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(54) Process for producing lubricating base oils

(57) Process for producing lubricating base oils,
which process comprises the steps of:

- (a) contacting a hydrowax obtained as the bottom fraction of a hydrocracked effluent with a catalyst comprising platinum and/or palladium on a refractory oxide carrier in the presence of hydrogen under such conditions that at least 10% by weight, preferably at least 25% by weight, of the hydrocarbons having a boiling point of 370 °C or higher, which are present in the hydrowax, is converted into hydrocarbons having a lower boiling point,
- (b) separating the product obtained in step (a) in at least one lighter distillate fraction and a heavy distillate fraction having a VI of 125 or higher, preferably of 135 or higher, and a kinematic viscosity at 100 °C of at least 3.5 centiStokes, and
- (c) dewaxing the heavy distillate fraction obtained in step (b).

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Description

The present invention relates to a process for producing lubricating base oils. More specifically, the present invention relates to a process for producing lubricating base oils having a high viscosity index (VI) using a hydrowax obtained as the bottom fraction of a hydrocracking treatment as the feedstock.

It is known that lubricating base oils having a very high VI, i.e. a VI of 125 or higher, can be produced from feedstocks containing relatively high amounts of waxy molecules, i.e. linear and slightly branched paraffins as well as long chain alkyl-aromatics and -naphthenics. Such waxy molecules, namely, have a very high VI of their own and accordingly, positively influence the VI of the product in which they are present. Concrete examples of such high wax content feedstocks are slack waxes and synthetic waxes produced by Fischer-Tropsch synthesis reactions. Slack waxes usually contain 50% by weight or more of wax, whilst synthetic waxes even have a wax content of 80% by weight or more. The present invention aims to provide a process wherein lubricating base oils having such high VI's are produced from a feedstock having a relatively low wax content, i.e. a wax content of less than 50% by weight, even of less than 30% by weight. More specifically, the present invention aims to provide a process for producing such lubricating base oils using a hydrocracker bottom fraction or hydrowax as the feedstock. The process of the present invention, accordingly, can be very suitably integrated in a refinery having hydrocracking capacity.

Processes for producing lubricating base oils from hydrowax are known in the art. In EP-A-0,272,729, for instance, a process is disclosed wherein a hydrocarbon feedstock containing flashed distillate produced in a residue conversion process is hydrocracked, after which the bottom fraction of the cracked effluent, i.e. the hydrowax, is dewaxed. The dewaxing treatment may be preceded or followed by a hydrotreatment step in order to hydrogenate any unsaturated components present. The preferred order is first dewaxing and then hydrotreating the dewaxed material. The final hydrogenation step increases the amount of saturated components present, whereby the hydrogenation of olefins into paraffinic and isoparaffinic components is favourable for the VI of the base oil finally obtained. However, the aromatic components present which are also hydrogenated have no or hardly any impact on the VI of the final base oil and consequently do not contribute to a high VI. As a result, base oils having a VI of 125 or higher cannot be obtained by the process according to EP-A-0,272,729.

The present invention aims to provide a process wherein lubricating base oils having a VI of 125 or higher can be produced in an effective way starting from a hydrowax obtained as the bottom fraction of a hydrocracked effluent.

Accordingly, the present invention relates to a process for producing lubricating base oils, which process comprises the steps of:

- (a) contacting a hydrowax obtained as the bottom fraction of a hydrocracked effluent with a catalyst comprising platinum and/or palladium on a refractory oxide carrier in the presence of hydrogen under such conditions that at least 10% by weight, preferably at least 25% by weight, of the hydrocarbons having a boiling point of 370 °C and higher, which are present in the hydrocracker bottom fraction, is converted into hydrocarbons having a lower boiling point,
- (b) separating the product obtained in step (a) in at least one lighter distillate fraction and a heavy distillate fraction having a VI of 125 or higher, preferably of 135 or higher, and a kinematic viscosity at 100 °C of at least 3.5 centiStokes, and
- (c) dewaxing the heavy distillate fraction obtained in step (b).

The feed used in the process according to the present invention is the bottom fraction of a hydrocracked effluent, which effluent in return is obtained from a hydrocracking operation. The expression "bottom fraction" indicates the fraction recovered from the effluent obtained from the hydrocracking operation at the bottom of the separation device wherein said effluent is separated. Accordingly, said bottom fraction -commonly referred to as hydrowax- is that fraction of the hydrocracked effluent containing the heaviest components. The hydrowax used as the feed in the process of the present invention is suitably obtained from the hydrocracked effluent at an effective cutpoint in the range of from 300 to 450 °C, preferably 310 to 380 °C. The effective cutpoint is the temperature above which at least at least 85% by weight and preferably at least 90% by weight, of the hydrocarbons present in the hydrowax recovered has its boiling point.

