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(54) Process to prepare base oils having different viscosity index

(57) Process to prepare two types of lubricating base oils, namely a base oil having a viscosity index of between 80-120 and a base oil having a viscosity index of greater than 120, wherein the base oils further have a saturates content of above 90 wt% and a sulphur content of below 0.03 wt% by performing a solvent extraction, a solvent dewaxing, a wax isomerisation and an oil hydrotreatment.

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Description

[0001] The invention relates to a process to prepare two types of lubricating base oils, namely a base oil having a viscosity index (VI) of between 80-120 and a base oil having a viscosity index of greater than 120 from the same feed. The base oils further have a saturates content of above 90 wt% and a sulphur content of below 0.03 wt%. The base oils having a VI of between 80 and 120 are also referred to as a API Group II base oils and the base oils having a VI of greater than 120 are also referred to as API Group III base oils as defined in API Publication 1509: Engine Oil Licensing and Certification System, "Appendix E-API Base Oil Interchangeability Guidelines for Passenger Car Motor Oil and Diesel Engine Oils". There exist an increasing demand for these products due to the fact that modern automobile engines operate under more severe conditions, requiring a lubricating oil which is formulated based on a base oil having the above specifications.

[0002] Lubricating base oils are conventionally prepared starting from a vacuum distillate or a deasphalted vacuum residue. These distillates are obtained by first distilling a petroleum crude feedstock at atmospheric conditions wherein a residue is obtained, which residue is subsequently distilled at reduced pressure obtaining vacuum distillates and a vacuum residue. Aromatics are removed from the vacuum distillate by means of solvent extraction resulting in an aromatic-poor solvent extracted product. In a subsequent step wax is removed from the solvent extracted product and a lubricating base oil product is obtained. Typically the wax is removed by solvent dewaxing. It has been found that the API Group II base oil product cannot be easily obtained by such a process from most petroleum crude sources.

[0003] WO-A-9802502 describes a process to prepare Group II and Group III base oils by hydrotreating a vacuum distillate, hydrodewaxing the hydrotreated oil and finally subjecting the dewaxed oil to a so-called hydrofinishing zone. In a possible embodiment the vacuum distillate is first subjected to a solvent extraction step. The solvent extraction step is used to influence the viscosity index of the resultant base oil.

[0004] A disadvantage of the process as described in WO-A-9802502 is that the Group II and the Group III base oils are not prepared at the same time. A further disadvantage is that when aiming at the high VI base oil grades a rather severe solvent extraction has to be applied resulting in a low base oil yield on feedstock.

[0005] The object of the present invention is to provide a process wherein a Group II and a Group III base oil is prepared from the same feedstock in the same complex or production facility.

[0006] This object is achieved with the following process. Process to prepare two types of lubricating base oils, namely a base oil having a viscosity index of between 80-120 and a base oil having a viscosity index of greater than 120, wherein the base oils further have a saturates content of above 90 wt% and a sulphur content of below 0.03 wt% by performing the following steps:

(a) removing part of aromatic compounds from a petroleum fraction boiling in the lubricating oil range by means of solvent extraction resulting in a solvent extracted product
(b) solvent dewaxing the solvent extracted product thereby obtaining an oil having a reduced pour point and a wax,
(c) subjecting the wax as obtained in step (b) to a hydroisomerisation step and a dewaxing step to obtain the base oil having a viscosity index of above 120,
(d) contacting the oil as obtained in step (b) to a severe hydrotreating step to obtain the base oil having a viscosity index of between 80 and 120.

[0007] Applicants have found that an API Group II base oil and an API Group III base oil can be prepared simultaneously using the process according to the invention. An additional advantage is that the process can be performed by adopting, or retrofitting, existing API Group I processes. These processes typically include a solvent extraction step as step (a) of the present invention and a solvent dewaxing step as step (b) of the present invention. By adding steps (c) and (d) to such an existing process one obtains a process which can make the more desired Group II and Group III base oils, while making optimal use of the existing production facilities.

[0008] For this invention the sulphur and nitrogen content expressed in weight percentage or ppmw is the amount of elemental sulphur or nitrogen relative to the total amount of the mixture referred to.

