feed is subjected to a TC treatment, from the product thus obtained a heavy fraction is separated and subjected to a combination of a HT and a DA treatment.

5 The embodiments belonging to class I form the subject matter of the present patent application. The embodiments belonging to classes II and III form the subject matter of Netherlands Patent Applications 8105660 and 8201119.

The embodiments to which the present patent application
10 relates may further be subdivided depending on whether the heavy fraction separated from the product from the HT is used as feed for the DA treatment (class IA), or as a feed component for the TC (class IB). In the embodiments belonging to class IB the heavy fraction separated from the TC treatment is used as feed for the
15 DA treatment.

The present patent application therefore relates to a process for the production of hydrocarbon oil distillates from asphaltenes-containing hydrocarbon mixtures, in which an asphaltenes-containing hydrocarbon mixture (stream 1) is subjected to a catalytic hydro-
20 treatment (HT) in which an asphaltenes-containing feed is converted into a product having a reduced asphaltenes content from which one or more distillate fractions and a heavy fraction (stream 2) are separated, in which stream 2 is subjected to a combination of the following two treatments: solvent deasphalting
25 (DA) in which an asphaltenes-containing feed is converted into a product from which a deasphalted oil fraction (stream 3) and an asphaltic bitumen fraction (stream 4) are separated and thermal cracking (TC) in which one feed or two individual feeds are converted into a product which contains less than 20% w C_4^-
30 hydrocarbons and from which one or more distillate fractions and a heavy fraction (stream 5) are separated, in which stream 3 is used as the feed or as a feed component for the TC treatment and in which stream 2 is used either as a feed component for the TC

treatment with stream 5 being used as the feed for the DA treatment, or as the feed for the DA treatment.

In the process according to the invention the feed used is an asphaltenes-containing hydrocarbon mixture. A suitable parameter for the assessment of the asphaltenes content of a hydrocarbon mixture as well as of the reduction of the asphaltenes content which appears when an asphaltenes-containing hydrocarbon mixture is subjected to a HT, is the Ramsbottom Carbon Test value (RCT). The higher the asphaltenes content of the hydrocarbon mixture, the higher the RCT. Preferably, the process is applied to hydrocarbon mixtures which boil substantially above 350°C and more than 35% w of which boils above 520°C and which have an RCT of more than 7.5% w. Examples of such hydrocarbon mixtures are residues obtained in the distillation of crude mineral oils and also heavy hydrocarbon mixtures obtained from shale and tar sand. If required, the process may also be applied to heavy crude mineral oils, residues obtained in the distillation of products formed in the thermal cracking of hydrocarbon mixtures and asphaltic bitumen obtained in the solvent deasphalting of asphaltenes-containing hydrocarbon mixtures. The process according to the invention can very suitably be applied to residues obtained in the vacuum distillation of atmospheric distillation residues from crude mineral oils. If an atmospheric distillation residue from a crude mineral oil is available as feed for the process according to the invention, it is preferred to separate a vacuum distillate therefrom by vacuum distillation and to subject the resulting vacuum residue to the HT. The separated vacuum distillate may be subjected to thermal cracking or to catalytic cracking in the presence or in the absence of hydrogen to convert it into light hydrocarbon oil distillates. The separated vacuum distillate is very suitable for use as a feed component for the TC treatment, together with stream 3.

The process according to the invention is a three-step process in which in the first step an asphaltenes-containing feed (stream 1) is subjected to a HT for the production of a product

with a reduced asphaltenes content from which one or more distillate fractions and a heavy fraction (stream 2) are separated. In the second and third steps of the process stream 2 is subjected to a combination of a DA treatment and a TC treatment.

5 Asphaltenes-containing hydrocarbon mixtures usually include a considerable percentage of metals particularly vanadium and nickel. When such hydrocarbon mixtures are subjected to a catalytic treatment, for instance a HT for the reduction of the asphaltenes content, as is the case in the first step of the
10 process according to the invention, these metals are deposited on the catalyst used in the HT and thus shorten its effective life. In view of this, asphaltenes-containing hydrocarbon mixtures having a vanadium + nickel content of more than 50 parts per million by weight (ppmw) should preferably be subjected to a
15 demetallization treatment before they are contacted with the catalyst used in the HT. This demetallization may very suitably be carried out by contacting the asphaltenes-containing hydrocarbon mixture, in the presence of hydrogen, with a catalyst consisting more than 80% w of silica. Both catalysts completely consisting of
20 silica and catalysts containing one or more metals having hydrogenating activity - in particular a combination of nickel and vanadium - emplaced on a carrier substantially consisting of silica, are suitable for the purpose. When in the process according to the invention the asphaltenes-containing feed is subjected to a
25 catalytic demetallization treatment in the presence of hydrogen, this demetallization may be carried out in a separate reactor. Since the catalytic demetallization and the HT for the reduction of the asphaltenes content can be carried out under the same conditions, the two processes may very suitably be carried out in
30 the same reactor containing a bed of the demetallization catalyst and a bed of the catalyst used in the HT, successively.

