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A process for the production of low-asphaltenes hydrocarbon mixtures.

Deasphalted oils and distillates are produced from asphaltenes-containing hydrocarbons by two-step solvent-deasphalting (yielding a high quality DAO-1, a DAO-2 of lower quality and asphalt) and converting the DAO-2 or the asphalt by catalytic hydrotreatment into a product having a reduced RCT, which is separated by distillation into distillate fraction(s) and a residue which is subjected to thermal or catalytic cracking or which is used as feed component for solvent-deasphalting and the cracked product is separated by distillation into distillate fraction(s) and a residue which is used as feed component in solvent-deasphalting, or by subjecting the DAO-2 to thermal or catalytic cracking and/or the asphalt to thermal cracking and converting a distillation residue of the cracked product(s) by catalytic hydrotreatment into a product having a reduced RCT, which is separated by distillation into distillate fraction(s) and a residue which is used as feed component for solvent-deasphalting.

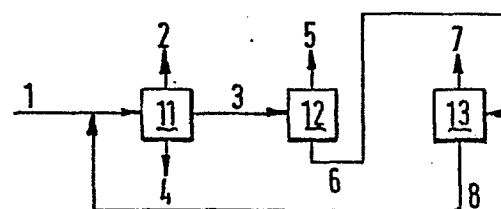


FIG.1

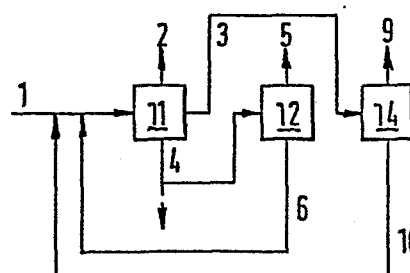
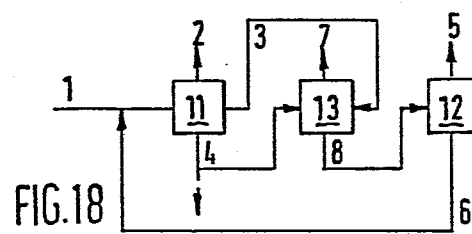


FIG.8

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A PROCESS FOR THE PRODUCTION OF LOW-ASPHALTENES
HYDROCARBON MIXTURES

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

5 In the atmospheric distillation of crude mineral oil for the production of light hydrocarbon oil distillates, such as gasoline, kerosine and gas oil, an asphaltenes-containing residue is obtained as by-product.

10 These residues, which usually contain a substantial quantity of sulphur and metals in addition to asphaltenes, were initially used as fuel oil. In view of the need for light hydrocarbon oil distillates and the decreasing mineral oil reserves, several treatments have already been proposed aiming at producing light hydrocarbon oil distillates from atmospheric residues. For example, it is possible to separate a deasphalted oil from an atmospheric residue by solvent-deasphalting and to subject said deasphalted oil to catalytic cracking, optionally in the presence of hydrogen. 15 It is also possible to separate an atmospheric residue into a vacuum distillate and a vacuum residue by vacuum distillation, to separate a deasphalted oil from the vacuum residue by solvent-deasphalting and subjecting both the vacuum distillate and the 20 deasphalted oil to catalytic cracking, optionally in the presence of hydrogen.

A drawback of the conventional solvent-deasphalting, in which an asphaltenes-containing feed is separated in one step into a 25 deasphalted oil as desired main product and an asphalt as by-product, is that for realizing a sufficiently high yield of deasphalted oil, one usually has to accept a deasphalted oil of insufficient quality. In this connection the quality of the deasphalted oil is meant to be its suitability for conversion into

hydrocarbon oil distillates by catalytic cracking optionally in the presence of hydrogen. Said suitability is higher according as the deasphalted oil has, inter alia, a lower asphaltenes, metal and sulphur content. By subjecting a deasphalted oil of insufficient quality to a pretreatment, it can as yet be made suitable for conversion into hydrocarbon oil distillates by catalytic cracking optionally in the presence of hydrogen.

It has been found that the above-mentioned drawback of the conventional solvent-deasphalting can be alleviated to some extent by carrying out the solvent-deasphalting as a two-step process, in which the asphaltenes-containing hydrocarbon mixture is separated into a deasphalted oil of high quality (for the sake of brevity termed below "deasphalted oil 1"), a deasphalted oil of lower quality (for the sake of brevity termed below "deasphalted oil 2") and an asphalt. Deasphalted oil 1 differs from deasphalted oil 2 mainly by a substantially lower asphaltenes, metal and sulphur content. Comparison of the results of the one-step process with those of the two-step process shows that starting from an equal quantity of an asphaltenes-containing hydrocarbon mixture for the production of an equal total quantity of deasphalted oil, which deasphalted oil is of insufficient quality in the one-step process, the two-step process yields two deasphalted oils of which deasphalted oil 1 is suitable as such for conversion into hydrocarbon oil distillates by catalytic cracking optionally in the presence of hydrogen. A deasphalted oil of insufficient quality is admittedly also obtained in the two-step process, but in a considerably smaller quantity than in the one-step process.

Since solvent-deasphalting has in practice been found to be suitable for the production of deasphalted oils from various asphaltenes-containing hydrocarbon mixtures and a two-step solvent-deasphalting process has moreover been found to yield better results than a one-step process, it was ascertained to what extent it would be possible to obtain a better result by combining the two-step solvent-deasphalting process with aftertreatment(s) of the deasphalted oil 2 and/or the asphalt and application of a

residual fraction of the aftertreated product(s) as a feed component for the two-step solvent-deasphalting, than when using just a two-step solvent-deasphalting process. An investigation into catalytic hydrotreatment, in which a feed is converted into a product with a reduced Ramsbottom Carbon Test value (RCT), catalytic cracking and thermal cracking as possible aftertreatments was conducted. In all cases the resulting products were separated by distillation into one or more distillate fractions and a residual fraction and at least one of the resultant residual fractions was used as a feed component for the two-step solvent-deasphalting. In the evaluation of the result the yield and the quality of the deasphalted oils and the asphalt play a prominent part. The yield of light product is also of great importance. In this connection by quality of asphalt is meant the suitability to serve as a fuel oil component. Said suitability is higher according as the asphalt has a lower metal and sulphur content and a lower viscosity and density. Compared with a mode of operation in which just a two-step solvent-deasphalting is used, the combinations tested generally resulted in a higher yield of deasphalted oil 1 and a considerable yield of hydrocarbon oil distillate. Some combinations have been found to yield deasphalted oils and/or asphalt of a better quality.

The present invention therefore relates to a process for the production of deasphalted oils and hydrocarbon oil distillates from asphaltenes-containing hydrocarbon mixtures, characterized in that an asphaltenes-containing hydrocarbon mixture is separated by two-step solvent-deasphalting into a deasphalted oil 1 of high quality, a deasphalted oil 2 of lower quality and an asphalt, that the deasphalted oil 2 or the asphalt is converted by a catalytic hydrotreatment into a product having a reduced RCT which is separated by distillation into one or more distillate fractions and a residual fraction, that the residual fraction is subjected to thermal or catalytic cracking or used as a feed component for solvent-deasphalting and the cracked product obtained is separated

by distillation into one or more distillate fractions and a residual fraction, which latter fraction is used as a feed component for solvent-deasphalting, or that the deasphalted oil 2 is subjected to thermal or catalytic cracking and/or that the asphalt is subjected to thermal cracking and that a distillation residue of the cracked product(s) is converted by a catalytic hydrotreatment into a product with a reduced RCT that is separated by distillation into one or more distillate fractions and a residual fraction which is used as a feed component for solvent-deasphalting.

As regards the feeds used for each of the aftertreatments as well as when applying more than one aftertreatment and the sequence in which said treatments take place, a number of preferred embodiments will be discussed hereinafter. It is applicable to all the embodiments that the asphaltenes-containing hydrocarbon mixture used as feed is first separated by a two-step solvent-deasphalting treatment into a deasphalted oil 1, a deasphalted oil 2 and an asphalt and that at least one of the residual fractions obtained in the aftertreatment is used as a feed component for solvent-deasphalting, in particular the two-step solvent-deasphalting treatment referred to hereinabove.

A preferred embodiment of the process according to the present invention relates to a process for the production of a deasphalted oil and hydrocarbon oil distillates from asphaltenes-containing hydrocarbon mixtures, in which an asphaltenes-containing hydrocarbon mixture is separated by two-step solvent-deasphalting into a deasphalted oil 1 of high quality, a deasphalted oil 2 of lower quality and an asphalt, in which deasphalted oil 2 is converted by catalytic hydrotreatment into a product having a reduced RCT which is separated by distillation into one or more distillate fractions and a residual fraction, in which said residual fraction is converted by thermal or catalytic cracking into a cracked product which is separated by distillation into one or more distillate fractions and a residual fraction, the latter residual fraction being used as a feed component for the two-step solvent-deasphalting.