Hydrocracking is a conversion process which is well known in the art and basically involves catalytically converting hydrocarbon molecules into smaller hydrocarbon molecules in the presence of hydrogen. A variety of feedstocks can be used for hydrocracking operations, including inter alia distillate fractions, vacuum flashed distillates obtained from other hydrocarbon conversion processes and atmospheric residues. Hydrocracking conditions usually comprise temperatures in the range of from 250 to 500 °C, hydrogen partial pressures in the range of from 1 to 300 bar, weight hourly space velocities of from 0.1 to 10 kg feed per litre of catalyst per hour and gas/feed ratios of from 100 to 5000 NI of gas per kg of feed. Hydrocracking catalysts are also known in the art and include both amorphous and zeolite-based catalysts. In general, a hydrocracking catalyst comprises at least one hydrogenation component of a Group VI metal and/or at least one hydrogenation component of a Group VIII metal and a carrier comprising an amorphous material, such as amorphous silica-alumina, silica or alumina, and/or a zeolite. Zeolites particularly useful in this connection comprise zeolite Y or a modification thereof, such as ultra-stable zeolite Y. The latter type of zeolites is most suitably applied.

Combinations of amorphous materials and zeolites may also be applied. Suitable Group VI metals are tungsten (W) and molybdenum (Mo), whilst suitable Group VIII metals are the non-noble metals nickel (Ni) and cobalt (Co) as well as the noble metals platinum (Pt) and palladium (Pd). Examples of suitable amorphous catalysts are those comprising as the hydrogenation component(s) NiMo, CoMo, NiW, CoW, Pt, Pd or PtPd. The hydrocracking operation may be a single stage operation, involving the use of one bed catalyst, or a two-stage operation, wherein two different catalyst beds are employed. The hydrowax used as the feed in the process of the present invention can in principle be obtained from any arbitrary hydrocracking operation.

In step (a) of the process according to the present invention the hydrowax is contacted with a catalyst comprising platinum and/or palladium on a refractory oxide carrier in the presence of hydrogen under such conditions that a 370 °C+ conversion of at least 10% by weight, preferably at least 25% by weight and even more preferably at least 35% by weight is attained. Suitably, the 370 °C+ conversion is kept below 80% by weight and more suitably below 70% by weight, as at too high conversion levels the yield of lubricating base oil product having a VI of 125 or higher is becoming less interesting from an economical point of view. A highly preferred 370 °C+ conversion is in the range of from 40 to 70% by weight. The expression "370 °C+ conversion" as used in this connection refers to the weight percentage of hydrocarbons present in the hydrowax having a boiling point of 370 °C or higher, which is converted into hydrocarbons having a lower boiling point. This implies that in step (a) both hydrogenation and hydrocracking reactions take place. Suitable reaction conditions include a reaction temperature in the range of from 350 to 550 °C, preferably from 365 to 500 °C, a hydrogen partial pressure in the range of from 10 to 300 bar, preferably 25 to 250 bar, a weight hourly space velocity in the range of from 0.1 to 10 kg/l/hr, preferably from 0.2 to 5 kg/l/hr, and a hydrogen to feed ratio in the range of from 100 to 5,000 NI/kg, preferably from 250 to 2,000 NI/kg.

The catalyst used in step (a) is a noble metal-based catalyst comprising platinum and/or palladium supported on a refractory oxide carrier. The total amount of platinum and/or palladium present in the catalyst is suitably in the range of from 0.1 to 5.0% by weight calculated as element based on total weight of carrier, more suitably in the range of from 0.2 to 2.0% by weight. If both present, the weight ratio of platinum to palladium (calculated as element) may vary within wide limits, but suitably is in the range of from 0.05 to 10, more suitably 0.1 to 5. In one preferred embodiment of the present invention the catalyst comprises platinum as the sole catalytically active metal, whilst in another preferred embodiment of the present invention the catalyst comprises a combination of platinum and palladium. Platinum and palladium may be present as element, as oxide and/or as sulphide.