Suitably catalysts for carrying out the HT are those containing at least one metal chosen from the group formed by nickel and cobalt and in addition at least one metal chosen from the

group formed by molybdenum and tungsten on a carrier, which carrier consists more than 40% w of alumina. Catalysts very suitable for use in the HT are those comprising the metal combinations nickel/molybdenum or cobalt/molybdenum on alumina as the carrier. The HT is preferably carried out at a temperature of from 300-500°C and in particular of from 350-450°C, a pressure of from 50-300 bar and in particular of from 75-200 bar, a space velocity of from 0.02-10 g.g.⁻¹.h⁻¹ and in particular of from 0.1-2 g.g.⁻¹.h⁻¹ and a H₂/feed ratio of from 100-5000 Nl.kg⁻¹ and in particular of from 500-2000 Nl.kg⁻¹. The conditions used in a catalytic demetal-
lization treatment in the presence of hydrogen, to be carried out if required, are subject to the same preference as those for the HT for the reduction of the asphaltenes content stated herein-
before.

The HT is preferably carried out in such a way that it yields a product the C₅⁺ fraction of which meets the following requirements:

- a) the RCT of the C₅⁺ fraction amounts to 20-70% of the feed (RCT), and
- b) the difference between the percentages by weight of hydrocarbon boiling below 350°C present in the C₅⁺ fraction and in the feed is at most 40.

It should be noted that in the catalytic demetallization, apart from reduction of the metal content, there will be some reduction of the RCT and some formation of C₅-350°C product. A similar phenomenon is seen in the HT, in which, apart from reduction of the RCT and formation of C₅-350°C product, there will be some reduction of the metal content. The requirements mentioned under a) and b) refer to the total RCT reduction and the total formation of C₅-350°C product (viz. including those occurring in a catalytic demetallization treatment that may be carried out).

The first step of the process according to the invention yields a product having a reduced asphaltenes content from which one or more distillate fractions and a heavy fraction (stream 2) are separated. The distillate fractions separated from the product

may be atmospheric distillates only, but it is preferred to separate a vacuum distillate from the product as well. This vacuum distillate may be converted into light hydrocarbon oil distillates in the ways stated hereinbefore.

5 In the process according to the invention the second or third step used is a DA treatment in which an asphaltenes-containing feed is converted into a product from which a deasphalted oil fraction (stream 3) and an asphaltic bitumen fraction (stream 4) are separated. Suitable solvents for carrying out the DA are
10 paraffinic hydrocarbons having of from 3-6 carbon atoms per molecule, such as n-butane and mixtures thereof, such as mixtures of propane and n-butane and mixtures of n-butane and n-pentane. Suitable solvent/oil weight ratios lie between 7:1 and 1:1 and in particular between 4:1 and 1:1. The DA treatment is preferably
15 carried out at a pressure in the range of from 20 to 100 bar. When n-butane is used as the solvent, the deasphalting is preferably carried out at a pressure of from 35-45 bar and a temperature of from 100-150°C.

 In the process according to the invention the second or third
20 step used is a TC treatment in which one feed or two separate feeds are converted into a product which contains less than 20% w C₄⁻ hydrocarbons and from which one or more distillate fractions and a heavy fraction (stream 5) are separated. The way in which the TC treatment is carried out is determined by the quality of the feeds
25 available for the TC.

 If the feed for the TC is composed of nothing but one or more streams having a relatively low asphaltenes content, such as stream 3 - optionally together with one or more vacuum distillates separated during the process - a TC treatment comprising a single
30 cracking unit will be sufficient. From the product formed one or more distillate fractions and a heavy fraction (stream 5) are separated. The distillate fractions separated from the product may be atmospheric distillates only, but it is preferred to separate a vacuum distillate from the product as well. This vacuum distillate
35 may be converted into light hydrocarbon oil distillates in the

ways stated hereinbefore. If the feed for the TC treatment is composed of nothing but one or more streams having a relatively low asphaltenes content, and a TC treatment is used which comprises only one cracking unit, then a heavy fraction of the cracked product is preferably recirculated to the cracking unit. For instance, starting from stream 3 as the feed for the TC treatment, a product may be prepared from which one or more atmospheric distillates are separated by distillation and subsequently part of the atmospheric residue may be recirculated to the cracking unit.

If the feed for the TC treatment is composed of both of one or more streams having a relatively low asphaltenes content, such as stream 3 - optionally together with one or more vacuum distillates separated during the process - and of a relatively asphaltenes-rich stream, such as stream 4 or stream 2 obtained as vacuum residue, it is preferred to carry out a TC treatment comprising two cracking units and to crack the two feeds separately to form products from which one or more distillate fractions and a heavy fraction (stream 5) are separated. The distillate fractions separated from the products may be atmospheric distillates only, but it is preferred to separate a vacuum distillate from the products as well. The separated vacuum distillate may be converted into light hydrocarbon distillates in the manners described hereinbefore. As is the case when a TC treatment comprising a single cracking unit is used, so also when a TC treatment comprising two cracking units is used, a heavy fraction from the cracked product from the cracking unit in which the relatively low asphaltenes feed is processed will preferably be recirculated to that cracking unit. When a TC treatment comprising two cracking units is used, a relatively low-asphaltenes heavy fraction may, if desired, be separated from the product obtained in the cracking unit in which the relatively asphaltenes-rich feed is cracked and be used as a feed component for the cracking unit in which the relatively low-asphaltenes feed is processed. When a TC treatment comprising two cracking units is used, it is not

necessary for the distillation of the cracked products (atmospheric and, optionally, vacuum distillation) to be carried out in separate distillation units. If desired, the cracked products or fractions therefrom may be combined and distilled together.