In this embodiment (class I) the deasphalted oil 2 is subjected to a catalytic hydrotreatment. Class I can be further subdivided depending on whether the distillation residue of the hydrotreated product is subjected to thermal cracking (class IA) or to catalytic cracking (class IB).

A preferred embodiment of class I comprises a process wherein the residual fraction separated from the product of the catalytic hydrotreatment is subjected to thermal cracking and that the asphalt is used as a feed component for thermal cracking.

A further preferred embodiment of the process according to the present invention relates to a process for the production of deasphalted oils and hydrocarbon oil distillates from asphaltenes-containing hydrocarbon mixtures, in which an asphaltenes-containing hydrocarbon mixture is separated by two-step solvent-deasphalting into a deasphalted oil 1 of high quality, a deasphalted oil 2 of lower quality and an asphalt, in which the asphalt is converted by catalytic hydrotreatment into a product having a reduced RCT which is separated by distillation into one or more distillate fractions and a residual fraction and in which the residual fraction is used as a feed component for the solvent-deasphalting or is converted by thermal or catalytic cracking into a cracked product which is separated by distillation into one or more distillate fractions and a residual fraction, the latter residual fraction being used as a feed component for solvent-deasphalting.

In this embodiment (class II) the asphalt is subjected to a catalytic hydrotreatment. Class II can be further subdivided depending on whether the distillation residue of the hydrotreated product is used as a feed component for solvent-deasphalting, in particular two-step solvent-deasphalting (class IIA) or is subjected to thermal cracking (class IIB) or to catalytic cracking (class IIC).

A preferred embodiment of class II comprises a process wherein the residual fraction separated from the product of the catalytic hydrotreatment is used as a feed component for solvent-deasphalting and that the deasphalted oil 2 is converted by

thermal or catalytic cracking into a cracked product which is separated by distillation into one or more distillate fractions and a residual fraction that is used as a feed component for solvent-deasphalting.

- 5 A further preferred embodiment of class II comprises a process wherein the residual fraction separated from the product of the catalytic hydrotreatment is converted by thermal or catalytic cracking into a cracked product and that the deasphalted oil 2 is used as a feed component for thermal or catalytic cracking and
10 that a distillation residue of the thermally or catalytically cracked product is used as a feed component for solvent-deasphalting.

- A third preferred embodiment of the process according to the present invention relates to a process for the production of deasphalted oils and hydrocarbon oil distillates from asphaltene-
15 containing hydrocarbon mixtures, in which an asphaltene-containing hydrocarbon mixture is separated by two-step solvent-deasphalting into a deasphalted oil 1 of high quality, a deasphalted oil 2 of lower quality and an asphalt, in which the deasphalted oil 2 is subjected to thermal or catalytic cracking and/or in which the
20 asphalt is subjected to thermal cracking, in which a distillation residue of the cracked product is converted by catalytic hydrotreatment into a product with a reduced RCT that is separated by distillation into one or more distillate fractions and a residual fraction and in which the residual fraction is used as a feed
25 component for solvent-deasphalting, in particular two-step solvent-deasphalting.

- In this embodiment (class III) the deasphalted oil 2 is subjected to thermal or catalytic cracking and/or the asphalt is subjected to thermal cracking. Class III can be further subdivided
30 depending on whether the apparatus in which the process is carried out contains in addition to a two-step solvent-deasphalting section and a catalytic hydrotreatment section, either a thermal cracking section (class IIIA) or a catalytic cracking section (class IIIB), or both a thermal and a catalytic cracking section
35 (class IIIC), in which the deasphalted oil 2 and/or the asphalt

separated in the two-step solvent-deasphalting section is/are further processed.

A preferred embodiment of class III comprises a process wherein the deasphalted oil 2 is thermally or catalytically
5 cracked and that the asphalt is used as a feed component for the catalytic hydrotreatment.

A further preferred embodiment of class III comprises a process wherein the deasphalted oil 2 is catalytically cracked and that the asphalt is thermally cracked and that the mixture of the
10 distillation residues of the cracked products is subjected to catalytic hydrotreatment.

In the process according to the invention the feed used is an asphaltenes-containing hydrocarbon mixture. The process is preferably applied to hydrocarbon mixtures mainly boiling above 350°C
15 and more than 35% by weight boiling above 520°C and having an RCT above 7.5% by weight. Examples of such hydrocarbon mixtures are residues obtained in the distillation of crude mineral oils as well as heavy hydrocarbon mixtures obtained from shale and tar sand. If desired, the process can also be used for heavy crude
20 mineral oils and for residues obtained in the distillation of products formed in the thermal cracking of hydrocarbon mixtures. The process according to the invention is very suitable to be applied to residues obtained in the vacuum distillation of atmospheric distillation residues of crude mineral oils. The process
25 according to the invention is further very suitable to be applied to residues obtained in the vacuum distillation of atmospheric distillation residues of products formed in the thermal cracking of asphaltenes-containing hydrocarbon mixtures. If an atmospheric distillation residue is available as feed for the process according
30 to the invention, it is preferred to separate therefrom a vacuum distillate by vacuum distillation and subject the resultant vacuum residue to the process according to the invention. The separated vacuum distillate can be converted into light hydrocarbon oil distillates by subjecting it to thermal cracking or
35 catalytic cracking optionally in the presence of hydrogen.

In the process according to the invention the feed is subjected to a two-step solvent-deasphalting. Suitable solvents for carrying out the deasphalting treatment are paraffinic hydrocarbons with 3-7 carbon atoms per molecule, such as propane, n-butane, iso-butane, n-pentane, iso-pentane and mixtures thereof, such as mixtures of propane with n-butane and mixtures of n-butane with iso-butane. Suitable solvent/oil weight ratios lie between 7:1 and 1:1. The solvent-deasphalting is preferably carried out at elevated temperature and pressure. The two-step solvent-deasphalting can in principle be carried out in two manners.

Firstly the feed may be subjected to an extraction under mild conditions in which the feed is separated into a deasphalted oil 1 and a "light" asphalt and in the second step the light asphalt is subsequently subjected to a second extraction in which it is separated into a deasphalted oil 2 and the final asphalt as by-product. In both steps the same solvent can be used, the degree of extraction being controlled by means of the temperature (temperature in the first step higher than in the second step). It is also possible to use different solvents, for example propane in the first step and n-butane in the second step.

Secondly, the feed may be subjected to an extraction under heavier conditions in which the feed is separated into a deasphalted oil and the final asphalt as by-product and in the second step the deasphalted oil is subsequently separated into a deasphalted oil 1 and a deasphalted oil 2. To this end the mixture of deasphalted oil and solvent from the extractor should only be supplied to a settler in which the temperature is higher than that applied in the first step.

The asphaltenes-containing hydrocarbon mixtures used as feed in the process according to the invention usually contain a substantial quantity of metals, especially vanadium and nickel. In the two-step solvent-deasphalting treatment some of these metals find their way into the deasphalted oil 2 or the asphalt. In the catalytic hydrotreatment of the deasphalted oil 2, the asphalt or the distillation products obtained therefrom by thermal

or catalytic cracking at least part of said metals deposits on the catalyst and consequently shortens its life. It is therefore preferred to subject a deasphalted oil 2, an asphalt or a cracking residue or a mixture of a cracking residue and an asphalt having a vanadium + nickel content above 50 parts per million by weight (ppmw) to a demetallization treatment before contacting it with the catalyst applied in the catalytic hydrotreatment. Said demetallization can very suitably be carried out by contacting the product(s) to be demetallized in the presence of hydrogen with a catalyst consisting more than 80% by weight of silica. Both catalysts completely consisting of silica and catalysts containing one or more metals having hydrogenation activity, in particular a combination of nickel and vanadium, present on a carrier support substantially consisting of silica, are suitable for said purpose. If in the process according to the invention a catalytic demetallization in the presence of hydrogen is applied said demetallization can be carried out in a separate reactor. Since the catalytic demetallization and the catalytic hydrotreatment to reduce the RCT can be carried out under the same conditions, the two processes can also very suitably be carried out in the same reactor, consecutively containing a bed of the demetallization catalyst and a bed of the catalyst used in the catalytic hydrotreatment.

Suitable catalysts for carrying out the catalytic hydrotreatment are those containing at least one metal chosen from the group formed by nickel and cobalt and at least one metal chosen from the group formed by molybdenum and tungsten on a carrier consisting more than 40% by weight of alumina. Very suitable catalysts for carrying out the catalytic hydrotreatment are those containing the metal combination nickel/molybdenum or cobalt/-molybdenum on alumina. The catalytic hydrotreatment 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 an H₂/feed

ratio of from 100-5000 Nl.kg⁻¹ and in particular of from 500-2000 Nl.kg⁻¹. As regards the conditions applied in an optional catalytic demetallization to be carried out in the presence of hydrogen, the same preference holds as stated above for the catalytic hydrotreatment to reduce the RCT.

The catalytic hydrotreatment is preferably carried out in such a manner that a product is obtained the C₅⁺ fraction of which fulfils the following requirements:

- a) the RCT of the C₅⁺ fraction is less than 50% of the RCT of the feed to be hydrotreated, and
- b) the quantity of hydrocarbons boiling below 350°C in the C₅⁺ fraction is less than 40% by weight.

