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PROCESS TO PREPARE A LUBRICATING BASE OIL

Field of invention

The invention is related to a process to prepare a lubricating base oil having a high saturates content and a high viscosity index starting from a vacuum distillate feedstock.

Background of the invention

US-A-5976354 discloses a process to make base oils having a high viscosity index (VI) and a low aromatics content from a waxy distillate feedstock. The majority of the aromatics are first removed by means of solvent extraction. The extracted oil is subsequently subjected to a hydrotreating step followed by a catalytically dewaxing step and finally to a aromatics saturation step.

A disadvantage of the process of US-A-5973354 is that when base oils are to be made having a high VI the yield will drop dramatically. This is due to the more severe solvent extraction and hydrotreating process conditions which are required in order to arrive at the high VI base oil.

An alternative processing route to high viscosity index base oils is by starting from a slack wax feed as for example described in EP-A-324528. In the disclosed process slack wax feed is first hydrocracked/hydroisomerised and the resultant oil product is subjected to a catalytic dewaxing step followed by a hydrotreating step.

A disadvantage of the process described in EP-A-324528 is that although high VI base oils are prepared the yield on feed is still not high.

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EP-A-921184 discloses a process in which a blend of a waxy distillate feedstock and a Fischer-Tropsch wax consisting predominately of normal paraffins is subjected to a hydrocracking process. The hydrocracked blend is subsequently subjected to a solvent dewaxing step. It was shown that higher VI base oils are obtained using this blended feedstock. However the yield of base oils calculated on the total feed was lower when starting from the blend of mineral waxy distillate and Fischer-Tropsch derived wax.

US-A-6576120 describes a process wherein a partly isomerised Fischer-Tropsch wax is catalytically dewaxed using a Pt-ZSM-5/silica containing catalyst to a base oil having a pour point of -30 °C and a VI of 151.

US-A-6080301 and US-A-6165949 disclose base oil as prepared from a Fischer-Tropsch wax and their use in lubricant formulations.

The object of the present invention is to make a base oil having a high saturates content and a high VI in a high yield starting from a vacuum distillate feedstock.

Summary of the invention

This object has been achieved with the following process. Process to prepare a lubricating base oil having a saturates content of greater than 90 wt% and a viscosity index of greater than 100 starting from a vacuum distillate feedstock by performing the following steps:

- (a) contacting the vacuum distillate feedstock with an extraction solvent selective for extracting aromatic compounds from the vacuum distillate,
- (b) mixing the extracted oil obtained in step (a) with a feed comprising of more than 50 wt% wax or

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comprising of more than 80 wt% of paraffins and having a pour point greater than 0 °C,
(c) hydrotreating the blend obtained in step (b),
(d) catalytically dewaxing the hydrotreated oil obtained
5 in step (c) to obtain the lubricating base oil and
(e) contacting the dewaxed oil with an aromatics saturation catalyst.

Detailed description of the invention

Applicants found that by mixing a waxy and or
10 paraffinic feed to the extracted oil the yield to high VI base oil can be significantly improved. This is explained by the fact that the paraffins in the waxy feed, for example a Fischer-Tropsch wax, will enhance the VI. Thus the severity of both the solvent extraction and the
15 hydrotreatment may be reduced resulting in an overall higher oil yield.

Detailed description of the invention

The vacuum distillate feed to step (a) is suitably a fraction boiling in the base oil boiling range. Such a
20 feed is also referred to as a mineral waxy distillate. The base oil boiling range boils suitably above 350 and more typically above 370 °C. From distillate feeds it is possible to prepare base oil products having a kinematic viscosity at 100 °C of above 2 cSt and typically between
25 2 and 15 cSt. Such distillate feeds are preferably obtained by distillation of a suitably mineral crude petroleum source at atmospheric pressure conditions. The residue thus obtained is subsequently further distilled at vacuum pressure conditions into one or more waxy
30 distillate fractions and a so-called vacuum residue. These waxy distillate fractions can be suitably used as feed to step (a). The feedstock preferably has an initial boiling point in the range of from about 500°F. (260 °C)

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to about 650 °F.(343 °C) and a 95% boiling point generally in the range of 800 °F.(427 °C) to 950 °F (510 °C).