5 The TC treatment both of relatively low-asphaltenes feeds and of relatively asphaltenes-rich feeds should preferably be carried out at a temperature of from 400-525°C and a space velocity of from 0.01-5 kg fresh feed per litre cracking reactor volume per minute.

10 As has been observed hereinbefore, the embodiments to which the present patent application relates and which fall within class I may be subdivided depending on whether stream 2 is used as the feed for the DA treatment (class IA), or as a feed component for the TC treatment (class IB). In the embodiments falling within
15 class IB stream 5 is used as the feed for the DA treatment.

The various embodiments falling within class IA are illustrated schematically in Figure I. The various streams, fractions and reaction zones are indicated by three digit numbers, the first of which refers to the Figure concerned. Thus, the vacuum residue
20 (302) for instance, refers to stream 2 as described hereinbefore in the context of Figure 3. According to Figure I the process is carried out in an apparatus comprising a HT zone (106), a DA zone (107) and a TC zone (108), successively. An asphaltenes-containing hydrocarbon mixture (101) is subjected to a HT and the
25 hydrotreated product is separated into one or more distillate fractions (109) and a residual fraction (102). Stream 102 is subjected to a DA treatment and the product is separated into a deasphalted oil (103) and an asphaltic bitumen (104). Stream 103 is subjected to a TC treatment and the cracked product is se-
30 parated into one or more distillate fractions (110) and a residual fraction (105). In addition to this embodiment (IA1), in which streams 104 and 105 are not subjected to further processing, Figure I includes the following seven embodiments:

- IA2 The use of at least part of stream 104 as a feed component for the HT. No further processing of stream 105.
- IA3 The use of at least part of stream 104 as a feed component for the TC treatment. No further treatment of stream 105.
- 5 stream 105.
- IA4 The use of part of stream 104 as a feed component for the HT and as a feed component for the TC treatment. No further processing of stream 105.
- IA5-IA7 Embodiments substantially corresponding with those described under IA2-IA4, respectively, but with at least part of stream 105 being used as a feed component for the HT.
- 10 the HT.
- IA8 The use of at least part of stream 105 as a feed component for the HT. No further processing of stream 104.
- 15 The various embodiments falling within class IB are represented schematically in Figure II. According to this Figure the process is carried out in an apparatus comprising a HT zone (206), a TC zone (207) and a DA zone (208). An asphaltenes-containing hydrocarbon mixture (201) is subjected to a HT and the hydro-
- 20 treated product is separated into one or more distillate fractions (209) and a residual fraction (202). Stream 202 is subjected to a TC treatment and the cracked product is separated into one or more distillate fractions (210) and a residual fraction (205). Stream 205 is subjected to a DA treatment and the product is separated
- 25 into a deasphalted oil (203) and an asphaltic bitumen (204). Stream 203 is used as a feed component for the TC treatment. In addition to this embodiment (IB1), in which stream 204 is not subjected to further processing Figure II includes another embodiment (IB2) in which at least part of stream 204 is used as a
- 30 feed component for the HT.

In the embodiments where it is the object to achieve the most complete conversion possible of stream (201) into hydrocarbon oil distillates, a so-called "bleed stream" should preferably be separated from one of the heavy streams of the process. In this way the build-up of undesirable heavy components during the process can be obviated.

Three flow diagrams for the preparation of hydrocarbon oil distillates from asphaltenes-containing hydrocarbon mixtures according to the invention will hereinafter be explained in more detail with the aid of Figures III-V.

Flow diagram A (based on embodiment IA5)

See Figure III.

The process is carried out in an apparatus comprising, successively a HT zone composed of a unit for catalytic hydrotreatment (306), a unit for atmospheric distillation (307) and a unit for vacuum distillation (308), a DA zone (309) and a TC zone composed of a thermal cracking unit (310), a second unit for atmospheric distillation (311) and a second unit for vacuum distillation (312). An asphaltenes-containing hydrocarbon mixture (301) is mixed with a recirculation stream (313) and the mixture (314) is subjected together with hydrogen (315) to a catalytic hydrotreatment. The hydrotreatment product (316) is separated by atmospheric distillation into a gas fraction (317), an atmospheric distillate (318) and an atmospheric residue (319). The atmospheric residue (319) is separated by vacuum distillation into a vacuum distillate (320) and a vacuum residue (302). The vacuum residue (302) is separated by solvent deasphalting into a deasphalted oil (303) and an asphaltic bitumen (304). The deasphalted oil (303) is mixed with an atmospheric residue (321) and the mixture (322) is subjected to thermal cracking. The asphaltic bitumen (304) is divided into two portions (323) and (324) and portion (324) is mixed with a vacuum residue (305) to form the recirculation stream (313). The thermally cracked product (325) is separated by atmospheric dis-

tillation into a gas fraction (326), an atmospheric distillate (327) and an atmospheric residue (328). The atmospheric residue (328) is divided into two portions (321) and (329) and portion (329) is separated by vacuum distillation into a vacuum distillate
5 (330) and a vacuum residue (305).

Flow diagram B (based on embodiment IA6)

See Figure IV.