It should be noted that in the catalytic demetallization, apart from reduction of the metal content, normally some reduction of the RCT and formation of C₅-350°C product occur. Something similar normally applies to the catalytic hydrotreatment in which, apart from reduction of RCT and formation of C₅-350°C product, some reduction of the metal content takes place. As regards the requirements stated above under a) and b) it should be noted that they relate to the total reduction of the RCT and the formation of C₅-350°C product (that is including those occurring in an optional catalytic demetallization).

In the catalytic hydrotreatment a product with a reduced RCT is obtained from which one or more distillate fractions and a residual fraction 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. Said vacuum distillate can be converted into light hydrocarbon oil distillates in the manners stated hereinbefore.

In some of the embodiments of the process according to the invention a distillation residue of the hydrotreated product is subjected to thermal or catalytic cracking. One or more distillate fractions are then separated from the cracked product. Said distillate fraction(s) may be atmospheric distillate(s) only, but it is preferred to separate a vacuum distillate from the cracked

product(s). Said vacuum distillate can be converted into light hydrocarbon oil distillates in the manners stated hereinbefore.

A number of embodiments of the process according to the invention (designated as IA-1, IA-2, IB, IIA-1 to IIA-3 inclusive, IIB-1, IIB-2, IIC-1, IIC-2, IIIA-1 to IIIA-4 inclusive, IIIB-1, IIIB-2 and IIIC) are discussed in some detail hereinafter.

The embodiments IA-1 and IA-2 are characterized in that the apparatus in which they are carried out contains in addition to a two-step solvent-deasphalting section and a catalytic hydrotreatment section, a thermal cracking section. In the embodiment IA-1 a distillation residue of the hydrotreated product is used as feed for the thermal cracking section and asphalt is separated off as final product. In the embodiment IA-2 both a distillation residue of the hydrotreated product and the asphalt are used as feed components for the thermal cracking section. Embodiment IB is characterized in that the apparatus in which it is carried out contains a catalytic cracking section in addition to a two-step solvent-deasphalting section and a catalytic hydrotreatment section.

The embodiments IIA-1 to IIA-3 inclusive are characterized in that the distillation residue of the hydrotreated product is used as a feed component for the two-step solvent-deasphalting. In the embodiment IIA-1 the deasphalted oil 2 is separated off as final product. In the embodiments IIA-2 and IIA-3 the deasphalted oil 2 is subjected to thermal and catalytic cracking respectively and a distillation residue of the cracked product is used as a feed component for the two-step solvent-deasphalting. The embodiments IIB-1, IIB-2, IIC-1 and IIC-2 are characterized in that the distillation residue of the hydrotreated product is subjected to thermal (IIB-1 and IIB-2) or catalytic (IIC-1 and IIC-2) cracking. In the embodiments IIB-1, IIB-2, IIC-1 and IIC-2 a distillation residue of the cracked product is used as a feed component for the two-step solvent-deasphalting. In the embodiments IIB-1 and IIC-1 the deasphalted oil 2 is separated off as final product. In the embodiments IIB-2 and IIC-2 the deasphalted oil 2 is used as a

feed component for the thermal and catalytic cracking section respectively.

The embodiments IIIA-1 to IIIA-4 inclusive are characterized in that the apparatus in which they are carried out consecutively consists of a two-step solvent-deasphalting section, a thermal cracking section and a catalytic hydrotreatment section. In the embodiment IIIA-1 the deasphalted oil 2 is subjected to thermal cracking and the asphalt is separated off as final product. Embodiment IIIA-2 is a variant of the embodiment IIIA-1 in which the asphalt is mixed with the distillation residue of the thermally cracked product and the mixture is subjected to catalytic hydrotreatment. In the embodiment IIIA-3 the asphalt is subjected to thermal cracking and the deasphalted oil 2 is separated off as final product. In the embodiment IIIA-4 both the deasphalted oil 2 and the asphalt are thermally cracked.

The embodiments IIIB-1 and IIIB-2 are characterized in that the apparatus in which they are carried out consecutively consists of a two-step solvent-deasphalting section, a catalytic cracking section and a catalytic hydrotreatment section. In the embodiment IIIB-1 the deasphalted oil 2 is subjected to catalytic cracking and the asphalt is separated off as final product. Embodiment IIIB-2 is a variant of the embodiment IIIB-1 in which the asphalt is mixed with the distillation residue of the catalytically cracked product and the mixture is subjected to catalytic hydro-treatment.

Embodiment IIIC is characterized in that the apparatus in which it is carried out consecutively consists of a two-step solvent-deasphalting section, a thermal cracking section, a catalytic cracking section and a catalytic hydrotreatment section. In embodiment IIIC the asphalt is thermally cracked, the deasphalted oil 2 is catalytically cracked and a mixture of the two cracking residues is subjected to catalytic hydrotreatment.

The embodiments IA-1, IA-2 and IB are diagrammatically shown in Figures 1, 2 and 3 respectively. The embodiments IIA-1 to IIA-3 inclusive, IIB-1, IIB-2, IIC-1 and IIC-2 are diagrammatically

shown in Figures 6-12 respectively. The embodiments IIIA-1 to IIIA-4 inclusive, IIIB-1, IIIB-2 and IIIC are diagrammatically shown in Figures 15-21 respectively. The following streams and sections are designated throughout the Figures 1-3, 6-12 and 15-21 respectively with the following numerals:

- stream 1 = asphaltenes-containing feed
- stream 2 = deasphalted oil 1
- stream 3 = deasphalted oil 2
- stream 4 = asphalt
- 10 stream 5 = hydrocarbon oil distillate ex catalytic hydro-treatment
- stream 6 = residue ex catalytic hydrotreatment
- stream 7 = hydrocarbon oil distillate ex thermal cracking
- stream 8 = residue ex thermal cracking
- 15 stream 9 = hydrocarbon oil distillate ex catalytic cracking
- stream 10 = residue ex catalytic cracking
- section 11 = two-step solvent-deasphalting
- section 12 = catalytic hydrotreatment
- section 13 = thermal cracking
- 20 section 14 = catalytic cracking

In the embodiment IA-2 aiming at the highest possible conversion of the asphaltenes-containing feed into deasphalted oil 1 and hydrocarbon oil distillates it is preferred to separate a "bleed stream" from the asphalt stream. It can thus be prevented that a build-up of undesired heavy components takes place in the process. When the process according to the invention takes place according to embodiment IA-2 in which the streams subjected to thermal cracking consist of a relatively low-asphaltenes stream 6 and a relatively asphaltenes-rich stream 4, it is preferred to use a thermal cracking section containing two cracking units and to crack the two types of feed separately into products from which one or more distillate fractions and a residual fraction are separated. When in the application of embodiment IA-2 use is made of a thermal cracking section containing two cracking units, a heavy fraction of the cracked product from the cracking unit in

which stream 6 is treated is preferably recycled to said cracking unit. If in the application of embodiment IA-2 use is made of a thermal cracking section containing two cracking units, it is possible, if desired, to separate a relatively low-asphaltenes fraction from the product obtained in the cracking unit in which stream 4 is cracked, and said relatively low-asphaltenes fraction can be used as feed component for the cracking unit in which stream 6 is treated. When using a thermal cracking section containing two cracking units, it is not necessary for the distillation of the cracked products (atmospheric and optionally vacuum distillation) to take place in separate distillation units. If desired, the cracked products or fractions thereof can be combined and distilled together. Two flow diagrams for the production of deasphalted oil and hydrocarbon oil distillates from asphaltenes-containing hydrocarbon mixtures according to class I will be further illustrated below with reference to Figures 4 and 5.

Two flow diagrams for the preparation of deasphalted oil and hydrocarbon oil distillates from asphaltenes-containing hydrocarbon mixtures according to class II will be further illustrated below with reference to Figures 13 and 14.

In the embodiments aiming at the highest possible conversion of the asphaltenes-containing feed into deasphalted oil and hydrocarbon oil distillates according to class III it is preferred to separate a "bleed stream" from the asphalt stream. It can thus be prevented that a build-up of undesired heavy components takes place in the process. When the process according to the invention takes place according to embodiment IIIA-4 in which the streams subjected to thermal cracking consist of a relatively low-asphaltenes stream 3 and a relatively asphaltenes-rich stream 4, it is preferred to use a thermal cracking section containing two cracking units and to crack the two types of feed separately into products from which one or more distillate fractions and a residual fraction are separated. When in the application of embodiment IIIA-4 use is made of a thermal cracking section containing two cracking units, a heavy fraction of the cracked product from the cracking unit in

which stream 3 is treated is preferably recycled to said cracking unit. When in the application of embodiment IIIA-4 use is made of a thermal cracking section containing two cracking units, it is possible, if desired, to separate a relatively low-asphaltenes fraction from the product obtained in the cracking unit in which stream 4 is cracked, and said relatively low-asphaltenes fraction can be used as a feed component for the cracking unit in which stream 3 is treated. When using a thermal cracking section containing two cracking units, it is not necessary for the distillation of the cracked products (atmospheric and optionally vacuum distillation) to take place in separate distillation units. If desired, the cracked products or fractions thereof can be combined and distilled together. Two flow diagrams for the production of deasphalted oil and hydrocarbon oil distillates from asphaltenes-containing hydrocarbon mixtures according to class III will be further illustrated below with reference to Figures 22 and 23.