[0009] Suitable petroleum fractions for use in step (a) are 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. The boiling range of such a vacuum distillate fraction is usually between 300 and 620 °C, suitably between 350 and 580 °C. However, deasphalted residual oil fractions, suitably deasphalted vacuum residues, may also be applied.

[0010] Solvent extraction in step (a) is a widely applied technology when preparing base oils and is for example described in "Lubricating base oil and wax processing", by Avilino Sequeira, Jr., 1994, Marcel Dekker Inc. New York, pages 81-118. Solvent extraction is suitably performed with for example N-methyl-2-pyrrolidone, furfural, phenol and sulphur dioxide as extraction solvent. Often used solvents are N-methyl-2-pyrrolidone and furfural. In the solvent extraction aromatic compounds are partly removed from the hydrocarbon mixture, thereby increasing the viscosity index of the product. Amounts of sulphur and nitrogen are also re-

moved in the solvent extraction process.

[0011] Solvent dewaxing in step (b) is performed by chilling the feedstock with a solvent whereby the wax molecules crystallise. The wax crystals are subsequently removed by filtration and the solvent is recovered. Examples of possible solvents are methylethylketone/toluene, methylisobutylketone, methylisobutylketone/methylethylketone, dichloroethylene/methylenechloride, and propane. Examples of possible solvent dewaxing processes are described in the earlier mentioned textbook "Lubricating base oil and wax processing", by Avilino Sequeira, Jr., 1994, Marcel Dekker Inc. New York, pages 153-192.

[0012] The pour point of the oil as obtained in step (b) is preferably below -15 °C and more preferably below -21 °C. Especially when making base oils which are to be used in applications which have to operate in a cold climate low pour points are desirable. Another advantage of a lower pour point oil obtained in step (b) is that more wax will be separated in step (b) and thus more high VI base oils may be prepared in step (c).

[0013] In step (c) the wax will be used to make the Group III type base oils. Hydroisomerisation catalyst for use in step (c) will suitably comprise a hydrogenation component supported on an amorphous silica-alumina carrier. Suitable hydrogenation components are the metals of Groups VIB and VIII of the Periodic Table of the Elements, or sulphides or oxides thereof. Preference is given to catalysts comprising as the hydrogenation component one or more of the metals molybdenum, chromium, tungsten, platinum, palladium, nickel, iron and cobalt, or their oxides and/or sulphides.

[0014] For use in step (c) in which hydrocarbon feeds comprising substantial amounts of nitrogen- and sulphur-containing compounds are used, catalysts comprising combinations of one or more of the metals cobalt, iron and nickel, and one or more of the metals chromium, molybdenum and tungsten are preferred. Especially preferred catalysts for use in treating such feeds comprise, in combination, cobalt and molybdenum, nickel and tungsten and nickel and molybdenum. Examples of suitable commercially available catalyst are the LH-21 and LH-22 type of catalyst as obtainable from the Criterion Catalyst Company (Houston). Optionally the catalyst may contain an additional amount of fluorine to increase the acidity of the catalyst. An example of a possible commercially available catalyst is the fluorided C-454 catalyst as obtainable from Criterion Catalyst Company.

[0015] The catalysts are preferably used in their sulphidic form. Sulphidation of the catalyst may be effected by any of the techniques known in the art. For example, sulphidation may be effected by contacting the catalyst with a sulphur-containing gas, such as a mixture of hydrogen and hydrogen sulphide, a mixture of hydrogen and carbon disulphide or a mixture of hydrogen and a mercaptan, such as butylmercaptan. Alternatively, sulphidation may be carried out by contacting the catalyst with hydrogen and a sulphur-containing hydrocarbon oil, such as sulphur-containing kerosine or gas oil. The sulphur may also be introduced into the hydrocarbon oil by the addition of a suitable sulphur-containing compound, for example dimethyldisulphide or tertiononylpolysulphide. The amounts of metals present in the catalyst may vary between very wide limits. Typically, the catalyst comprises from 10 to 100 parts by weight of the Group VIB metal, if present, preferably from 25 to 80 parts weight, per 100 parts by weight of carrier. The Group VIII metal is typically present in an amount of from 3 to 100 parts by weight, more preferably from 25 to 80 parts by weight, per 100 parts by weight of carrier.