The process is carried out in an apparatus comprising, successively, a HT zone composed of a unit for catalytic hydrotreatment
10 (406), a unit for atmospheric distillation (407) and a unit for vacuum distillation (408), a DA zone (409) and a TC zone composed of a thermal cracking unit (410), a second unit for atmospheric distillation (411), a second thermal cracking unit (412), a third unit for atmospheric distillation (413) and a second unit for
15 vacuum distillation (414). An asphaltenes-containing hydrocarbon mixture (401) is mixed with a vacuum residue (415) and the mixture (416) is subjected together with hydrogen (417) to a catalytic hydrotreatment. The hydrotreated product (418) is separated by atmospheric distillation into a gas fraction (419), an atmospheric
20 distillate (420) and an atmospheric residue (421). The atmospheric residue (421) is separated by vacuum distillation into a vacuum distillate (422) and a vacuum residue (402). The vacuum residue (402) is separated by solvent deasphalting into a deasphalted oil (403) and an asphaltic bitumen (404). The deasphalted oil (403) is
25 mixed with atmospheric residue (423) and the mixture (424) is converted in the second thermal cracking unit into a product (425) which is split up by atmospheric distillation into a gas fraction (426), an atmospheric distillate (427) and an atmospheric residue (428). The atmospheric residue (428) is divided into two portions
30 (423) and (429). The asphaltic bitumen (404) is converted in the first thermal cracking unit into a product (430) which is separated by atmospheric distillation into a gas fraction (431) an atmospheric distillate (432) and an atmospheric residue (433). Gas fractions (426) and (431) are combined to form mixture (434).

Atmospheric distillates (427) and (432) are combined to form mixture (435). Atmospheric residues (429) and (433) are combined to form mixture (436) which is separated by vacuum distillation into a vacuum distillate (437) and a vacuum residue (405). Vacuum residue (405) is divided into two portions (415) and (438).

Flow diagram C (based on embodiment IB2)

See Figure V.

The process is carried out in an apparatus comprising, successively, a HT zone composed of a unit for catalytic hydrotreatment (506), an atmospheric distillation unit (507) and a vacuum distillation unit (508), a TC zone composed of a thermal cracking unit (509), a second atmospheric distillation unit (510), a second thermal cracking unit (511), a third atmospheric distillation unit (512) and a second vacuum distillation unit (513), and a DA zone (514). An asphaltenes-containing hydrocarbon mixture (501) is mixed with an asphaltic bitumen (515) and the mixture (516) is subjected, together with hydrogen (517) to a catalytic hydrotreatment. The hydrotreated product (518) is separated by atmospheric distillation into a gas fraction (519), an atmospheric distillate (520) and an atmospheric residue (521). The atmospheric residue (521) is separated by vacuum distillation into a vacuum distillate (522) and a vacuum residue (502). The vacuum residue (502) is converted by thermal cracking into a product (523) which by atmospheric distillation is separated into a gas fraction (524), an atmospheric distillate (525) and an atmospheric residue (526). The atmospheric residue (526) is mixed with an atmospheric residue (527) and the mixture (528) is separated by vacuum distillation into a vacuum distillate (529) and a vacuum residue (505). The vacuum residue (505) is separated by solvent deasphalting into a deasphalted oil (503) and an asphaltic bitumen (504). The deasphalted oil (503) is mixed with an atmospheric residue (530) and the mixture (531) is subjected to thermal cracking to form a product (532) which by atmospheric distillation is separated into a gas fraction (533), an atmospheric distillate (534) and an atmospheric residue (535). The atmospheric residue (535) is

divided into two portions (527) and (530). Gas fractions (524) and (533) are combined to form mixture (536). Atmospheric distillates (525) and (534) are combined to form mixture (537). Asphaltic bitumen (504) is divided into two portions (515) and (538).

5 The present patent application also includes apparatuses for carrying out the process according to the invention substantially corresponding with those schematically represented in Figures I-V.

 The invention is now elucidated with the aid of the following Examples.

10 The starting mixtures used in the process according to the invention were three asphaltenes-containing hydrocarbon mixtures obtained as residues in the vacuum distillation of atmospheric distillation residues from crude mineral oils from the Middle East. All three vacuum residues boiled substantially above 520°C;
15 they had RCT's of 18.8, 14.5 and 17.1% w, respectively. The process was carried out according to flow diagrams A-C. The following conditions were used in the various zones:

 In all the flow diagrams the unit for catalytic hydrotreatment comprised two reactors, the first of which was filled with a
20 Ni/V/SiO₂ catalyst containing 0.5 parts by weight (pbw) of nickel and 2.0 pbw of vanadium per 100 pbw of silica, and the second of which was filled with a Co/Mo/Al₂O₃ catalyst containing 4 pbw of cobalt and 12 pbw of molybdenum per 100 pbw of alumina. The catalytic hydrotreatment was carried out at a hydrogen pressure of
25 150 bar, a space velocity, measured for both the reactors, of 0.5 kg feed per litre catalyst per hour, a H₂/feed ratio of 1000 Nl per kg and an average temperature of 410°C in the first reactor and 385°C in the second reactor.

 In all the flow diagrams the DA treatment was carried out at
30 a pressure of 40 bar using n-butane as solvent.

 In all the flow diagrams the TC treatment was carried out in one or two cracking coils at a pressure of 20 bar and a space velocity of 0.4 kg fresh feed per litre cracking coil volume per minute.

Further information concerning the conditions under which the DA treatment and the TC treatment were carried out is given in the Table.