5 In step (a) aromatics are extracted by contacting the feedstock with a suitable extraction solvent. These processes are well known in base oil manufacturing and are for example described in Lubricant Base Oil and Wax Processing, Avilino Sequeira, Jr, Marcel Dekker Inc., New York, 1994, Chapter 5. Suitable solvents are well
10 known, as are process conditions. Common suitable solvents include N-methyl-pyrrolidone, furfural, phenol and sulphur dioxide. In the process of the present invention a less severe extraction is allowed, preferably less than 50 wt% of the aromatics content of the waxy
15 raffinate feedstock needs to be removed from said waxy distillate feedstock in step (a).

In step (b) the extracted oil as obtained in step (a), which is poor in aromatics relative to the original feedstock is blended with a feed comprising of
20 more than 50 wt% wax or comprising of more than 80 wt% of paraffins and having a pour point greater than 0 °C. The feedstock employed in the process of the invention preferably contains greater than about 70% wax. The paraffinic feed more preferably has a pour point of
25 greater than 10 °C and even more preferably more than 30 °C. The paraffinic feed more preferably comprises of more than 80 wt% paraffins and even more preferably more than 90 wt% paraffins, wherein the paraffins may be normal and/or iso-paraffins.

30 Examples of the above described feed are synthetic oils such as prepared by the Fischer-Tropsch synthesis process, high pour point polyalphaolefins, foots oils, synthetic waxes such as normal polyalphaolefin waxes,

slack waxes, deoiled waxes and microcrystalline waxes. Foots oil is prepared by separating oil from for example a slack wax. The isolated oil is referred to as foots oil.

5 A preferred waxy feed are slack waxes having a wax content of above 50 wt% and more preferably above 70 wt%. A preferred paraffinic feed are those obtained in the Fischer-Tropsch process. More preferably a partly isomerised Fischer-Tropsch derived wax is used. By using
10 such a partly isomerised wax a less severe catalytic dewaxing is required which also is beneficial for the final base oil yield. An additional advantage of using a partly isomerised Fischer-Tropsch wax is that it is more easily transported from the typical remote Fischer-
15 Tropsch location to the base oil manufacturing location. The partly isomerised Fischer-Tropsch wax is also referred to in this application as FT Waxy Raffinate. The FT Waxy Raffinate preferably has an initial boiling point of greater than 300 °C and a T95wt% recovery boiling
20 point of between 450 and 600 °C. The partly isomerised wax is different from a normal-paraffin wax in that it has a relatively large oil content and a relatively smaller wax content, wherein the wax content is indicative for the presence of normal paraffins.

25 The wax content as used in this description is measured by solvent dewaxing at -27 °C in MEK/Toluene. The wax content of the FT Waxy Raffinate is preferably above 5 wt%, more preferably between 10 and 80 wt%, even more preferably between 20 and 60 wt% and even more
30 preferably below 40 wt%. The FT Waxy Raffinate is suitably prepared by hydrocracking a wax as obtained in the Fischer-Tropsch synthesis reaction and recovering the above distillate or residual fraction from the effluent

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of the hydrocracking step. Examples of illustrative processes to prepare such a partly isomerised Fischer-Tropsch wax are disclosed in WO-A-02070630 and in EP-A-0668342. An example of a commercially available FT Waxy Raffinate is SMDS Waxy Raffinate as obtainable from Shell MDS (Malaysia) Sdn Bhd.

The content of the paraffinic and/or waxy feed component in the total feed to step (c) is preferably between 5 and 50 wt%, more preferably between 5 and 30 wt% and even more preferably between 5 and 15 wt%. It has been found that even with such relatively small amounts of paraffinic and/or waxy feed a relatively large increase in base oil yield is achieved when intending to prepare the higher VI base oils. It is also found that waxy distillate feedstocks, which are less suited to make the high VI base oils, may nevertheless find application in the present invention.

In step (c) is generally operated to remove nitrogen and sulfur from the blend obtained in step (b). This process is referred to as hydrodesulfurization/ (302 °C) hydrodenitrogenation, HDS/HDN. Generally speaking, the HDS/HDN is conducted at a temperature in the range of from about 575 °F (302 °C). to about 780 °F (416 °C). Usually, the temperature will be in the range of from about 600 °F. to about 760 °F (404 °C). Preferably, the temperature will be in the range of about 625 °F (329 °C). to about 730 °F (388 °C). Hydrogen will generally be present at a hydrogen partial pressure in the range of from about 150 psig to about 3500 psig, and total pressure will generally be in the range of from about 200 psig to about 4,000 psig. Usually, hydrogen partial pressure will be in the range of from about

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350 psig to about 1400 psig and a total pressure will be in the range of from about 400 psig to about 1500 psig.