Flow diagram 1* (based on embodiment IA-1)

See Figure 4.

The process is carried out in an apparatus consecutively consisting of a two-step solvent-deasphalting section 111, a catalytic hydrotreatment section built up of a catalytic hydrotreatment unit 115, a first atmospheric distillation unit 116 and a first vacuum distillation unit 117 and a thermal cracking section built up of a thermal cracking unit 118, a second atmospheric distillation unit 119 and a second vacuum distillation unit 120. An asphaltenes-containing hydrocarbon mixture 101 is mixed with a recycle stream 108 and the mixture 122 is separated by two-step solvent-deasphalting into a deasphalted oil 1 (stream 102), a deasphalted oil 2 (stream 103) and an asphalt (104). The deasphalted oil 2 (stream 103) together with hydrogen 123 is subjected to catalytic hydrotreatment. The hydrotreated product 124

* The various streams and apparatuses in the flow diagrams are referred to by three-digit numbers, the first digit corresponds with the diagram concerned.

is separated by atmospheric distillation into a gas fraction 125, an atmospheric distillate 105A and an atmospheric residue 126. The atmospheric residue 126 is separated by vacuum distillation into a vacuum distillate 105B and a vacuum residue 106. The vacuum residue 106 is thermally cracked and the cracked product 127 is separated by atmospheric distillation into a gas fraction 128, an atmospheric distillate 107A and an atmospheric residue 129. The atmospheric residue 129 is separated by vacuum distillation into a vacuum distillate 107B and a vacuum residue 108.

10 Flow diagram 2 (based on embodiment IB)

See Figure 5.

The process is mainly carried out in the same manner as that described under flow diagram 1, except that the thermal cracking unit 118 present in flow diagram 1 has been replaced by a catalytic cracking unit 221 in flow diagram 2.

15 Flow diagram 3 (based on embodiment IIA-3)

See Figure 13.

The process is carried out in an apparatus consecutively consisting of a two-step solvent-deasphalting section 311, a catalytic hydrotreatment section built up of a catalytic hydrotreatment unit 315, a first atmospheric distillation unit 316, a first vacuum distillation unit 317 and a catalytic cracking section built up of a catalytic cracking unit 321, a second atmospheric distillation unit 319 and a second vacuum distillation unit 320. An asphaltene-containing hydrocarbon mixture 301 is mixed with a recycle stream 306 and a recycle stream 310 and the mixture 322 is separated by two-step solvent-deasphalting into a deasphalted oil 1 (stream 302), a deasphalted oil 2 (stream 303) and an asphalt 304. The asphalt 304 is separated into two portions 304A and 304B. Portion 304B is subjected to catalytic hydrotreatment together with hydrogen 323. The hydrotreated product 324 is separated by atmospheric distillation into a gas fraction 325, an atmospheric distillate 305A and an atmospheric residue 326. The atmospheric residue 326 is separated by vacuum distillation into a vacuum distillate 305B and a vacuum residue 306. The deasphalted

oil 2 (stream 303) is catalytically cracked and the cracked product 327 is separated by atmospheric distillation into a gas fraction 328, an atmospheric distillate 309A and an atmospheric residue 329. The atmospheric residue 329 is separated by vacuum
5 distillation into a vacuum distillate 309B and a vacuum residue 310.

Flow diagram 4 (based on embodiment IIB-2)

See Figure 14.

The process is mainly carried out in the same manner as
10 that described under flow diagram 3, except for the following differences:

- a) The catalytic cracking unit 321 present in flow diagram 3 has been replaced by a thermal cracking unit 418 in flow diagram 4.
- 15 b) Stream 406 is not recycled but mixed with stream 403 to form the mixture 430 that is thermally cracked.

Flow diagram 5 (based on embodiment IIIA-4)

See Figure 22.

The process is carried out in an apparatus consecutively
20 consisting of a two-step solvent-deasphalting section 511, a thermal cracking section built up of a thermal cracking unit 518, a first atmospheric distillation unit 519 and a first vacuum distillation unit 520 and a catalytic hydrotreatment section built
25 up of a catalytic hydrotreatment unit 515, a second atmospheric distillation unit 516 and a second vacuum distillation unit 517. An asphaltenes-containing hydrocarbon mixture 501 is mixed with a recycle stream 506 and the mixture 522 is separated by two-step solvent-deasphalting into a deasphalted oil 1 (stream 502), a deasphalted oil 2 (stream 503) and an asphalt 504. The asphalt 504
30 is separated into two portions (504A and 504B). Portion 504B and deasphalted oil 2 (stream 503) are thermally cracked and the cracked product 527 is separated by atmospheric distillation into a gas fraction 528, an atmospheric distillate 507A and an atmospheric residue 529. The atmospheric residue 529 is separated by
35 vacuum distillation into a vacuum distillate 507B and a vacuum

residue 508. The vacuum residue 508 is subjected to catalytic hydrotreatment together with hydrogen 523. The hydrotreated product 524 is separated by atmospheric distillation into a gas fraction 525, an atmospheric distillate 505A and an atmospheric residue 526. The atmospheric residue 526 is separated by vacuum distillation into a vacuum distillate 505B and a vacuum residue 506.

Flow diagram 6 (based on embodiment IIIB-2)

See Figure 23.

10 The process is mainly carried out in the same manner as that described under flow diagram 5, with the following differences:

- a) The thermal cracking unit 518 present in flow diagram 5 has been replaced by a catalytic cracking unit 621 in flow diagram 6.
- b) Stream 604B is not cracked but mixed with stream 610 to form the mixture 630 that is subjected to catalytic hydrotreatment.

The present application also relates to apparatuses for carrying out the process according to the invention, substantially corresponding with those diagrammatically shown in Figures 1-23.

20 The invention is now illustrated with reference to the Examples 1-6.

In the process according to the invention the starting material was an asphaltenes-containing hydrocarbon mixture obtained as residue in the vacuum distillation of an atmospheric distillation residue of a crude mineral oil. The vacuum residue mainly boiled above 520°C and had an RCT of 18.8% by weight, a total vanadium and nickel content of 167 ppmw and a sulphur content of 5.4% by weight. The process was carried out according to the flow diagrams 1-6 respectively. The following conditions were applied in the various sections.

30 In the processes described in the flow diagrams the two-step solvent-deasphalting was carried out by contacting the feed to be deasphalted in the first step in an extractor with an n-butane/isobutane mixture (weight ratio 65:35) at a temperature of 110°C, a pressure of 40 bar and a solvent/oil weight ratio of 2:1 and, after separation of the asphalt, separating the deasphalted oil

into a deasphalted oil 1 and a deasphalted oil 2 in the second step in a settler at a temperature of 140°C and a pressure of 40 bar.

In the processes described in the flow diagrams the catalytic hydrotreatment unit consisted of two reactors the first of which was filled with an 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 an Ni/Mo/Al₂O₃ catalyst containing 4 pbw of nickel and 12 pbw of molybdenum per 100 pbw of alumina. The catalysts were used in a volume ratio of 1:4. The catalytic hydrotreatment was carried out at a hydrogen pressure of 150 bar, a space velocity (measured over both reactors) of 0.5 kg feed/catalyst/h, an H₂/feed ratio of 1000 Nl per kg and an average temperature of 410°C in the first reactor and of 390°C in the second reactor.

In the process described in flow diagram 1 the thermal cracking was carried out in a cracking coil at a pressure of 10 bar, a space velocity of 2.5 kg of fresh feed per cracking coil volume per minute and a temperature of 460°C (measured at the cracking coil outlet).

In the processes described in flow diagrams 2, 3 and 6 the catalytic cracking was carried out at a temperature of 510°C, a pressure of 2.2 bar, a space velocity of 2 kg.kg⁻¹.h⁻¹ and a catalyst regeneration rate of 1.0 part by weight of catalyst per 1000 pbw of oil and using a zeolitic cracking catalyst.

In the process described in flow diagram 4, the thermal cracking was carried out as described for flow diagram 1, but at a space velocity of 0.4 kg of fresh feed per cracking coil volume per minute and in the process described in flow diagram 5, the thermal cracking was carried out in two cracking coils under conditions as described for flow diagram 1, but at space velocities of 0.4 and 2.5 kg of fresh feed per cracking coil volume per minute for asphalt and deasphalted oil 2 respectively.