		<u>TABLE</u>		
5	Example	1	2	3
	Carried out according to flow diagram	A	B	C
	Flow diagram represented in Figure	III	IV	V
10	<u>DA</u>			
	Solvent/oil weight ratio	3:1	3:1	2:1
	Temperature, °C	115	115	118
	<u>TC</u>			
	Number of cracking units	1	2	2
15	Temperature in first cracking unit, °C*	---	460	490
	Temperature in second cracking unit, °C*	480	490	500
20	Recirculation ratio in second cracking unit (pbw residue per pbw fresh feed)	2	2	2

* The cracking temperatures given were measured at the outlet of the cracking coils.

Example 1

100 pbw 520°C⁺ vacuum residue (301) having an RCT of 18.8% w yielded the various streams in the following quantities:

130.3 pbw mixture (314) having an RCT of 23.8% w, a product (316) the C₅⁺ fraction of which had an RCT of 10.4% w,

17.1 pbw C₅-350°C atmospheric distillate (318),
106.0 " 350°C⁺ atmospheric residue (319),
31.7 " 350-520°C vacuum distillate (320),
74.3 " 520°C⁺ vacuum residue (302),
53.5 " deasphalted oil (303),
20.8 " asphaltic bitumen (304),
6.0 " portion (323),
14.8 " portion (324),
20.0 " C₅-350°C atmospheric distillate (327),
6.0 " portion (323),
14.8 " portion (324),
20.0 " C₅-350°C atmospheric distillate (327),
30.1 " 350°C⁺ atmospheric residue (329),
14.6 " 350-520°C vacuum distillate (330),
15.5 " 520°C⁺ vacuum residue (305) and
30.3 " recirculation stream (313).

Example 2

100 pbw 520°C⁺ vacuum residue (401) having an RCT of 14.5% w yielded the various streams in the following quantities:

121.2 pbw mixture (416) having an RCT of 19.5% w, a product (418) the C₅⁺ fraction of which had an RCT of 9.1% w,

18.7 pbw C₅-350°C atmospheric distillate (420),
96.0 " 350°C⁺ atmospheric residue (421),
28.1 " 350-520°C vacuum distillate (420),
67.9 " 520°C⁺ vacuum residue (402),
46.2 " deasphalted oil (403),
21.7 " asphaltic bitumen (404),

20.2 pbw C_5 -350°C atmospheric distillate (435),
44.3 " 350°C⁺ atmospheric residue (436),
14.6 " 350-520°C vacuum distillate (437),
29.7 " 520°C⁺ vacuum residue (405),
5 8.5 " portion (438) and
21.2 " portion (415).

Example 3

100 pbw 520°C⁺ vacuum residue (501) having an RCT of 17.1% w
yielded the various streams in the following quantities:
10 125.3 pbw mixture (516) having an RCT of 21.8% w, a product
(518), the C_5 ⁺ fraction of which had an RCT of 9.8% w,
18.9 pbw C_5 -350°C atmospheric distillate (520),
99.8 " 350°C⁺ atmospheric residue (521),
28.4 " 350-520°C vacuum distillate (522),
15 71.4 " 520°C⁺ vacuum residue (502),
75.2 " 350°C⁺ atmospheric residue (528),
14.7 " 350-520°C vacuum distillate (529),
60.5 " 520°C⁺ vacuum residue (505),
25.2 " deasphalted oil (503),
20 35.3 " asphaltic bitumen (504),
18.7 " C_5 -350°C atmospheric distillate (537),
25.3 " portion (515) and
10.0 " portion (538).

C L A I M S

1. A process for the production of hydrocarbon oil distillates from asphaltenes-containing hydrocarbon mixtures, characterized in that an asphaltenes-containing hydrocarbon mixture (stream 1) is subjected to a catalytic hydrotreatment (HT) in which an asphaltenes-containing feed is converted into a product having a reduced asphaltenes content, from which one or more distillate fractions and a heavy fraction (stream 2) are separated, that stream 2 is subjected to a combination of the following two treatments: solvent deasphalting (DA) in which an asphaltenes-containing feed is converted into a product from which a de-asphalted oil fraction (stream 3) and an asphaltic bitumen fraction (stream 4) are separated and thermal cracking (TC) in which one feed or two individual feeds are converted into a product which contains less than 20% w C_4^- hydrocarbons and from which one or more distillate fractions and a heavy fraction (stream 5) are separated, that stream 3 is used as the feed or as a feed component for the TC treatment and that stream 2 is used either as a feed component for the TC treatment with stream 5 being used as the feed for the DA treatment, or as the feed for the DA treatment.
 2. A process as claimed in claim 1, characterized in that stream 2 is used as the feed for the DA treatment and that at least part of stream 4 is used as a feed component for the HT and/or as a feed component for the TC treatment and/or at least part of stream 5 is used as a feed component for the HT.
 3. A process as claimed in claim 1, characterized in that stream 2 is used as a feed component for the TC treatment and that at least part of stream 4 is used as a feed component for the HT.
 4. a process as claimed in any one of claims 1-3, characterized in that the stream 1 used is a hydrocarbon mixture which boils substantially above 350°C and more than 35% w of which boils above

520°C and which has an RCT of more than 7.5% w such as a residue obtained in the vacuum distillation of an atmospheric distillation residue from the crude mineral oil.