The weight hourly space velocities (WHSV) is suitably in the range of from 0.1 to 10 kg of oil per litre of catalyst per hour (kg/l/hr), and preferably from 0.5 to 5 kg/l/hr, more preferably from 0.5 to 2.0 kg/l/hr and hydrogen to oil ratios in the range of from 100 to 2000 litres of hydrogen per litre of oil.

A preferred catalyst having HDS/HDN activity under these conditions generally, a non-noble-metal-containing HDS/HDN catalyst. Suitable HDS/HDN catalysts generally comprise alumina or silica alumina and carry Group VIII and/or Group VIB metals as the catalytically active agent. Most preferably, the catalytically active HDS/HDN agent is selected from the group consisting of nickel/molybdenum, cobalt/molybdenum and nickel/tungsten.

The Group VIII component generally comprises about 0.1 to about 30% by weight, preferably about 1 to about 15% by weight of the final catalytic composite calculated on an elemental basis. The Group VIB component comprises about 0.05 to about 30% by weight, preferably about 0.5 to about 15% by weight of the final catalytic composite calculated on an elemental basis.

The hydrogenation components of the HDS/HDN catalyst will most likely be present in the oxide form after calcination in air and may be converted to the sulfide form if desired by contact at elevated temperatures with a reducing atmosphere comprising hydrogen sulfide, a mercaptan or other sulfur containing compound. It is preferred that the catalyst(s) used in the HDS/HDN zone is essentially free of any noble metal such as platinum or palladium. Further disclosure of possible catalysts and operating conditions are described in detail in the

afore-mentioned US-A-59763545, which publication is incorporated by reference.

Step (c) is performed in the presence of a suitable dewaxing catalysts, which catalysts are preferably heterogeneous catalysts comprising a molecular sieve and optionally in combination with a metal having a hydrogenation function, such as the Group VIII metals. Molecular sieves, and more suitably intermediate pore size zeolites, have shown a good catalytic ability to reduce the pour point of the base oil precursor fraction under catalytic dewaxing conditions. Preferably the intermediate pore size zeolites have a pore diameter of between 0.35 and 0.8 nm. Suitable intermediate pore size zeolites are ZSM-5, ZSM-12, ZSM-22, ZSM-23, SSZ-32, ZSM-35 and ZSM-48, of which ZSM-12, ZSM-23, ZSM-22, SSZ-32 are most preferred because of their additional isomerisation selectivities. Another preferred group of molecular sieves are the silica-aluminaphosphate (SAPO) materials of which SAPO-11 is most preferred as for example described in US-A-4859311. ZSM-5 may optionally be used in its HZSM-5 form in the absence of any Group VIII metal. The other molecular sieves are preferably used in combination with an added Group VIII metal. Suitable Group VIII metals are nickel, cobalt, platinum and palladium. Examples of possible combinations are Ni/ZSM-5, Pt/ZSM-23, Pd/ZSM-23, Pt/ZSM-48 and Pt/SAPO-11. Further details and examples of suitable molecular sieves and dewaxing conditions are for example described in WO-A-9718278, US-A-5053373, US-A-5252527 and US-A-4574043.

The dewaxing catalyst suitably also comprises a binder. The binder can be a synthetic or naturally occurring (inorganic) substance, for example clay, silica

and/or metal oxides. Natural occurring clays are for example of the montmorillonite and kaolin families. The binder is preferably a porous binder material, for example a refractory oxide of which examples are:

5 alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary compositions for example silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. More preferably a
10 low acidity refractory oxide binder material which is essentially free of alumina is used. Examples of these binder materials are silica, zirconia, titanium dioxide, germanium dioxide, boria and mixtures of two or more of these of which examples are listed above. The most
15 preferred binder is silica.

A preferred class of dewaxing catalysts comprise intermediate zeolite crystallites as described above and a low acidity refractory oxide binder material which is essentially free of alumina as described above, wherein
20 the surface of the aluminosilicate zeolite crystallites has been modified by subjecting the aluminosilicate zeolite crystallites to a surface dealumination treatment. These catalysts may be advantageously used because they allow small amounts of sulphur and nitrogen
25 in the feed. A preferred dealumination treatment is by contacting an extrudate of the binder and the zeolite with an aqueous solution of a fluorosilicate salt as described in for example US-A-5157191 or US-B-6576120. Examples of suitable dewaxing catalysts as described
30 above are silica bound and dealuminated Pt/ZSM-5, silica bound and dealuminated Pt/ZSM-23, silica bound and dealuminated Pt/ZSM-12, silica bound and dealuminated

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Pt/ZSM-22, as for example described in US-B-6576120 and EP-B-832171.

