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(54) Process for the preparation of lubricating base oils

(57) Process for the preparation of a lubricating base oil comprising the steps of:

(a) contacting a hydrocarbon oil feed in a first stage with hydrogen in the presence of a catalyst comprising at least one Group VIII noble metal component on an refractory oxide support;
(b) contacting the liquid effluent in a second stage with hydrogen in the presence of a hydroconversion catalyst under hydroconversion conditions, and
(c) recovering at least one lubricating base oil having a viscosity index of at least 80.

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Description

The present invention relates to a process for the preparation of a lubrication base oil, which process involves two successive hydroconversion stages.

Two stage hydroconversion processes for preparing lubricating base oils are well known in the art, and examples of such processes are disclosed in British Patent Specification No. 1,546,504, European Patent Application No. 0,321,298 and U.S. Patents Nos. 3,494,854; 3,459,656; 3,974,060 and 4,518,485. From these disclosures it becomes apparent that the first stage of a two stage hydroconversion process is usually aimed at removing nitrogen- and sulphur-containing compounds present in the hydrocarbon oil feed and to hydrogenate the aromatic compounds present in the feed to at least some extent. In the second stage the aromatics content is subsequently further reduced by hydrogenation and/or hydrocracking, whilst dewaxing of the effluent from the first stage by hydroisomerisation of waxy molecules often takes place as well. The hydroconversion catalysts used in first and second stage should accordingly be able to adequately serve their respective purposes. From the aforementioned prior art documents it becomes clear that first stage catalysts normally comprise a Group VIII non-noble metal component and a Group VIB metal component on a refractory oxide support. First stage catalysts generally applied, then, include nickel-molybdenum, nickel-tungsten or cobalt-molybdenum on an alumina, silica-alumina or fluorided alumina support. Suitable second stage catalysts comprise a Group VIII noble metal component, optionally together with a Group VIB metal component, on an refractory oxide support. As the Group VIII metal component platinum and/or palladium, either in elemental form or as oxide or sulphide, are disclosed to be useful. As the refractory oxide support aluminosilicates (zeolitic materials) as well as inorganic oxides (such as e.g. silica, alumina and amorphous silica-alumina) or mixtures thereof may be applied.

Although many of the aforementioned prior art two stage hydroconversion processes perform satisfactory, there is always an incentive for further improving the efficiency of a process. In particular the first stage operating temperature leaves room for improvement. Due to the relatively high operating temperature applied in the first hydroconversion stage, namely, the formation of polynuclear aromatic compounds in this first stage is favoured. These polynuclear aromatic compounds formed must then be removed in the second stage, which implies that hydroconversion conditions in this second stage should be sufficiently severe to hydrogenate and/or hydrocrack said polynuclear polyaromatic compounds. On the other hand, decreasing the first stage operating temperature will result in less conversion of the feedstock into valuable products, which is undesired from an economic perspective.

The present invention aims to provide a two stage hydroconversion process for preparing lubricating base oils, whereby the first stage can be operated at a lower operating temperature than conventionally applied, whilst still obtaining products having an excellent viscosity index at a commercially attractive yield. It will be evident that such a process will put less stringent demands on the equipment to be used and hence can be operated at lower operating costs, whilst still maintaining a commercially attractive yield. Moreover, less formation of polynuclear aromatic species also implies that less of these species will remain in the final base oil, which is desired from both environmental and base oil quality considerations. Thus, the present invention aims to provide an improved two stage hydroconversion process for preparing lubricating base oils. More specifically, the present invention aims to provide a process for the preparation of a lubricating base oil, which process allows the production of high viscosity index lubricating base oils at less demanding operating conditions, whilst still having a commercially attractive yield.

These aims have been achieved by selecting a specific first stage hydroconversion catalyst, which is more active than the first stage catalysts conventionally applied and thus allows a lower operating temperature for obtaining the same yield as with a conventional first stage catalyst.