[0016] Catalysts for use in the treatment of waxes which contain low concentrations of nitrogen- and sulphur-containing compounds preferably comprise platinum and/or palladium as the hydrogenation component, with platinum being a particularly suitable metal for inclusion in catalysts for such use. Platinum and palladium are typically present in the catalyst in amounts of from 0.05 to 5.0 parts by weight, preferably from 0.1 to 2.0 parts by weight, more preferably from 0.2 to 1.0 parts by weight, per 100 parts by weight of carrier. An example of a possible commercially available catalyst is C-624 as obtainable from Criterion Catalyst Company. Optionally the catalyst may contain an additional amount of fluorine to increase the acidity of the catalyst. If the nitrogen and sulphur content in the wax is above 10 ppm 500 ppm respectively a hydrotreatment step is preferably performed prior to contacting the wax with a hydroisomerisation catalyst comprising a noble metal. Typical hydrotreatment processes are the HDS and HDN processes which make use of well known NiMo, CoMo and NiCoMo containing catalyst on an alumina carrier.

[0017] The catalyst carrier of the hydrosiomerisation catalyst in step (c) may comprise any suitable amorphous silica-alumina. The amorphous silica-alumina preferably contains alumina in an amount in the range of from 2 to 75% by weight, more preferably from 10 to 60% by weight. A very suitable amorphous silica-alumina product for use in preparing the catalyst carrier comprises 45% by weight silica and 55% by weight alumina and is commercially available (ex. Criterion Catalyst Company, USA).

[0018] More preferably the amorphous silica-alumina carrier has a certain degree of macroporous pores. The macroporosity of the carrier is suitably in the range of from 5% vol to 50% vol, wherein the macroporosity is defined as the volume percentage of the pores having a diameter greater than 50 nm, more preferably greater than 100 nm. More preferably the carrier has a macroporosity of at least 10% vol, even more preferably at least 15% vol and most preferably at least 20% vol. Especially preferred catalysts for use in the process comprise a carrier having a macroporosity of at least 25% vol. Catalysts comprising carriers having a high macroporosity may suffer the disadvantage that the catalyst has a low resistance to damage by crushing. According-

ly, the macroporosity is preferably no greater than 40% vol, more preferably no greater than 38% vol, even more preferably no greater than 35% vol. The side crushing strength of the catalyst is suitably above 75 N/cm, more preferably above 100 N/cm. The bulk crushing strength of the catalyst is suitably above 0.7 MPa, more preferably above 1 MPa.

[0019] References to the total pore volume are to the pore volume determined using the Standard Test Method for Determining Pore Volume Distribution of Catalysts by Mercury Intrusion Porosimetry, ASTM D 4284-88, at a maximum pressure of 4000 bar, assuming a surface tension for mercury of 484 dyne/cm and a contact angle with amorphous silica-alumina of 140°. The total pore volume of the carrier as measured by the above method, is typically in the range of from 0.6 to 1.2 ml/g, preferably in the range of from 0.7 to 1.0 ml/g, more preferably in the range of from 0.8 to 0.95 ml/g.

[0020] It will be appreciated that a major portion of the total pore volume is occupied by pores having a pore diameter smaller than 100 nm, that is meso- and micropores. Typically, a major portion of those meso- and micropores has a pore diameter in the range of from 3.75 to 10 nm. Preferably, from 45 to 65% vol of the total pore volume is occupied by pores having a pore diameter in the range of from 3.75 to 10 nm.

[0021] In addition to amorphous silica-alumina, the carrier may also comprise one or more binder materials. Suitable binder materials include inorganic oxides. Both amorphous and crystalline binders may be applied. Examples of binder materials comprise silica, alumina, clays, magnesia, titania, zirconia and mixtures thereof. Silica and alumina are preferred binders, with alumina being especially preferred. The binder, if incorporated in the catalyst, is preferably present in an amount of from 5 to 50% by weight, more preferably from 15 to 40% by weight, on the basis of total weight of the carrier. Catalysts comprising a carrier without a binder are preferred for use in the process of this invention.