Beside the noble metal(s), the catalyst used in step (a) may also comprise at least one Group VIB metal component. Particularly when palladium is used as the noble metal, the presence of a Group VIB metal component may be beneficial. Suitable Group VIB metal components include the oxides and sulphides of chromium, molybdenum or tungsten, but also these metals in elemental form. Of these, the tungsten and chromium components are preferred. If present, a Group VIB metal component is suitably present in an amount of from 1 to 35% by weight, more suitably from 5 to 30% by weight, calculated as element and based on total weight of carrier. Examples of very suitable noble metal-based catalysts, accordingly, are those comprising palladium and tungsten or palladium and chromium.

The carrier used comprises a refractory oxide. Suitable refractory oxides include zeolites, alumina, amorphous silica-alumina, fluorinated alumina or mixtures of two or more of these. Of these, amorphous silica-alumina, zeolites and mixtures of these are preferred, whereby the use of amorphous silica-alumina is particularly preferred. Suitable zeolites are the same as those described above to be suitably applied in hydrocracking catalysts, i.e. (modified) zeolite Y. Suitable amorphous silica-alumina carrier materials comprise in the range of from 10 to 70% by weight of alumina and are commercially available. If the carrier comprises an amorphous silica-alumina and/or zeolite as the refractory oxide, it may also contain a binder. The use of binder materials in catalysts is well known in the art. Typical binder materials are silica and alumina. In general, the mutual weight ratio of binder to refractory oxide may vary between wide limits, but suitably is in the range of from 0 (i.e. no binder) to 5, suitably 0 to 4. A particularly preferred catalyst comprises platinum and palladium on an amorphous silica-alumina carrier.

The product obtained from step (a) is subsequently separated in step (b) into at least one lighter distillate fraction and a heavy distillate fraction having a VI of 125 or higher, preferably of 135 or higher, and a kinematic viscosity at 100 °C (Vk100) of at least 3.5 centiStokes, whereby the Vk100 preferably does not exceed 12.0 centiStokes. Very good results have been obtained when aiming at a heavy fraction having a VI above 135 and a Vk100 in the range of from 4.5 to 7.5. It will be appreciated by those skilled in the art that the combination of VI and Vk100 will determine the effective cutpoint for the heavy fraction, i.e. that temperature above which at least 85% by weight and preferably at least 90% by weight of the hydrocarbons in said heavy fraction has its boiling point. In practice this effective cutpoint will be in the range of from 350 to 500 °C, suitably 375 to 475 °C. The lighter distillate fraction(s) obtained will have a VI below the VI of the heavy fraction as well as a lower Vk100. Still, these lighter fractions will have commercially attractive properties making them useful as lubricating base oils -after dewaxing- in applications not requiring extra high VI values.

The dewaxing carried out in step (c) may in principle be carried out via any known dewaxing process. Examples of suitable dewaxing operations are the conventional solvent dewaxing processes, particularly those wherein methylethylketone, toluene or a mixture thereof is used as the dewaxing solvent, and the catalytic dewaxing processes. Both types of dewaxing operations are well known in the art. The most commonly applied solvent dewaxing process is the methyl

ethyl ketone (MEK) solvent dewaxing route, wherein MEK is used as the dewaxing solvent, possibly in admixture with toluene. Catalytic dewaxing generally involves cracking and/or isomerising linear and slightly branched paraffinic hydrocarbon molecules -which negatively influence the cold flow properties of the base oil- in the presence of hydrogen and a dewaxing catalyst. Suitable dewaxing catalysts which mainly favour cracking of paraffinic hydrocarbons are those comprising ZSM-5, ferrierite and/or silicalite and optionally a hydrogenation component. Examples of catalysts which mainly favour isomerisation of linear or slightly branched hydrocarbons, include catalysts comprising a silicoaluminophosphate (SAPO), such as e.g. SAPO-11, SAPO-31 and SAPO-41, ZSM-23 and SSZ-32. A catalytic dewaxing step may suitably be followed by a hydrofinishing step to hydrogenate any unsaturated species (olefins, aromatics) still left. For the purpose of the present invention it is preferred to use either solvent dewaxing or catalytic dewaxing by isomerisation, i.e. catalytic hydro-isomerisation.

The invention is further illustrated by the following examples.