Accordingly, the present invention relates to a process for the preparation of a lubricating base oil comprising the steps of:

(a) contacting a hydrocarbon oil feed in a first stage with hydrogen in the presence of a catalyst comprising at least one Group VIII noble metal component on a refractory oxide support;
(b) contacting the liquid effluent in a second stage with hydrogen in the presence of a hydroconversion catalyst under hydroconversion conditions, and
(c) recovering at least one lubricating base oil having a viscosity index of at least 80.

Suitable hydrocarbon oil feeds to be employed in step (a) of the process according to the present invention are mixtures of high-boiling hydrocarbons, such as for instance heavy oil fractions. Particularly those heavy oil fractions having a boiling range which is at least partly above the boiling range of lubricating base oils are suitable as hydrocarbon oil feeds for the purpose of the present invention. It has been found particularly suitable to use vacuum distillate fractions derived from an atmospheric residue, i.e. distillate fractions obtained by vacuum distillation of a residual fraction which in return is obtained by atmospheric distillation of a crude oil, as the feed. The boiling range of such a vacuum distillate fraction is usually between 300 and 620 °C, suitably between 350 and 550 °C. However, deasphalted residual oil fractions, including both deasphalted atmospheric residues and deasphalted vacuum residues, may also be applied, whilst synthetic waxy raffinates (Fischer-Tropsch waxy raffinates), slack waxes -particularly those obtained from the dewaxing

of hydrotreated waxy distillates- and hydrocracker bottom fractions (hydrowax) are also suitable feedstocks to be used in the process according to the present invention. Suitable hydrowaxes are those having an effective cutpoint of 320 °C or higher, preferably of 370 °C or higher.

The catalyst to be used in the first hydroconversion stage is a Group VIII noble metal-based catalyst. If a hydrocarbon oil feed is used which is not substantially free of sulphur- and nitrogen-containing compounds, this catalyst should be sulphided prior to operation in order to attain optimum catalyst activity and in order to ensure that the catalyst is sufficiently tolerant towards the sulphur- and nitrogen-containing compounds present in the feed. If the catalyst would not be sulphided in this case, its sulphur-tolerance would be too low under the operating conditions and the catalyst would consequently be rapidly poisoned when contacted with the hydrocarbon oil feed under the operating conditions. Only in case the hydrocarbon oil feed is substantially free of any sulphur- and nitrogen-containing compounds, for instance when using a synthetic wax as the feed, sulphiding of the noble metal-based catalyst can be dispensed with. In most cases, however, the noble metal-based catalyst must be sulphided prior to operation.

Sulphiding of the catalyst can be achieved by methods known in the art, such as for instance from European patent applications Nos. 0,181,254; 0,329,499; 0448,435 and 0,564,317 and from International patent applications Nos. WO 93/02793 and WO 94/25157. Sulphiding can be performed either ex situ or in situ by contacting the unsulphided catalyst with a suitable sulphiding agent, such as hydrogen sulphide. A hydrocarbon oil containing a substantial amount of sulphur-containing compounds may also be used as the sulphiding agent. Such oil is then contacted with the catalyst at a temperature which is gradually increased from ambient temperature to a temperature of between 150 and 250 °C. The catalyst is to be maintained at this temperature for between 10 and 20 hours. Subsequently, the temperature is to be raised gradually to the operating temperature. Still another option is to use the hydrocarbon oil feed, which usually contains a significant amount of sulphur-containing compounds, as the sulphiding agent. In this case the unsulphided catalyst may be contacted with the feed under conditions less severe than the operating conditions, thus causing the catalyst to become sulphided. Typically, the hydrocarbon oil feed should comprise at least 0.5% by weight of sulphur-containing compounds, said weight percentage indicating the amount of elemental sulphur relative to the total amount of feedstock, in order to be useful as a sulphiding agent. From a cost and efficiency perspective, it is generally preferred to sulphide the catalyst in situ, i.e. first loading the unsulphided catalyst into a reactor and thereafter contacting it with the sulphiding agent(s) under appropriate sulphiding conditions.