[0022] Step (c) is preferably conducted at elevated temperature and pressure. Typical operating temperatures for the process are in the range of from 290 °C to 430 °C, preferably in the range of from 310 °C to 415 °C, more preferably in the range of from 325 °C to 415 °C. Typical hydrogen partial pressures are in the range of from 20 to 200 bar, preferably in the range of from 80 to 160 bar, more preferably in the range of from 90 to 160 bar, in particular in the range of from 100 to 150 bar. The hydrocarbon feed is typically treated at a weight hourly space velocity in the range of from 0.5 to 1.5 kg/1/h, more preferably in the range of from 0.5 to 1.2 kg/1/h.

[0023] The oil as obtained in the hydroisomerisation step is subsequently dewaxed to obtain the API Group III base oil. Dewaxing may be by means of catalytic dewaxing. Preferably dewaxing is performed by means of solvent dewaxing as described above and more preferably use is made of the solvent dewaxing facilities, which are also used for performing step (b).

[0024] The oil as obtained in step (b) will suitably have a typical API Group I composition. For example the oil may contain sulphur in ranges from 100 to more than 1000 ppmw. The nitrogen content may be between 30 and 300 ppm. The saturates content is preferably higher than 70 wt%. Next to saturates the base oil mainly consists of aromatic and polar compounds. Examples of polar compounds are specific sulphur and nitrogen containing compounds. In step (d) the content of non-saturated compounds and sulphur needs to be reduced in order to obtain the desired Group II base oil. This may be done in a two-step process wherein first a hydrodesulphurisation (HDS) and denitrogenation (HDN) is performed followed by an aromatics saturation. In a more preferred embodiment all these reactions are performed in one step.

[0025] In a one step process the oil is contacted at the below hydrotreating process conditions with a catalyst comprising preferably at least one Group VIB metal component and at least one non-noble Group VIII metal component selected from the group of iron, nickel or cobalt supported on a refractory oxide carrier. Examples of suitable Group IVB metals are molybdenum (Mo) and tungsten (W). Examples of suitable non-noble Group VIII metals are nickel (Ni) and cobalt (Co). Suitable catalysts include those catalysts comprising as the non-noble Group VIII metal component one or more of nickel (Ni) and cobalt (Co) in an amount of from 1 to 25 percent by weight (wt%), preferably 2 to 15 wt%, calculated as element relative to total weight of catalyst and as the Group VIB metal component one or more of in an amount of from 5 to 30 wt%, preferably 10 to 25 wt%, calculated as element relative to total weight of catalyst. These metal components may be present in elemental, oxidic and/or sulphidic form and are supported on a refractory oxide carrier.

[0026] The refractory oxide support of the catalyst used in step (d) may be any inorganic oxide, alumino-silicate 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 and mixtures of two or more of these.

[0027] Phosphorus (P), may also be present in the catalyst used in step (d). The phosphorous content is preferably between 1 and 10 wt% as oxide.

[0028] Preferred catalyst, more preferably containing a phosphorus promoter, are cobalt/molybdenum on alumina having a cobalt content of between 1-5 wt% as oxide and 10-25 wt% molybdenum content as oxide; nickel/molybdenum on alumina having a nickel content 1-5 wt% as oxide and a molybdenum content of between 10-30 wt% as oxide of which commercially available catalyst C-424 of Criterion Catalyst Company (Houston, TX) is an example; and nickel/tungsten on alumina having a nickel content of between 1-5 wt% as oxide and a tungsten content of between 10-30 wt% as oxide. Ex-

amples of suitable commercial catalysts are C-424, DN-200, DN-3100 and DN-3300 as obtainable from the Criterion Catalyst Company in Houston (USA). In general, presulphiding is effected by contacting the unsulphided catalyst with a suitable sulphiding agent, such as hydrogen sulphide, elemental sulphur, a suitable polysulphide, a hydrocarbon oil containing a substantial amount of sulphur-containing compounds or a mixture of two or more of these sulphiding agents. Particularly for the in situ sulphidation a hydrocarbon oil containing a substantial amount of sulphur-containing compounds may suitably 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. A particular useful hydrocarbon oil presulphiding agent may be the base oil feed itself, which contains a significant amount of sulphur-containing compounds. In this case the unsulphided catalyst may be contacted with the feed under, for example, the operating conditions, thus causing the catalyst to become sulphided. Typically, the base 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.