Preferred catalysts have a content of molecular sieve of between 5 and 40 wt%. The average crystal size of the molecular sieve is preferably smaller than 0.5 μm and more preferably smaller than 0.1 μm as determined by the well-known X-ray diffraction (XRD) line broadening technique using the high intensity peak at about 20.9 2-theta in the XRD diffraction pattern.

Catalytic dewaxing conditions are known in the art and typically involve operating temperatures in the range of from 200 to 500 °C, suitably from 250 to 400 °C, hydrogen pressures in the range of from 10 to 200 bar, preferably between 20 and 100 bars. The weight hourly space velocities (WHSV) is suitably in the range of from 0.1 to 10 kg of oil per litre of catalyst per hour (kg/l/hr), and preferably from 0.2 to 5 kg/l/hr, more preferably from 0.5 to 3 kg/l/hr and hydrogen to oil ratios in the range of from 100 to 2,000 litres of hydrogen per litre of oil.

The dewaxed oil is contacted in step (d) with an aromatics saturation catalyst under aromatics saturation conditions. The aromatics saturation catalyst comprises preferably. Generally the aromatics saturation catalyst comprises oxides of platinum and palladium supported on an alumina matrix. To provide selectivity for aromatic molecules, the matrix usually contains dispersed zeolite which has a pore size for preferentially reacting aromatic molecules. Generally, only small amounts of platinum and palladium are used. The aromatics saturation catalyst will generally contain in the range of from about 0.1 wt % to about 5 wt % platinum and in the range

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of from about 0.1 wt % to about 5 wt % palladium, based on elemental weight of metal.

Operating temperature conditions in step (d) suitably does not exceed 350 °C and preferably is in the range of from 150 and 350 °C, more preferably from 180 to 300 °C. The operating pressure may range from 10 to 250 bar and preferably is in the range of from 20 to 175 bar. The WHSV may range from 0.1 to 10 kg of oil per litre of catalyst per hour (kg/l.h) and suitably is in the range from 0.5 to 6 kg/l.h.

Hydrotreating the blend of solvent refined waxy distillates and the paraffinic and/or waxy feed, for example FT Waxy Raffinate, to remove the sulfur and nitrogen in step (c) can be achieved at about the same hydroprocessing conditions (pressure, temperature, space velocity, hydrogen circulation rate) as selective dewaxing in step (d). A high degree of aromatic saturation in step (e) can also be achieved at these same hydroprocessing conditions. This makes it feasible to hydrotreat, dewax and remove the majority of feed aromatics in three sequential reactors in a reactor train forming a process unit as illustrated in detail in the afore mentioned US-A-5976354. If desired, the last two steps can be incorporated in the same process unit, e.g. the same reactor vessel.

The desired lubricating base oil having the high viscosity index of especially between 100 and 135 is recovered from the effluent of step (d). Such recovery suitably involves fractionation of the effluent to obtain a gaseous fraction and at least one liquid fraction as the lubricating base oil product. Fractionation can be attained by conventional methods, such as by distillation of the effluent from the second reaction zone under

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atmospheric or reduced pressure. Of these, distillation under reduced pressure, including vacuum flashing and vacuum distillation, is most suitably applied. The cutpoint(s) of the distillate fraction(s) is/are selected such that each product distillate recovered has the desired viscosity, viscosity index and pour point for its envisaged application.

The base oils as produced preferably have a pour point of below -18 °C and more preferably below -27 °C.

The kinematic viscosity at 100 °C is preferably between 2 and 15 cSt. The viscosity index is preferably above 90 and more preferably between 100 and 135. The saturates content is preferably above 90 wt%, more preferably above 95 wt% and even more preferably above 98 wt%. The sulphur content is below 100 ppmw, preferably below 50 ppmw, more preferably below 20 ppmw.

The invention will be illustrated by means of a calculated example. In this example it is aimed at preparing a base oil having a saturates content of 98 wt% and the viscosity index of 115-118 by means of a process according to the main claim and by means of the same process but without blending any FT Waxy Raffinate to the solvent extracted oil. The FT Waxy Raffinate used in this simulation is the Shell MDS Waxy Raffinate having the properties in Table 1. The content of Shell MDS Waxy Raffinate in the blend is 10 wt%.