5. A process as claimed in any one of claims 1-4, characterized in that one or more vacuum distillates separated from one or more of streams 1, 2 and 5 are used together with stream 3 as feed components for the TC treatment.

6. A process as claimed in any one of claims 1-5, characterized in that in the HT for the reduction of the asphaltenes content of the feed a catalyst is used which comprises at least one metal chosen from the group formed by nickel and cobalt and in addition at least one metal chosen from the group formed by molybdenum and tungsten on a carrier, which carrier consists more than 40% w of alumina.

7. A process as claimed in any one of claims 1-6, characterized in that the HT is carried out at a temperature of from 350-450°C, a pressure of from 75-200 bar, a space velocity of from 0.1-2 g.g⁻¹.hour⁻¹ and a H₂/feed ratio of from 500-2000 Nl.kg⁻¹.

8. A process as claimed in any one of claims 1-7, characterized in that the HT is carried out in such a manner that a product is obtained whose C₅⁺ fraction meets the following requirements:

a) the RCT of the C₅⁺ fraction is 20-70% of the RCT of the feed and

b) the difference between the percentages by weight of hydrocarbons boiling above 350°C present in the C₅⁺ fraction and in the feed is at most 40.

9. A process as claimed in any one of claims 1-8, characterized in that the DA treatment is carried out using n-butane as the solvent at a pressure of from 35-45 bar and a temperature of from 100-150°C.

10. A process as claimed in any one of claims 1-9, characterized in that if the feed for the TC treatment is composed both of stream 3, if desired together with one or more vacuum distillates

separated during the process, and of stream 2 or at least part of stream 4, a TC treatment is carried out which comprises two cracking units and that the two types of feed are cracked separately.

5 11. A process as claimed in any one of claims 1-10, characterized in that in the TC of stream 3 a heavy fraction of the cracked product is recirculated to the cracking unit in which the cracking of stream 3 is carried out.

12. A process as claimed in any one of claims 1-11, characterized
10 in that the TC treatment is carried out at a temperature of from 400-525°C and a space velocity of from 0.01-5 kg fresh feed per litre of cracking reactor volume per minute.

13. A process for the preparation of hydrocarbon oil distillates from asphaltenes-containing hydrocarbon mixtures substantially as
15 described hereinbefore and in particular with reference to the Examples.

14. Hydrocarbon oil distillates prepared according to a process as described in claim 13.

15. Apparatuses for carrying out the process as claimed in claim
20 13, characterized in that these apparatuses substantially correspond with those schematically shown in Figures I-V.