The refractory oxide support of the first stage hydrotreating catalyst may be any inorganic oxide, aluminosilicate or combination of these, optionally in combination with an inert binder material. Examples of suitable refractory oxides include inorganic oxides, such as alumina, silica, titania, zirconia, boria, silica-alumina, fluorided alumina, fluorided silica-alumina and mixtures of two or more of these. In a preferred embodiment an acidic carrier such as alumina, silica-alumina or fluorided alumina is used as the refractory oxide carrier. The refractory oxide support may also be an aluminosilicate. Both synthetic and naturally occurring aluminosilicates may be used. Examples are zeolite beta, faujasite and zeolite Y. A preferred aluminosilicate to be applied is alumina- or silica-bound zeolite Y.

The Group VIII noble metal component of the first stage hydroconversion catalyst suitably is a platinum (Pt) and/or a palladium (Pd) component. If the catalyst is sulphided prior to operation, the noble metal component will usually be present as a sulphide during normal operation, but part of it may very well be present in elemental and/or oxide form. Beside the Group VIII noble metal component, a non-noble Group VIII metal component and/or a Group VIB metal component may be present as well on the catalyst. Accordingly, nickel (Ni), cobalt (Co) and/or chromium (Cr), molybdenum (Mo) or tungsten (W) -suitably in their sulphide form- may also be present on the catalyst. Of the Group VIB metals, tungsten and chromium are preferred. Examples of very suitable first stage catalysts, then, are those noble metal based-catalysts disclosed in European Patent Application No. 0,653,242 and International Patent Application No. WO 96/03208. Specific examples of suitable catalysts include PdCr and PdW on silica-bound zeolite Y, on alumina-bound zeolite Y, on fluorided alumina-bound zeolite Y, on silica-alumina or on fluorided alumina. Other examples are Pt on silica-alumina, PtPd on silica-bound zeolite Y, PtPd on alumina-bound zeolite Y and PtPd on silica-alumina. All catalysts mentioned preferably are sulphided prior to operation. Particularly preferred first stage catalysts are sulphided PdW on silica- or alumina-bound zeolite Y, sulphided PdW on silica-alumina and sulphided PdW on fluorided alumina.

The second hydroconversion stage, i.e. step (b), of the process according to the present invention may involve hydrogenation, hydrodesulphurisation, hydrodenitrogenation, hydroisomerisation of paraffinic molecules and any combination of two or more of these processes, depending on the type of hydroconversion catalyst used. Hydrocracking of paraffinic molecules may also occur in step (b), but only as a (minor) side reaction to one or more of the hydroconversion reactions mentioned above. Accordingly, the hydroconversion catalyst to be used in step (b) will not be a catalyst specifically suited for hydrocracking of paraffinic molecules.

The hydroconversion catalyst used in step (b) of the process according to the present invention, i.e. the second stage catalyst, in principle may be any catalyst known to be active in the hydrogenation, hydrodesulphurisation, hydrodenitrogenation and/or hydroisomerisation of the relevant hydrocarbons with the purpose of manufacturing lubricating base oils.

Accordingly, a first class of suitable second stage catalysts are the hydrogenation catalysts comprising at least one Group VIII metal component and optionally at least one Group VIB metal component as the hydrogenating compo-

nent(s). Such catalysts have hydrogenation activity and may also have hydrodesulphurisation and/or hydrodenitrogenation activity. Usually they do not possess any relevant hydroisomerisation activity. Suitable Group VIII metal components include both noble and non-noble metals and/or compounds thereof, usually oxides and/or sulphides. The second stage catalyst may accordingly comprise one or more of the non-noble Group VIII metals nickel (Ni) or cobalt (Co) and/or one or more of the noble Group VIII metals Pt and Pd. In this connection it is noted that if a noble metal component is present on the second stage catalyst, this catalyst is suitably at least partly sulphided prior to operation in order to increase its sulphur tolerance. It will be understood that the extent of sulphidation depends on the sulphur content of the first stage effluent. At sufficiently low sulphur content of the first stage effluent, sulphidation of a second stage noble metal-based catalyst may be dispensed with.