For comparison a test was also carried out in which the vacuum residue was subjected to a two-step solvent-deasphalting

for the production of a deasphalted oil 1 and a deasphalted oil 2 (Example 7) as well as a test in which the vacuum residue was subjected to one-step solvent-deasphalting for the production of a deasphalted oil 3 (Example 8). In Example 7 the two-step solvent-deasphalting was mainly carried out in the same manner as described in the Examples 1-6, with the exception that the temperature in the settler described in Example 7 was 144°C. The one-step solvent-deasphalting described in Example 8 was carried out in the same manner as the first step of the two-step solvent-deasphalting described in the Examples 1-6.

In all the tests the asphaltenes-containing hydrocarbon mixture (1) used as starting material was 100 parts by weight of vacuum residue.

The quantities of various streams obtained in the experiments described in the Examples 1-6 and the RCT's of certain streams are stated in Table I.

Table II gives a survey of the yield of final products obtained in the Examples 1-8.

Table III gives a survey of the properties of the final products obtained in the Examples 1-8.

TABLE I

Example No.	1	2	3	4	5	6
Example carried out according to flow diagram No.	1	2	3	4	5	6
Flowdiagram shown in Fig. No.	4	5	13	14	22	23
Quantity in parts by weight						
C ₅ -350°C atmospheric distillate (5A)	6.1	5.8	8.7	9.0	9.2	9.4
C ₅ -350°C " " (7A)	2.4	-	-	9.6	12.4	-
C ₅ -350°C " " (9A)	-	7.1	18.0	-	-	18.2
350-520°C vacuum distillate (5B)	9.0	8.6	13.0	13.7	13.8	13.9
350-520°C " " (7B)	4.7	-	-	18.9	14.0	-
350-520°C " " (9B)	-	1.5	3.5	-	-	3.6
deasphalted oil 1 (stream .02)	37.3	36.4	44.3	42.0	42.0	42.3
asphalt (4 or 4A)	40.2	38.1	5.0	5.0	5.0	5.0

RCT of the various streams in parts by weight

deasphalted oil 2 (stream .03)	9.9	14.5	45.1 ^x	37.9 ^x	30.9 ^{xx}	- ^{xx}
C ₅ ⁺ fraction of product (.24)	0.7	1.6	3.5	2.7	3.9	4.5

x asphalt (4B)

xx 520°C⁺ vacuum residue (.08) for the mixture (.30) - and 35.3 pbw

TABLE II

Example No.	1	2	3	4	5	6	7	8
<u>Yield in parts by weight</u>								
hydrocarbon oil distillates	22.2	23.0	43.2	51.2	49.4	45.1	-	-
deasphalted oil 1	37.3	36.4	44.3	42.0	42.0	42.3	22.0	-
" " 2	-	-	-	-	-	-	40.2	-
" " 3	-	-	-	-	-	-	-	62.2
asphalt	40.2	38.1	5.0	5.0	5.0	5.0	37.8	37.8

TABLE III

Example No.	1	2	3	4	5	6	7	8
RCT, % by wt	(deasphalted oil 1 " " 2 " " 3 asphalt)	2.6 - - 39.7	2.8 - - 45.1	2.6 - - 37.9	2.5 - - 27.4	3.1 - - 44.7	1.8 8.2 - 39.5	- - 5.9 39.5
V + Ni content, ppmw	(deasphalted oil 1 " " 2 " " 3 asphalt)	4.4 - - 387	3.9 - - 360	3.8 - - 347	4.3 - - 281	4.1 - - 356	2.9 26 - 411	- - 18 411
Sulphur content, % by wt	(deasphalted oil 1 " " 2 " " 3 asphalt)	3.4 - - 7.1	3.0 - - 6.6	3.5 - - 8.3	3.4 - - 5.8	3.1 - - 6.5	3.2 4.5 - 7.2	- - 4.1 7.2

The following applies to Tables I-III.

The advantage of two-step solvent-deasphalting compared with one-step solvent-deasphalting is apparent when comparing the results of Examples 7 and 8.

- 5 The advantage of the process according to the invention compared with two-step solvent-deasphalting is apparent when comparing the results of Examples 1-6 with those of Example 7. By subjecting the deasphalted oil 2 to catalytic hydrotreatment, thermally or catalytically cracking a distillation residue of the
- 10 hydrotreated product and using a distillation residue of the cracked product as a feed component for solvent-deasphalting, (see Examples 1 and 2), it is ensured that the deasphalted oil 2 is practically completely converted into valuable hydrocarbon oil distillates and deasphalted oil 1.
- 15 By subjecting the asphalt to catalytic hydrotreatment using a distillation residue of the hydrotreated product as a feed component for solvent-deasphalting optionally after the application of catalytic or thermal cracking and, moreover, cracking the deasphalted oil 2 thermally or catalytically and using a distil-
- 20 lation residue of the cracked product as a feed component for solvent-deasphalting (see Examples 3 and 4), it is ensured that a substantial part of the asphalt is converted and the deasphalted oil 2 is practically completely converted into valuable hydrocarbon distillates and deasphalted oil 1.
- 25 By thermally or catalytically cracking the deasphalted oil 2, subjecting the distillation residue of the cracked product to catalytic hydrotreatment and using the distillation residue of the hydrotreated product as a feed component for solvent-deasphalting and, moreover, subjecting the asphalt to catalytic hydrotreatment
- 30 optionally after thermal cracking and using a distillation residue of the hydrotreated product as a feed component for solvent-deasphalting (see Examples 5 and 6), it is ensured that the asphalt is for a substantial part and the deasphalted oil 2 is practically completely converted into valuable hydrocarbon oil
- 35 distillates and deasphalted oil 1.

C L A I M S

1. A process for the production of deasphalted oils and hydrocarbon oil distillates from asphaltenes-containing hydrocarbon mixtures, characterized in that an asphaltenes-containing hydrocarbon mixture is separated by two-step solvent-deasphalting
5 into a deasphalted oil 1 of high quality, a deasphalted oil 2 of lower quality and an asphalt, that the deasphalted oil 2 or the asphalt is converted by a catalytic hydrotreatment into a product having a reduced RCT which is separated by distillation into one or more distillate fractions and a residual fraction, that the
10 residual fraction is subjected to thermal or catalytic cracking or used as a feed component for solvent-deasphalting and the cracked product obtained is separated by distillation into one or more distillate fractions and a residual fraction, which latter fraction is used as a feed component for solvent-deasphalting, or
15 that the deasphalted oil 2 is subjected to thermal or catalytic cracking and/or that the asphalt is subjected to thermal cracking and that a distillation residue of the cracked product(s) is converted by a catalytic hydrotreatment into a product with a reduced RCT that is separated by distillation into one or more
20 distillate fractions and a residual fraction which is used as a feed component for solvent-deasphalting.
2. A process according to claim 1, characterized in that an asphaltenes-containing hydrocarbon mixture is separated by
25 two-step solvent-deasphalting into a deasphalted oil 1 of high quality, a deasphalted oil 2 of lower quality and an asphalt, that the deasphalted oil 2 is converted by catalytic hydrotreatment into a product having a reduced RCT which is separated by
distillation into one or more distillate fractions and a residual fraction that said residual fraction is converted by thermal or
30 catalytic cracking into a cracked product that is separated by distillation into one or more distillate fractions and a residual fraction and that the latter residual fraction is used as a feed

component for solvent-deasphalting.

3. A process as claimed in claim 2, characterized in that the residual fraction separated from the product of the catalytic hydrotreatment is subjected to thermal cracking and that the asphalt is used as a feed component for thermal cracking.

4. A process according to claim 1, characterized in that an asphaltenes-containing hydrocarbon mixture is separated by two-step solvent-deasphalting into a deasphalted oil 1 of high quality, a deasphalted oil 2 of lower quality and an asphalt, that the asphalt is converted by catalytic hydrotreatment into a product having a reduced RCT which is separated by distillation into one or more distillate fractions and a residual fraction and that the residual fraction is used as a feed component for solvent-deasphalting or is converted by thermal or catalytic cracking into a cracked product which is separated by distillation into one or more distillate fractions and a residual fraction, the latter residual fraction being used as a feed component for solvent-deasphalting.

5. A process as claimed in claim 4, characterized in that the residual fraction separated from the product of the catalytic hydrotreatment is used as a feed component for solvent-deasphalting and that the deasphalted oil 2 is converted by thermal or catalytic cracking into a cracked product which is separated by distillation into one or more distillate fractions and a residual fraction that is used as a feed component for solvent-deasphalting.

6. A process as claimed in claim 4, characterized in that the residual fraction separated from the product of the catalytic hydrotreatment is converted by thermal or catalytic cracking into a cracked product, that the deasphalted oil 2 is used as a feed component for thermal or catalytic cracking and that a distillation residue of the thermally or catalytically cracked product is used as a feed component for solvent-deasphalting.