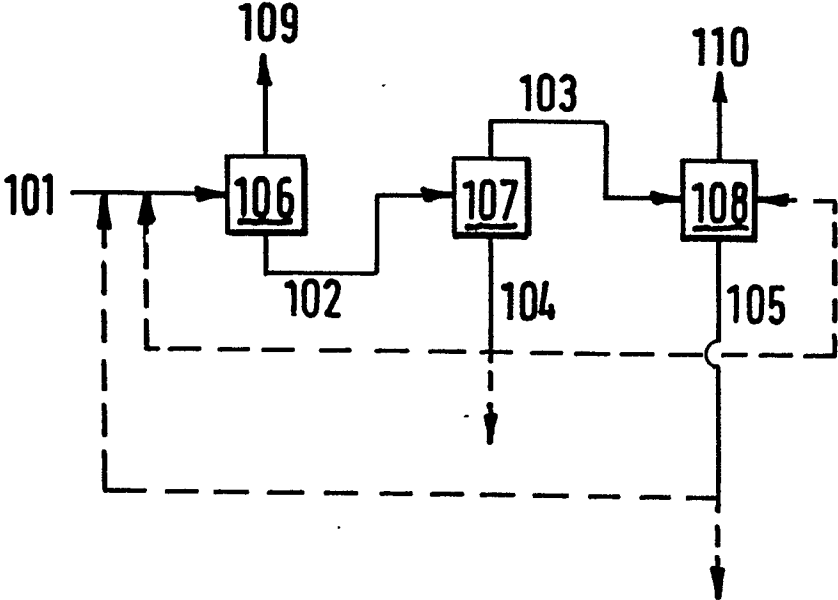


FIG. I

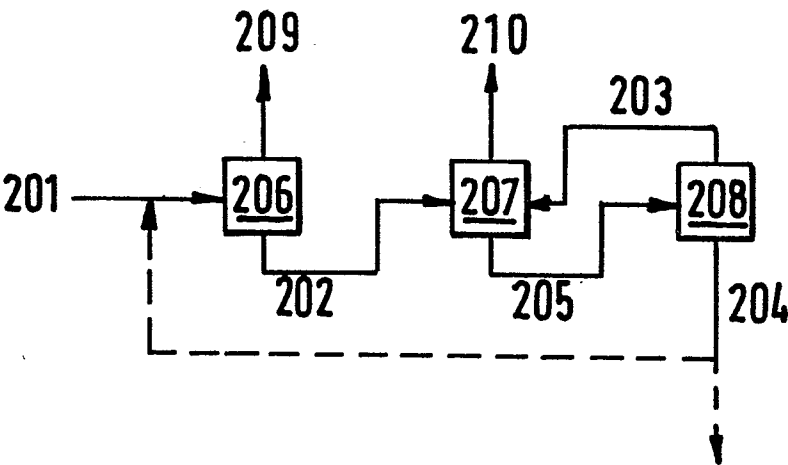


FIG II

FIG. III

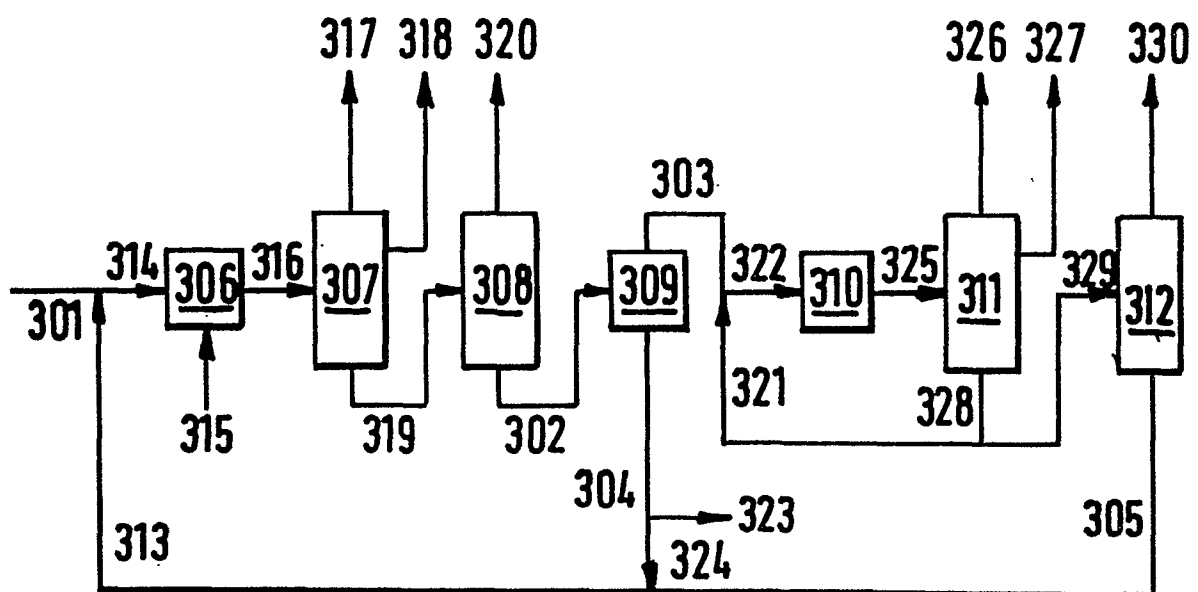


FIG. IV

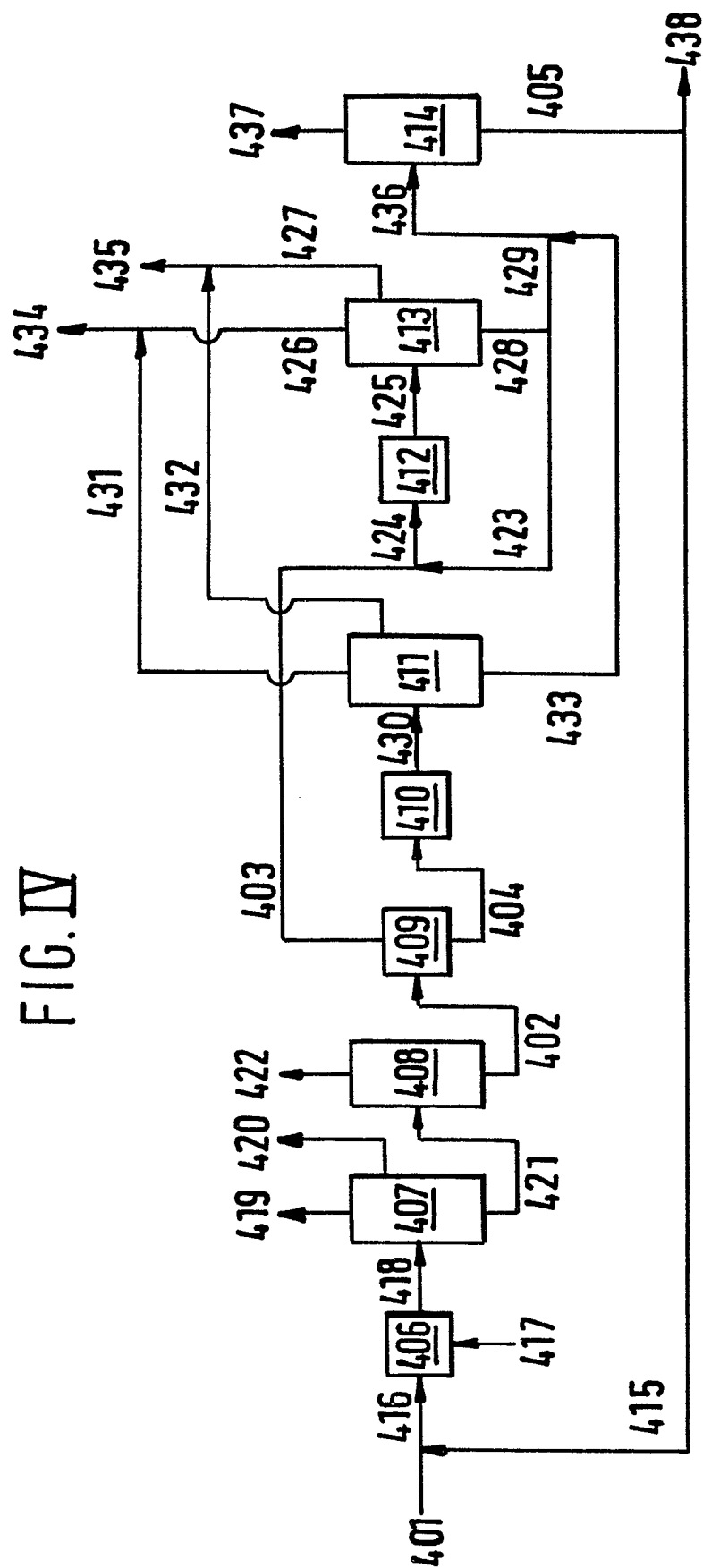
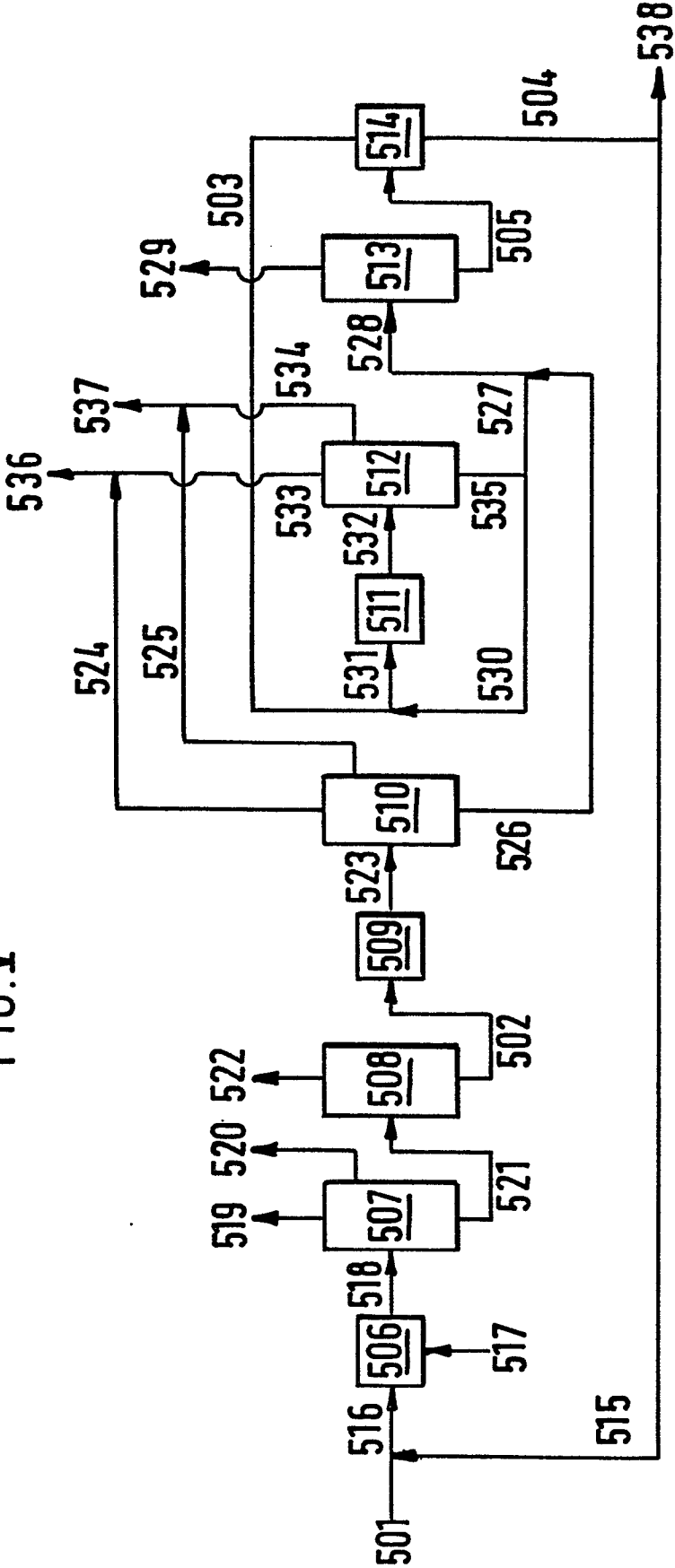


FIG.V





DOCUMENTS CONSIDERED TO BE RELEVANT			EP 82201560.8
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
A	<u>US - A - 3 730 875</u> (W.K.T. GLEIM et al.) * Claims; column 2, line 40 - column 4, line 75 * --	1	C 10 G 69/02
A	<u>GB - A - 2 031 011</u> (CHIYODA CHEMICAL ENGINEERING & CONSTRUCTION COMPANY LIMITED) * Claims; page 1, lines 30-52 * --	1	C 10 G
A	<u>GB - A - 1 560 148</u> (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) * Claims; page 1, line 35 - page 3, line 20 * --	1	
A	<u>US - A - 4 191 636</u> (Y. FUKUI et al.) * Claims; column 3, line 37 - column 5, line 16 * ----	1	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl. ³)
Place of search		Date of completion of the search	Examiner
VIENNA		17-03-1983	STÖCKLMAYER
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			