In addition to the Group VIII metal component, the second stage catalyst may also comprise a Group VIB metal component, which may be Cr, Mo and/or W in elemental, oxide and/or sulphide form. The second stage catalyst support also is an refractory oxide support and includes the same supports as listed above for the first stage catalyst. In case the second stage catalyst comprises a non-noble Group VIII metal, it may be advantageous to use phosphorus (P) as a promoter. Examples of suitable second stage catalysts, then, include NiMo(P) on alumina or fluorided alumina, CoMo(P) on alumina, NiW on fluorided alumina, PdW on silica-alumina, fluorided alumina or silica-bound zeolite Y.

A second class of suitable second stage catalysts are those catalysts having predominantly hydroisomerisation activity. These catalysts are used, if the main objective of step (b) is to lower the pour point of the first stage effluent, i.e. dewaxing. Hydroisomerisation catalysts are well known in the art and usually are based on an intermediate pore size zeolitic material, suitably comprising at least one Group VIII metal component, preferably Pt and/or Pd. Suitable zeolitic materials, then, include ZSM-5, ZSM-22, ZSM-23, ZSM-35, SSZ-32, ferrierite, zeolite beta, mordenite and silica-aluminophosphates, such as SAPO-11 and SAPO-31. Examples of suitable hydroisomerisation catalysts are, for instance, described in International Patent Application No. WO 92/01657. Since hydroisomerisation catalysts generally are relatively quickly poisoned by sulphur-containing compounds, the first stage effluent must have a low sulphur content prior to entry in the second stage.

The amounts of the different metals present on first and second stage catalyst may vary between wide limits. A Group VIII noble metal may suitably be present on first and second stage catalyst in an amount ranging from 0.1 to 10, preferably 0.2 to 5, percent by weight (% wt), which weight percentage indicates the amount of metal (calculated as element) relative to total weight of catalyst. Similarly, a non-noble Group VIII metal may suitably be present on the second stage catalyst in an amount of from 1 to 25% wt, preferably 2 to 15% wt, calculated as element relative to total weight of catalyst. If present at all, a Group VIB metal is suitably present on first and second stage in an amount of from 5 to 30% wt, preferably 10 to 25% wt, calculated as element relative to total weight of catalyst.

Operating conditions in the first and second hydroconversion stage are those conventionally applied in the relevant hydroconversion operations. Accordingly, the operating temperature may range from 250 to 500 °C, the operating pressure may range from 10 to 250 bar, the weight hourly space velocity (WHSV) may range from 0.1 to 10 kg of oil per litre of catalyst per hour (kg/l.h), preferably from 0.5 to 5 kg/l.h, and the hydrogen to oil ratio is suitably in the range from 100 to 2,000 litres of hydrogen per litre of oil. However, as already stated above, at a given final yield of lubricating base oil, the first stage catalyst used in accordance with the present invention allows a lower first stage operating temperature, thus reducing the amount of polynuclear aromatic species formed in this first hydroconversion stage and hence allowing less severe conditions in the second hydroconversion stage. In this connection it is noted that an activity gain in the first hydrotreatment stage of only three degrees Celsius may already significantly reduce the amount of polynuclear aromatics formed.

Before being subjected to the second stage hydroconversion, the liquid effluent of the first stage may first be treated to remove undesired gaseous species, such as hydrogen sulphide (H_2S) and ammonia (NH_3). Particularly for feeds containing substantial amounts of sulphur- and nitrogen-containing compounds, such as vacuum distillates derived from an atmospheric residue, such interstage treatment could be very advantageous. H_2S may, for instance, be removed by absorption in an aqueous amine solution. A di-isopropanolamine solution is very useful in this respect. A preferred option, however, is to remove H_2S and NH_3 simultaneously from the first stage effluent by passing said effluent through a high pressure stripper prior to introduction into the second stage. In this way the content of both these undesired gases in the first stage effluent can be effectively reduced to very low levels, suitably below 10 ppm each. Such low levels of H_2S and NH_3 allow the use of second stage catalysts which have a higher sensitivity to sulphur and nitrogen, such as (unsulphided) noble metal-based catalysts. The use of these kind of catalysts in the second hydroconversion stage, in return, allows the manufacture of higher quality base oils, such as technical grade white oil. Using noble metal-based catalysts in both hydroconversion stages may even allow the production of medicinal oil, which must be free of aromatics, nitrogen compounds and sulphur compounds, if the first stage is operated at a sufficiently low temperature, thus preventing the formation of polynuclear aromatics.

