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54 **Process for the manufacture of lubricating base oils from naphthenic feedstocks.**

57 Process for the manufacture of naphthenic base oils having a viscosity index of up to 100 by catalytically converting a naphthenic feedstock at elevated temperature and pressure in the presence of hydrogen, in which process a hydrogen partial pressure of at least 100 bar is applied in the presence of a fluorided, nickel containing catalyst also comprising tungsten and/or molybdenum.

Good quality naphthenic base oils containing reduced amounts of aromatic compounds, in particular polycyclic aromatic compounds, are prepared in high yields.

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PROCESS FOR THE MANUFACTURE OF LUBRICATING BASE OILS FROM NAPHTHENIC FEEDSTOCKS

The present invention relates to a process for the manufacture of lubricating base oils from naphthenic feedstocks as well as to lubricating base oils thus prepared.

One of the major problems associated with the production of naphthenic base oils from naphthenic feedstocks concerns the presence of naphthenic acids in the feeds to be processed. A pre-treatment is required to reduce substantially the amount of naphthenic acids present in the feedstock as they are unacceptable from a process and product quality point of view.

Reduction of the amount of naphthenic acids can be achieved by applying a classic clay treatment or a more recent catalytic hydrofinishing treatment, which moreover also reduces considerably the amount of sulphur and nitrogen in the feed. Reference is made to US Patent Specification 2,734,019 wherein a naphthenic lubricating oil fraction is treated with a cobalt molybdate on alumina catalyst at an elevated temperature and a moderate pressure (well below 60 bar) to give a product with a substantially reduced sulphur content and a reduced nitrogen content whilst the neutralization number has been reduced substantially to zero.

It should be noted, however, that the total aromatics content of the naphthenic feedstock described in said US patent specification, being at least 35 %v, has only been reduced marginally (i.e. by some 3-5 %v) by said treatment over the cobalt molybdate catalyst. Since it becomes increasingly important -for a variety of reasons -to reduce the amount of aromatics present in lubricating base oils, in particular those aromatic compounds referred to as polycyclic aromatics as measured by the IP 346 method, to rather low levels, preferably not exceeding 10 %w, it will be clear that the prior art process leaves much to desire.

It has now been found that naphthenic feedstocks, i.e. feeds containing both naphthenic acids and a considerable amount of aromatic compounds can be converted directly (i.e. without the necessity of a pre-treatment) into naphthenic base oils of good quality, having a viscosity index of up to 100 when use is made of certain fluorided nickel-containing catalysts under rather severe process conditions.

The present invention thus relates to a process for the manufacture of naphthenic base oils having a viscosity index of up to 100 by catalytically converting a naphthenic feedstock at elevated temperature and pressure in the presence of hydrogen,

which process is carried out at a hydrogen partial pressure of at least 100 bar in the presence of a fluorided, nickel-containing catalyst also comprising tungsten and/or molybdenum.

By using the specific catalyst and process conditions according to the present invention it has become possible to substantially reduce the aromatic content of the feedstock in a single operation, e.g. by at least 50 %w, and often by more than 90 %w, starting from feedstocks containing aromatic compounds in amounts of at least 35 %w.

It should be noted that the naphthenic feedstock can, of course, be subjected -if desired -to a neutralization pre-treatment as referred to hereinbefore so as to reduce almost completely the acidic components (whilst substantially leaving the aromatic compounds in the feedstock) but this is not necessary since it is the process according to the present invention which allows a substantial reduction of the initial aromatics content together with complete removal of the acidic components.

The process according to the present invention can be used advantageously in the manufacture of low viscosity index base oils (which are applied e.g. as base oils for cutting oils and as additive carriers) as well as of medium viscosity index base oils (which are applied e.g. as base oils for refrigerator oils, large engine lubricating oils as well as in white oil manufacture).

Naphthenic base oils having a low viscosity index can now be prepared in far higher yields and at a much lower polycyclic aromatic components level than is possible when using a conventional hydrotreatment and/or acid/clay treatment. It is now possible to reduce the polycyclic aromatic content to well below 10 %w and often to less than 6 %w, and even less than 3 %w which is of great importance from an environmental point of view.

Naphthenic base oils having a medium viscosity index can now be prepared in much higher yields by the process according to the present invention than is achievable by using common solvent extraction of neutralized feedstocks, followed, if desired, by a hydrofinishing step.