7. A process according to claim 1, characterized in that an asphaltenes-containing hydrocarbon mixture is separated by two-step solvent-deasphalting into a deasphalted oil 1 of high quality,

a deasphalted oil 2 of lower quality and an asphalt, that the deasphalted oil 2 is subjected to thermal or catalytic cracking and/or that the asphalt is subjected to thermal cracking, that a distillation residue of the cracked product(s) is converted by a catalytic hydrotreatment into a product with a reduced RCT that is separated by distillation into one or more distillate fractions and a residual fraction and that the residual fraction is used as a feed component for solvent-deasphalting.

8. A process as claimed in claim 7, characterized in that in the deasphalted oil 2 is thermally or catalytically cracked and that the asphalt is used as a feed component for the catalytic hydrotreatment.

9. A process as claimed in claim 7, characterized in that the deasphalted oil 2 is catalytically cracked, that the asphalt is thermally cracked and that the mixture of the distillation residues of the cracked products is subjected to catalytic hydrotreatment.

10. A process as claimed in one of claims 1-9, characterized in that the feed used is a hydrocarbon mixture mainly boiling above 350°C and more than 35% by weight boiling above 520°C and having an RCT above 7.5% by weight.

11. A process as claimed in claim 10, characterized in that the feed used is a residue obtained in the vacuum distillation of an atmospheric distillation residue of a crude mineral oil.

12. A process as claimed in any one of claims 1-11, characterized in that the two-step solvent-deasphalting is carried out by subjecting the feed in the first step to an extraction under mild conditions in which it is separated into a deasphalted oil 1 and a "light" asphalt and by subjecting the light asphalt in the second step to a second extraction in which it is separated into a deasphalted oil 2 and the final asphalt as by-product of the process.

13. A process as claimed in any one of claims 1-12, characterized in that the two-step solvent-deasphalting is carried out by subjecting the feed in the first step to an extraction under heavier conditions in which it is separated into a deasphalted oil

and a final asphalt as by-product of the process and by separating the deasphalted oil in the second step into a deasphalted oil 1 and a deasphalted oil 2.

14. A process as claimed in any one of claims 1-13, characterized in that in the catalytic hydrotreatment for the reduction of the RCT a catalyst is used containing at least one metal chosen from the group formed by nickel and cobalt and at least one metal chosen from the group formed by molybdenum and tungsten on a carrier consisting more than 40% by weight of alumina.

15. A process as claimed in claim 14, characterized in that in the catalytic hydrotreatment for reduction of the RCT a catalyst is used containing the metal combination nickel/molybdenum or cobalt/molybdenum on alumina as carrier.

16. A process as claimed in claim 14 or 15, characterized in that the feed for the catalytic hydrotreatment has a vanadium + nickel content above 50 ppmw and that in the catalytic hydrotreatment said feed is consecutively contacted with two catalysts, the first of which is a demetallization catalyst consisting more than 80% by weight of silica and the second catalyst is an RCT reduction catalyst as described in claim 14 or 15.

17. A process as claimed in claim 16, characterized in that the demetallization catalyst contains the metal combination nickel/vanadium on silica as carrier.

18. A process as claimed in any one of claims 1-17, characterized in that the catalytic hydrotreatment 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.h⁻¹ and an H₂/feed ratio of from 500-2000 NL.kg⁻¹.

19. A process as claimed in any one of claims 1-18, characterized in that the catalytic hydrotreatment is carried out in such a manner that a product is obtained the C₅⁺ fraction of which fulfils the following requirements:

- a) the RCT of the C₅⁺ fraction is less than 50% of the RCT of the stream subjected to the catalytic hydrotreatment, and
- b) the quantity of hydrocarbons boiling below 350°C in the C₅⁺

fraction is less than 40% by weight.

20. A process for the production of deasphalted oils and hydrocarbon oil distillates from asphaltenes-containing hydrocarbon mixtures as claimed in claim 1, substantially as described in the foregoing and in particular with reference to the Examples.

21. Deasphalted oils and hydrocarbon oil distillates produced by a process as described in claim 20.

22. Apparatuses for carrying out the process as claimed in claim 20, characterized in that said apparatuses substantially correspond with those diagrammatically shown in Figures 1-23.