[0029] If step (d) is performed in the preferred one step embodiment a relatively high operating pressure is preferred. The pressure is preferably greater than 100 bars, more preferably greater than 150 bars, even more preferably greater than 200 bars and in an even more preferred embodiment greater than 300 bars. The upper limit will be limited by the mechanical strength of the available reactors and preferably the pressure is lower than 1000 bars.

[0030] The temperature in step (d) is preferably between 250 and 450 °C. The actual temperature will depend largely on the content of sulphur and/or nitrogen and non-saturates in the feed. For example, higher temperatures result in higher reduction of S- and N-content. 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) and suitably is in the range from 0.2 to 5 kg/l.h.

[0031] After contacting the oil l step (d) with the above catalyst the Group II base oil is obtained after separating the lower boiling compounds and the hydrogen sulphide and ammonia as the S- and N-reaction products formed in step (d). The gaseous fraction will further contain any excess hydrogen, which has not reacted as well as some light hydrocarbons.

[0032] Suitably hydrogen sulphide and ammonia are removed from the gaseous fraction obtained resulting in a cleaned hydrogen containing gas, which is preferably recycled to step (d). Examples of suitably methods for removing hydrogen sulphide and ammonia are methods known in the art, such as an absorption treatment with a suitable absorption solvent, such as solvents based on one or more alkanolamines (e.g. mono-ethanolamine, di-ethanol-amine, methyl-di-ethanolamine and di-isopropanolamine).

Claims

1. Process to prepare two types of lubricating base oils, namely a base oil having a viscosity index of between 80-120 and a base oil having a viscosity index of greater than 120, wherein the base oils further have a saturates content of above 90 wt% and a sulphur content of below 0.03 wt% by performing the following steps:

   (a) removing part of aromatic compounds from a petroleum fraction boiling in the lubricating oil range by means of solvent extraction resulting in a solvent extracted product
   (b) solvent dewaxing the solvent extracted product thereby obtaining an oil having a reduced pour point and a wax,
   (c) subjecting the wax as obtained in step (b) to a hydroisomerisation step and a dewaxing step to obtain the base oil having a viscosity index of above 120,
   (d) contacting the oil as obtained in step (b) to a severe hydrotreating step to obtain the base oil having a viscosity index of between 80 and 120.

2. Process according to claim 1, wherein the petroleum fraction is a vacuum distillate boiling between 300 and 620 °C or a deasphalted residue.

3. Process according to any one of claims 1-2, wherein N-methyl-2-pyrrolidone, furfural, phenol or sulphur dioxide are used as extraction solvent in step (a).

4. Process according to any one of claims 1-3, wherein solvent dewaxing in step (b) is performed using methylethylketone/toluene, methylisobutylketone, methylisobutylketone/methylethylketone, dichloroethylene/methylenechloride, or propane as the dewaxing solvent.

5. Process according to any one of claims 1-4, wherein in step (b) the pour point is reduced to below -21 °C.

6. Process according to any one of claims 1-5, wherein the hydroisomerisation in step (c) is performed in the presence of a catalyst comprising a hydrogenation component and a silica-alumina carrier.

7. Process according to claim 6, wherein the hydrogenation component comprises a combination of, cobalt and molybdenum, nickel and tungsten and nickel and molybdenum.

8. Process according to claim 6, wherein the hydrogenation component comprises platinum and/or palladium and wherein the sulphur content in the wax is less than 500 ppm and the nitrogen content in the wax is less than 10 ppm.

9. Process according to any one of claims 1-8, wherein the catalyst used in step (d) is sulphided and comprises at least one Group VIB metal component and at least one non-noble Group VIII metal component selected from the group of iron, nickel or cobalt supported on a refractory oxide carrier.

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EUROPEAN SEARCH REPORT

Application Number
EP 03 29 3263

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	9 March 2004	Harf, J

CATEGORY OF CITED DOCUMENTS

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EUROPEAN SEARCH REPORT

Application Number
EP 03 29 3263

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 03 29 3263

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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