Thus, if the liquid effluent of the first hydroconversion stage is treated to remove H_2S and NH_3 prior to introduction into the second hydroconversion stage, the second stage catalyst suitably comprises a Pt and/or a Pd component as the Group VIII metal component. This catalyst may further comprise a Group VIB metal component, preferably based on W or Cr. In this mode of operation it may be advantageous to use the same noble metal-based catalyst in the first

and second hydroconversion stage. If, on the other hand, H_2S and NH_3 are not removed from the first stage effluent, whereas the feed used is not substantially free of any sulphur-and/or nitrogen-containing compounds, it is preferred to use a second stage catalyst comprising a nickel or cobalt component as the Group VIII metal component and a molybdenum or tungsten component as the Group VIB metal component. Suitable examples of any of these catalysts have already been described above.

Recovery of the lubricating base oil(s) in step (c) is usually attained by distillation of the second stage effluent. Each lubricating base oil is then recovered as a distillate fraction. Suitably the distillation is carried out under reduced pressure. However, atmospheric distillation may also be applied. The cutpoint(s) of the distillate fraction(s) is/are selected such that each base oil recovered has the desired viscosity.

If the second stage catalyst is a hydrogenation catalyst having no or hardly any hydroisomerisation activity, then a subsequent dewaxing step (d) is required to obtain lubricating base oils having sufficiently low pour points. Dewaxing can be achieved by catalytic dewaxing or solvent dewaxing. Both dewaxing techniques are well known in the art. For instance, suitable catalysts for use in catalytic dewaxing include catalysts based on ZSM-5, ZSM-23 or ZSM-35. Suitable dewaxing catalysts and dewaxing processes are for instance described in U.S. Patents Nos. 3,700,585; 3,894,938; 4,222,855; 4,229,282; 4,247,388 and 4,975,177. Solvent dewaxing is also a well known dewaxing process. 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. For the purpose of the present invention it is preferred to use the solvent dewaxing route.

If the second stage catalyst is a hydroisomerisation catalyst, then a separate dewaxing step after step (c) can be dispensed with. The lubricating base oil(s) obtained in step (c) in this case meet the specifications with respect to both viscosity index and pour point and accordingly no further pour point lowering treatment is necessary in that case. As already mentioned above, the first stage effluent must have a sufficiently low sulphur content before being contacted with a hydroisomerisation catalyst. If the hydrocarbon oil feed used in step (a) is a hydrowax or a synthetic waxy raffinate, which usually have low sulphur and nitrogen contents, then an interstage treatment for removing H_2S and NH_3 can be dispensed with and the first stage effluent can be directly passed to step (b). If, on the other hand, the hydrocarbon oil feed used in step (a) has relatively high sulphur and nitrogen contents, such as in the case of vacuum distillates of atmospheric residues, then an interstage removal of H_2S and NH_3 is required.

In general, the lubricating base oils eventually produced using the process according to the present invention have a viscosity index of at least 80, preferably at least 90 and more preferably at least 95, and a pour point of -6 °C or lower and preferably -9 °C or lower.

The invention will now be further illustrated by the following example without restricting the scope of the invention to this particular embodiment.

Example

A hydrocarbon oil vacuum distillate obtained by vacuum flashing of an atmospheric residue and having the properties as indicated in Table I was contacted in a first step with hydrogen in the presence of a presulphided catalyst comprising 4.3% wt Pd and 21.9% wt of W (both calculated as element relative to total weight of catalyst) on a fluorided alumina carrier (4.4% wt F, basis total carrier). The effluent of the first step was subsequently contacted in the second step with hydrogen in the presence of a conventional NiMoP/alumina catalyst (3.0% wt Ni, 13.0% wt Mo, 3.2% wt P, all calculated as element relative to total weight of catalyst). Reaction conditions applied in both steps and the properties of the final product after conventional solvent dewaxing at -20 °C are given in Tables II and III, respectively.