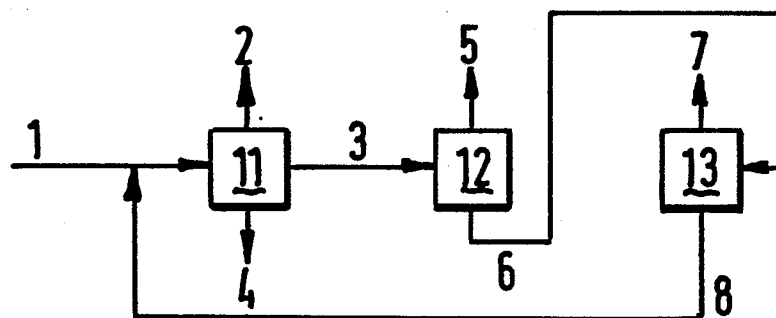


FIG. 1

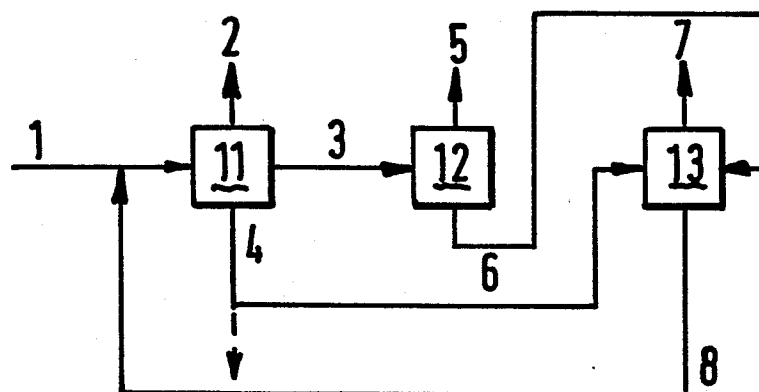


FIG. 2

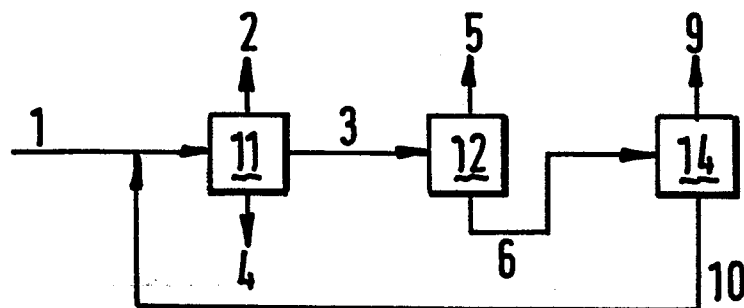


FIG. 3

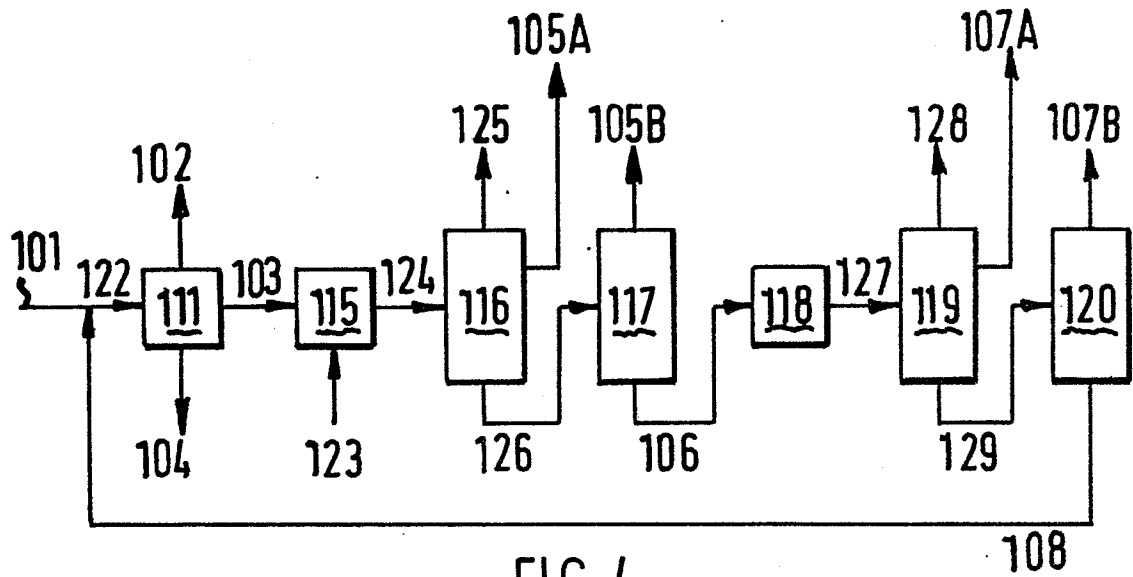


FIG. 4

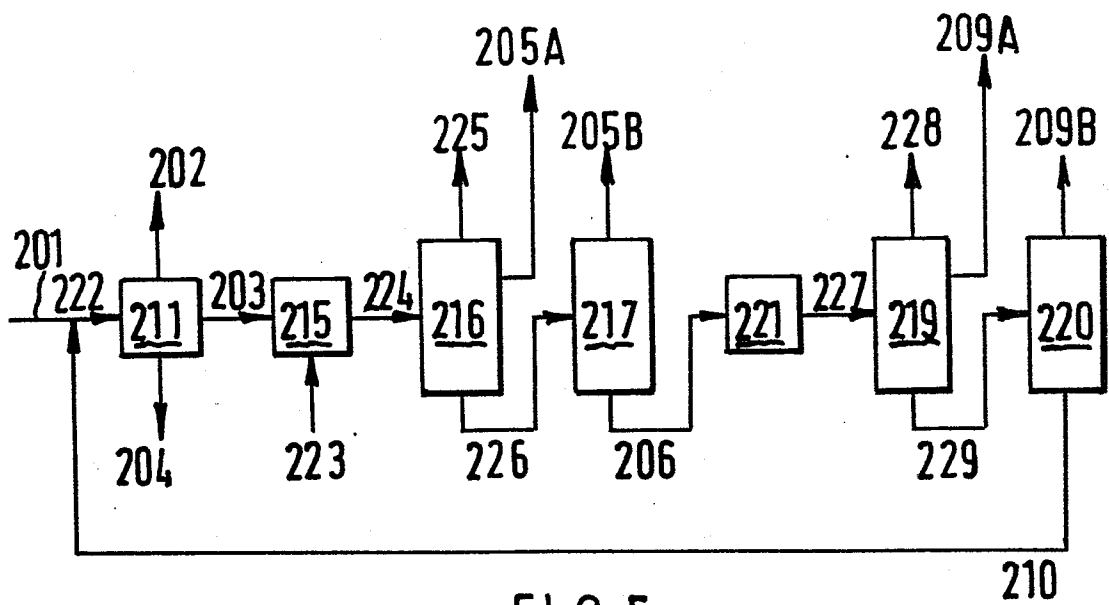


FIG. 5

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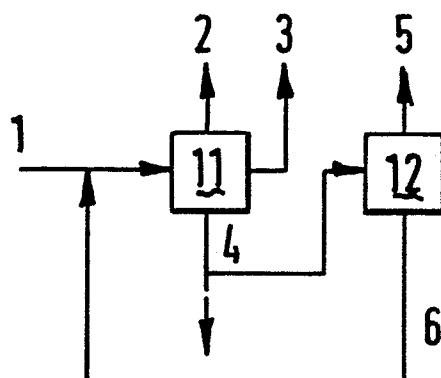


FIG. 6

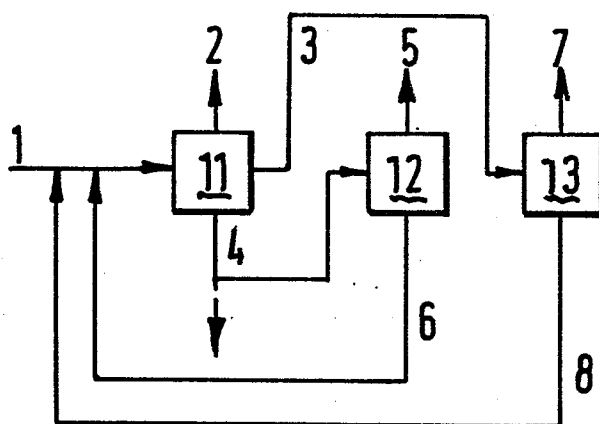


FIG. 7

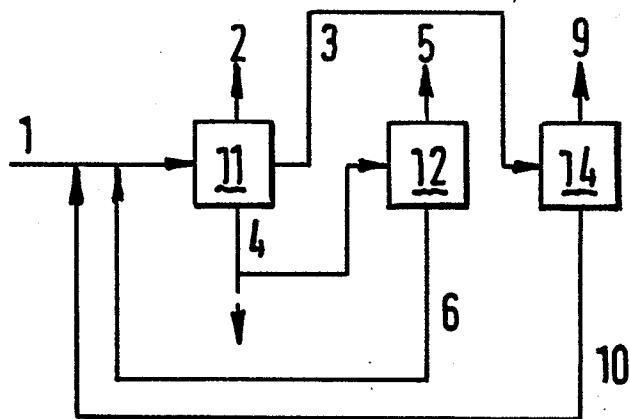


FIG. 8

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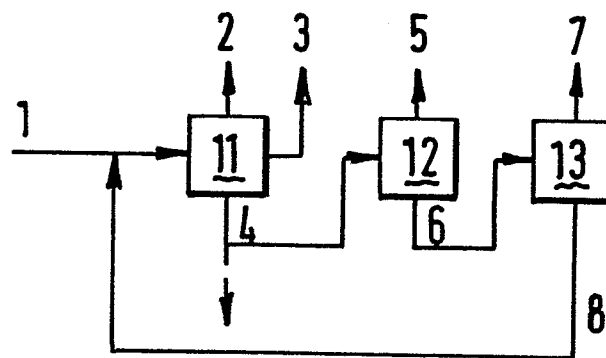