Table 1

Shell MDS Waxy Raffinate	
Flash point (°C)	225
Wax content	15 wt%
Congealing point (°C)	42

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When processing feedstock (i) alone a rather severe solvent extraction and hydrotreating step has to be performed in order to achieve a VI value of >115. As a base case the yield of these combined steps was about 60 wt% on feed. The dewaxing yield was between 80 and 85 wt% resulting in an overall yield of between 48 and 52 wt%.

When processing according to the invention we observed that a less severe solvent extraction/ hydrotreatment is required in order to arrive at the same base oil quality. This results in an oil yield in the extraction/ hydrotreating steps of between 75 and 80 wt%. Because some wax is introduced via the waxy feed, and less wax if the FT waxy Raffinate is used, a slightly less selective dewaxing step is expected having a oil yield of between 70 and 75 wt%. The overall oil yield was between 63-70wt% which is considerably higher than when no FT Waxy Raffinate is added to the feed of the hydrotreating step.

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C L A I M S

1. Process to prepare a lubricating base oil having a saturates content of greater than 90 wt% and a viscosity index of greater than 90 starting from a vacuum distillate feedstock by performing the following steps:

- 5 (a) contacting the vacuum distillate feedstock with an extraction solvent selective for extracting aromatic compounds from the vacuum distillate,
- (b) mixing the extracted oil obtained in step (a) with a feed comprising of more than 50 wt% wax or
10 comprising of more than 80 wt% of paraffins and having a pour point greater than 0 °C,
- (c) hydrotreating the blend obtained in step (b),
- (d) catalytically dewaxing the hydrotreated oil obtained in step (c) to obtained the lubricating base oil and
- 15 (e) contacting the dewaxed oil with an aromatics saturation catalyst.

2. Process according to claim 1, wherein the feed comprising of more than 50 wt% of wax in step (b) is a slack wax.

- 20 3. Process according to claim 1, wherein the feed comprising more than 80 wt% paraffins and a pour point of greater than 0 °C in step (b) is a partly isomerised Fischer-Tropsch wax having a wax content of between 10 and 80 wt%.

- 25 4. Process according to claim 3, wherein the partly isomerised Fischer-Tropsch wax has a wax content of between 20 and 60 wt%.

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5. Process according to any one of claims 1-4, wherein the blend obtained in step (b) comprises between 5 and 50 wt% of the paraffinic and/or waxy feed.

5 6. Process according to claim 5, wherein the blend obtained in step (b) comprises between 5 and 30 wt% of the paraffinic and/or waxy feed.

10 7. Process according to any one of claims 1-6, wherein step (c) is performed in the presence of a catalyst comprising one of the following combinations of metals selected from the group consisting of nickel/molybdenum, cobalt/molybdenum and nickel/tungsten.

15 8. Process according to any one of claims 1-7, wherein step (d) is performed in the presence of a catalyst comprising a Group VIII metal, one or more of the molecular sieves selected from the group of ZSM-5, ZSM-12, ZSM-22, ZSM-23, SSZ-32, ZSM-35, ZSM-48 or SAPO-11 and a binder.

20 9. Process according to claim 8, wherein the molecular sieve is one or more of the molecular sieves selected from the group of ZSM-12, ZSM-23, ZSM-22 or SSZ-32.

10. Process according to any one of claims 8-9, wherein the Group VIII is platinum.

25 11. Process according to any one of claims 8-10, wherein the content of molecular sieve in the catalyst is between 5 and 40 wt%.

30 12. Process according to any one of claims 8-11, wherein the average crystal size of the molecular sieve is smaller than 0.5 μm and more preferably smaller than 0.1 μm as determined by the X-ray diffraction (XRD) line broadening technique using the high intensity peak at about 20.9 2-theta in the XRD diffraction pattern.

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13. Process according to any one of claims 1-12, wherein the base oils as obtained have a pour point of below -18 °C and more preferably below -27 °C.

5 14. Process according to any one of claims 1-13, wherein the base oils as obtained have a kinematic viscosity at 100 °C is preferably between 2 and 15 cSt.

15. Process according to any one of claims 1-14, wherein the base oils as obtained have a viscosity index is between 100 and 135.

10 16. Process according to any one of claims 1-15, wherein the base oils as obtained have a saturates content of above 95 wt%.

17. Process according to any one of claims 1-16, wherein the base oils as obtained have a sulphur content of below
15 50 ppmw.