TABLE I

Feedstock characteristics	
Refractive Index at 70 °C	1.5010
Flash Point (°C)	213
Specific Gravity 70/4 °C	0.899
Vk80 (cSt)*	28.2
Vk100 (cSt)*	14.8
Sulphur (% wt)	2.68
Nitrogen (% wt)	0.13
Hydrogen (% wt)	12.0
C5 asphaltenes (% wt)	0.08
Wax content (% wt)	9.2

* Vk80 and Vk100 stand for kinematic viscosity in centistokes as determined at 80 °C and 100 °C, respectively

Comparative Example

The same procedure as described above was repeated, only this time with a first stage catalyst comprising 5.0% wt Ni and 23.1% wt W on a fluorided alumina carrier (4.6% wt F, basis total carrier). Process conditions and properties of the product obtained after conventional solvent dewaxing at -20 °C are listed in Tables II and III, respectively.

TABLE II

Process conditions				
Operating Condition	Example		Comparative Example	
	Step 1	Step 2	Step 1	Step 2
Temperature (°C)	380	390	400	390
WHSV (kg/l.h)	1.0	1.0	1.0	1.0
Gas rate (Nl/kg)	1500	1500	1500	1500
Pressure (bar)	140	140	140	140

TABLE III

Product properties		
	Example	Comparative Example
Yield (% wt on feed)	77	72
Vk100 (cSt)	9.55	9.88
VI	95	93

As can be seen from Tables II and III, the process according to the present invention requires a lower temperature in the first step, wherein the noble metal-based catalyst is used, whilst still obtaining a product having better VI and viscosity at a higher yield.

Claims

1. Process for the preparation of a lubricating base oil comprising the steps of:

   (a) contacting a hydrocarbon oil feed in a first stage with hydrogen in the presence of a catalyst comprising at least one Group VIII noble metal component on an refractory oxide support;
   (b) contacting the liquid effluent in a second stage with hydrogen in the presence of a hydroconversion catalyst under hydroconversion conditions, and
   (c) recovering at least one lubricating base oil having a viscosity index of at least 80.

2. Process according to claim 1, wherein the first stage catalyst comprises a platinum and/or palladium component as the Group VIII noble metal component.

3. Process according to claim 2, wherein the first stage catalyst further comprises a Group VIB metal component, preferably a tungsten or chromium component.

4. Process according to any one of the preceding claims, wherein the hydrocarbon oil feed is a vacuum distillate fraction derived from an atmospheric residue.

5. Process according to any one of the preceding claims, wherein the hydroconversion catalyst used in step (b) is a hydrogenation catalyst comprising at least one Group VIII metal component and optionally at least one Group VIB metal component.

6. Process according to claim 5 further comprising the step of (d) subjecting the lubricating oil(s) recovered in step (c) to a dewaxing treatment.

7. Process according to claim 5 or 6, wherein the hydroconversion catalyst used in step (b) comprises a palladium, nickel or cobalt component as the Group VIII metal component and a molybdenum or tungsten component as the Group VIB component.

8. Process according to any one of claims 5 to 7, wherein the liquid effluent from step (a) is first treated to remove hydrogen sulphide and ammonia before being contacted with hydrogen in step (b), preferably by passing said effluent through a high pressure stripper.

9. Process according to claim 8, wherein the hydroconversion catalyst used in step (b) comprises a platinum and/or a palladium component as the Group VIII metal component and as the Group VIB component, if present, a tungsten or chromium component.

10. Process according to any one of claims 1 to 4, wherein the liquid effluent from step (a) is first treated to remove hydrogen sulphide and ammonia before being contacted with hydrogen in step (b), preferably by passing said effluent through a high pressure stripper, and wherein the hydroconversion catalyst used in step (b) is a hydroisomerisation catalyst.

11. Process according to any one of claims 1 to 3, wherein the hydrocarbon oil feed is a hydrowax or a synthetic waxy raffinate and the effluent of step (a) is directly passed to step (b), wherein the hydroconversion catalyst is a hydroisomerisation catalyst.