FIG. 9

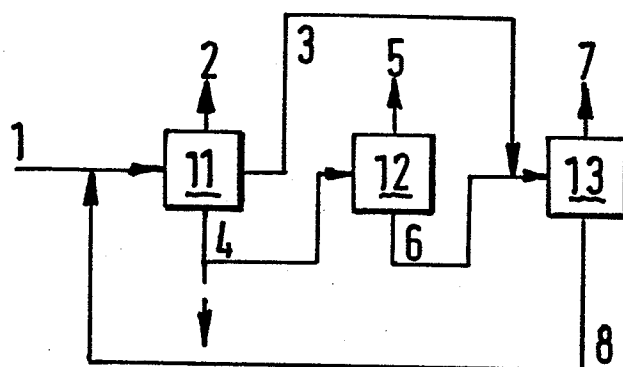


FIG. 10

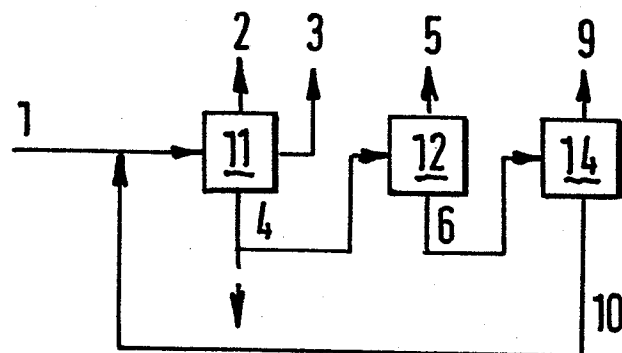


FIG. 11

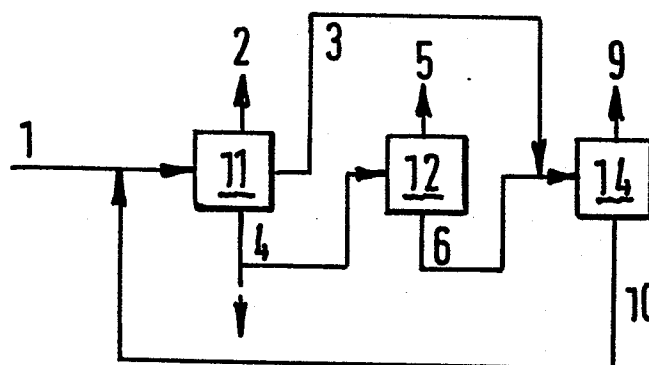
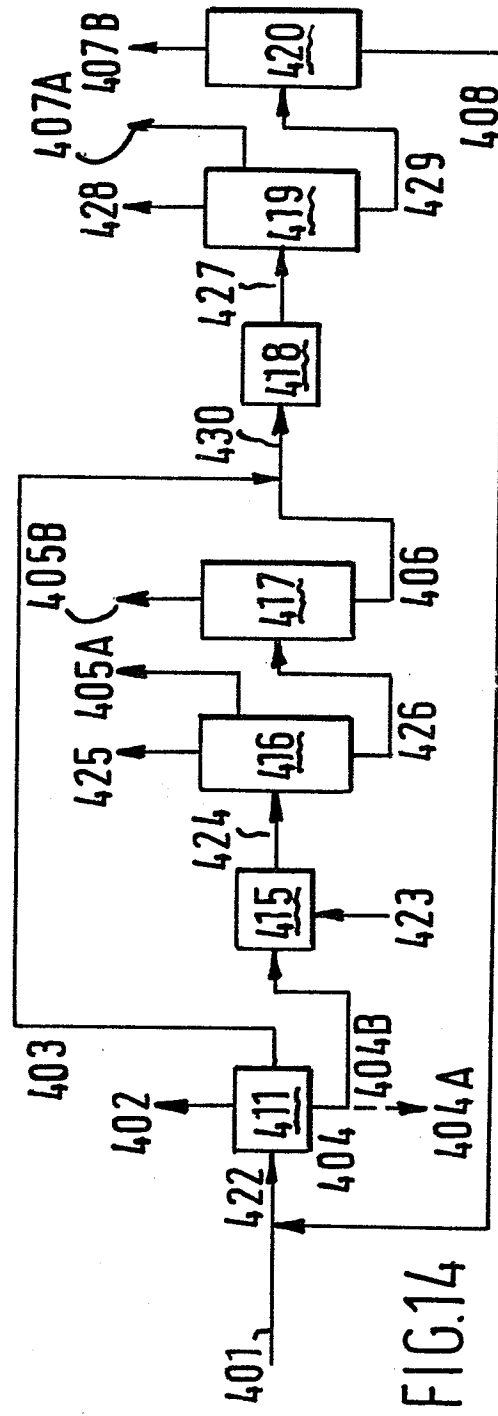
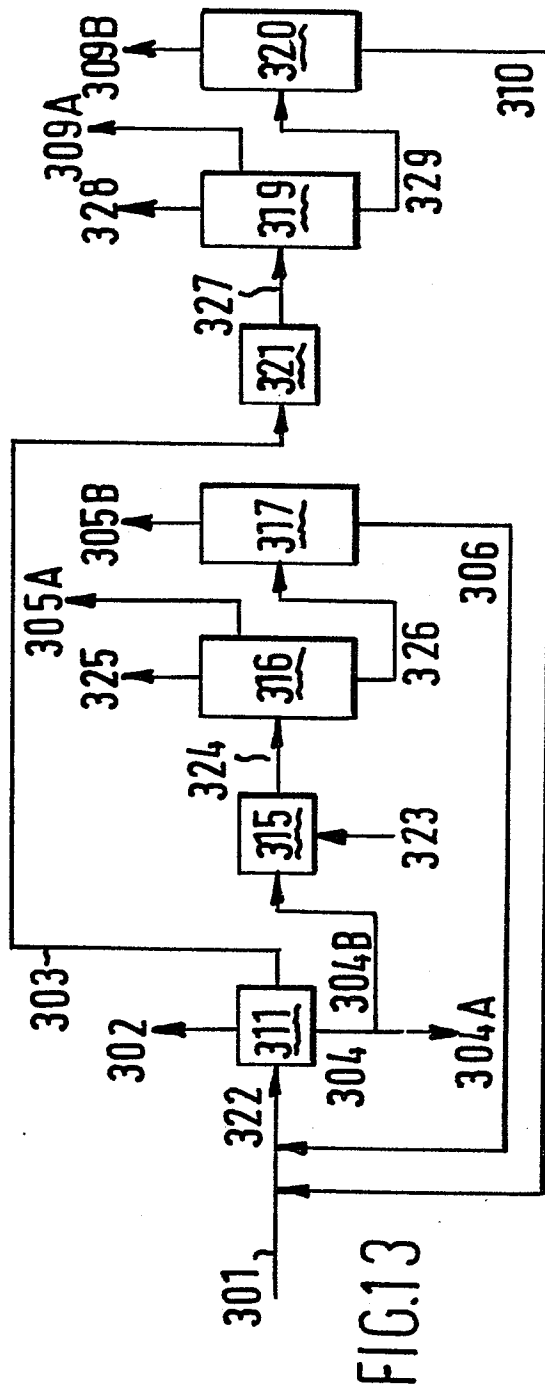
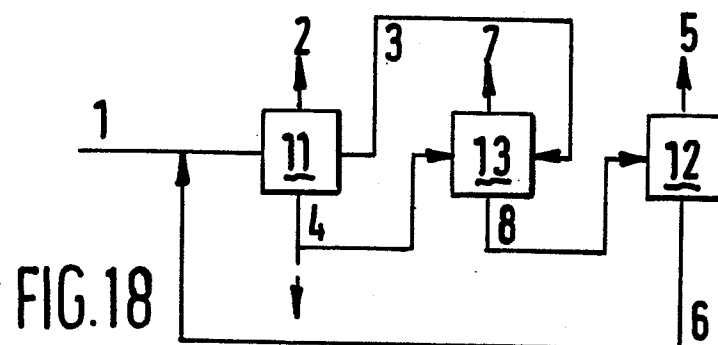
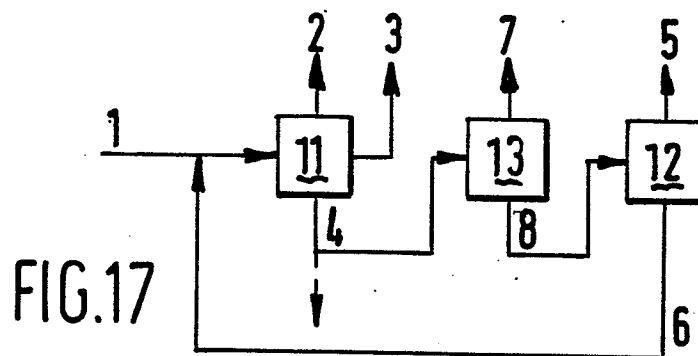
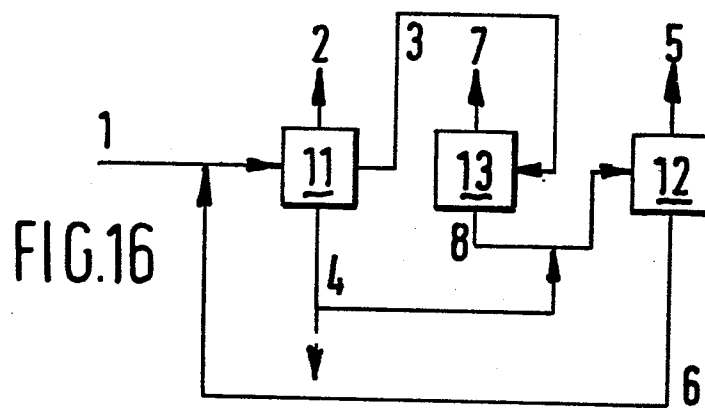
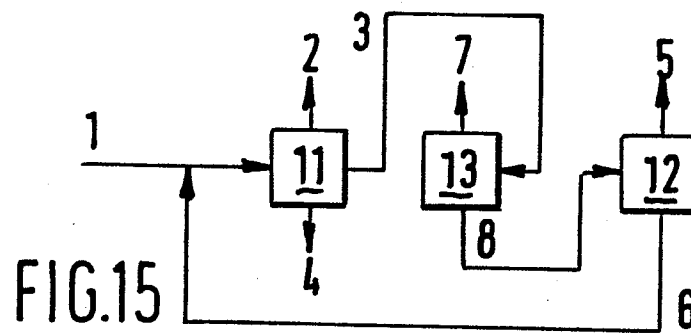


FIG. 12



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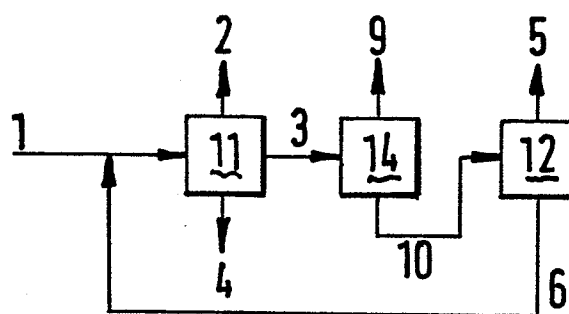


FIG. 19

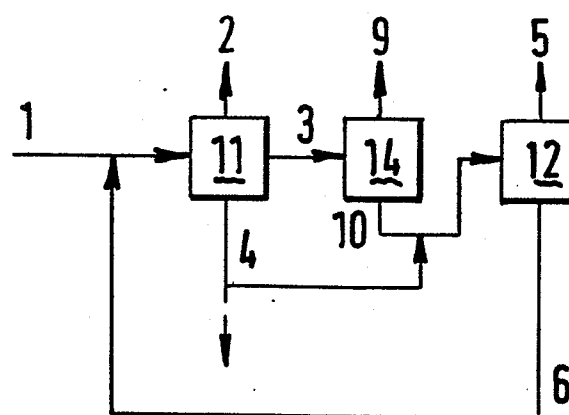


FIG. 20

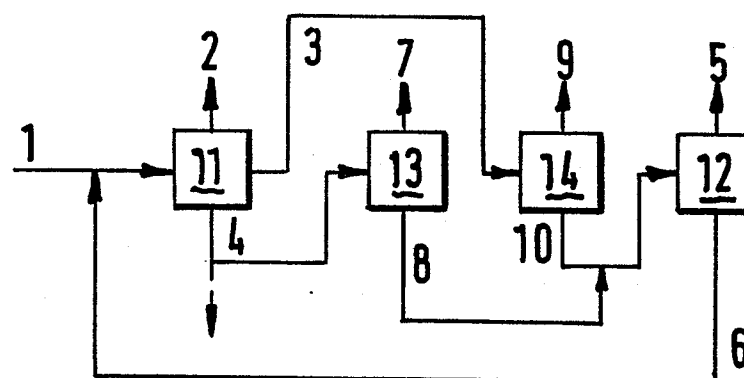


FIG. 21