Example 1

A hydrowax having a boiling point distribution as indicated in Table I, was contacted with a catalyst comprising 1.0% by weight of palladium and 0.3% by weight of platinum (both weight percentages being based on total weight of carrier) on an amorphous silica-alumina carrier having an alumina content of 45% by weight. Operating conditions were such that the 370 °C+ conversion was 49.5% by weight. This corresponded with an operating temperature of 390 °C, a hydrogen pressure of 190 bar, a weight hourly space velocity (WHSV) of 1.0 kg/l/hr and a gas rate of 750 NI/kg. The cracked effluent was separated at an effective cutpoint of 400 °C and the 400 °C+ fraction was solvent dewaxed via the conventional MEK/toluene dewaxing Process. The dewaxed product had a VI of 140.1, a Vk40 (kinematic viscosity at 40 °C) of 23.8 cSt and a Vk100 of 4.98 cSt at a yield of 36.7% by weight on feed.

TABLE I

Hydrowax composition	
Boiling point	distribution
IBP ¹	329 °C
IBP - 370 °C	8%wt
370 - 410 °C	22%wt
410 - 480 °C	40%wt
480 - 544 °C	20%wt
544 - 588 °C	6%wt
588 °C - FBP ²	4%wt
FBP	>620 °C

¹ IBP = Initial Boiling Point

² FBP = Final Boiling Point

Example 2

A hydrowax having a boiling point distribution as indicated in Table I, was contacted with the same catalyst as described in Example 1. Operating conditions were such that the 370 °C+ conversion was 28.8% by weight. This corresponded with an operating temperature of 380 °C, a hydrogen pressure of 190 bar, a weight hourly space velocity (WHSV) of 1.0 kg/l/hr and a gas rate of 750 NI/kg. The cracked effluent was separated into a 385 °C- fraction, a 385-450 °C fraction and a 450 °C+ fraction. The 385-450 °C fraction and the 450 °C+ fraction were solvent dewaxed via the conventional MEK/toluene dewaxing process. Properties of both dewaxed fractions are given in Table II.

TABLE II

Product Properties		
Properties	385-450 °C fraction	450 °C+ fraction
VI	116.0	135.1
Vk40 (cSt)	15.9	34.4
Vk100 (cSt)	3.67	6.45
Yield (%wt on feed)	36.7	25.7

Table II shows that a product having a VI of above 135 having good kinematic viscosity's at 40 and 100 °C is obtained, whilst the other dewaxed product obtained also has attractive properties as a lubricating base oil for those applications that do not require extra high VI values, i.e. a VI of 125 or higher.

Claims

1. Process for producing lubricating base oils, which process comprises the steps of:
 - (a) contacting a hydrowax obtained as the bottom fraction of a hydrocracked effluent with a catalyst comprising platinum and/or palladium on a refractory oxide carrier in the presence of hydrogen under such conditions that at least 10% by weight, preferably at least 25% by weight, of the hydrocarbons having a boiling point of 370 °C or higher, which are present in the hydrowax, is converted into hydrocarbons having a lower boiling point,
 - (b) separating the product obtained in step (a) in at least one lighter distillate fraction and a heavy distillate fraction having a VI of 125 or higher, preferably of 135 or higher, and a kinematic viscosity at 100 °C of a least 3.5 centiStokes, and
 - (c) dewaxing the heavy distillate fraction obtained in step (b).
2. Process according to claim 1, wherein the hydrowax is obtained from the hydrocracked effluent at an effective cut-point in the range of from 300 to 450 °C, preferably 310 to 380 °C.
3. Process according to claim 1 or 2, wherein the refractory oxide carrier is an amorphous silica-alumina, a zeolite Y based carrier or a mixture thereof.
4. Process according to any one of the preceding claims, wherein the catalyst used in step (a) comprises platinum and palladium on an amorphous silica-alumina carrier.
5. Process according to any one of the preceding claims, wherein step (a) is carried out at a temperature in the range of from 350 to 550 °C, preferably from 365 to 500 °C, a hydrogen partial pressure in the range of from 10 to 300 bar, preferably 25 to 250 bar, a weight hourly space velocity in the range of from 0.1 to 10 kg/l/hr, preferably from 0.2 to 5 kg/l/hr, and a hydrogen to feed ratio in the range of from 100 to 5,000 NI/kg, preferably from 250 to 2,000 NI/kg.
6. Process according to any one of the preceding claims, wherein the dewaxing in step (c) is carried out by solvent dewaxing.
7. Process according to any one of claims 1 to 5, wherein the dewaxing in step (c) is carried out by a catalytic hydro-isomerisation treatment, optionally followed by a hydrofinishing step.