Both neutralized and unneutralized naphthenic base oil feedstocks can be suitably applied in the process according to the present invention. Preferred feedstocks comprise unneutralized naphthenic distillates since they can be converted in a single operation into valuable naphthenic base oils. The naphthenic distillates to be used may contain up to 4 %w of sulphur and up to 0.8 %w of nitrogen compounds. The acid number may be as

high as 10 mg KOH/g. The naphthenic base oil feedstocks to be processed normally contain at least 35 %w of aromatic compounds and often even more than 65 %w.

It is also advantageous to use blends of two or more (un)neutralized naphthenic distillates as this increases the flexibility in the production of various grades of lubricating base oils depending on the composition of the blend to be processed and the severity of the conversion process itself.

The process according to the present invention has to be carried out at a hydrogen partial pressure of at least 100 bar (10⁴kPa) and preferably at a pressure between 100 and 200 bar. Temperatures between 280 °C and 425 °C can be suitably applied; preference is given to the use of temperatures between 325 and 400 °C, depending to some extent on the base oil feedstock to be processed and the base oil grade to be produced. Normally, the hydrotreatment according to the present invention will be carried out at a space velocity between 0.1 and 5 kg/kg.h, in particular between 0.2 and 2 kg/kg.h.

It has been found that the supported catalysts to be used in the process according to the present invention have to contain molybdenum and/or tungsten in addition to nickel.

The amount of nickel present in the catalyst can suitably vary between 1 and 20 %w, calculated as oxide on total catalyst composition, preference being given to amounts in the range of from 2 to 12 %w. The amounts of molybdenum and tungsten may vary between 10 and 40 %w, calculated as oxide on total catalyst composition, preference being given to amounts in the range between 10 and 30 %w. Preferred catalysts contain both nickel and tungsten.

The metals and/or metal compounds may be incorporated into the supports by any conventional technique, such as impregnation, dry-impregnation, precipitation and combinations thereof. It is also possible to prepare the catalysts by the hydrogel or the xerogel methods as described in British Patent Specifications 1,493,620 and 1,546,398.

Any suitable support material may be used such as refractory oxides conventionally used for hydrotreating catalysts, such as silica, alumina, magnesia, zirconia and mixtures thereof. Silica and alumina are preferred support materials, in particular alumina. Natural and synthetic crystalline aluminosilicates such as faujasite, in particular Y-faujasite, and ZSM-5 type carriers can also be applied.

The catalysts according to the present invention also contain fluorine. The amount of fluorine in the catalysts under operating conditions may vary between 0.5 and 10 %w, preferably between 2 and 8 %w, calculated on total catalyst. Fluorine can be

introduced into the catalyst by one or more of the fluorination techniques known in the art. Preference is given to the introduction of at least part of the fluorine required in the catalyst by means of in-situ fluorination. It is advantageous to incorporate substantially all fluorine required in the catalyst by in-situ fluorination, preferably in the initial stage of the hydrotreatment. It is also possible to supply, either continuously or intermittently, a small amount of fluorine, e.g. between 5 and 100 ppm, calculated on feedstock, during the hydrotreating process. This can be suitably achieved by adding an appropriate fluorine compound, e.g. difluoroethane or o-fluoro toluene, to the feedstock to be processed. The catalysts may also contain other compounds such as phosphorus or boria.

The catalyst can be applied in the form of spheres or extrudates. The extrudates may have different shapes depending on the extrusion equipment used during their preparation.

The present invention will now be illustrated by means of the following Examples.

Example 1

An unneutralized blend of various naphthenic distillates of South American origin, containing 1.8 %w of sulphur, a total nitrogen content of 760 ppm and an aromatics content of 55 %w, including 10.4 %w of polycyclic aromatic compounds was hydrotreated at a hydrogen partial pressure of 140 bar at a temperature of 345 °C and at a space velocity of 0.8 kg/kg.h over a commercially available fluorinated nickel-tungsten on alumina catalyst. Naphthenic base oils were obtained in a yield exceeding 95 %w, calculated on starting material. They contained less than 4 %w of polycyclic aromatic compounds, less than 250 ppm of nitrogen and not more than 0.25 %w of sulphur.

Example 2

An unneutralized blend of various naphthenic distillates of South American origin containing 1.8 %w of sulphur, a total nitrogen content of 760 ppm and an aromatic content of 55 %w, including 10.4 %w of polycyclic aromatic compounds was hydrotreated at a hydrogen partial pressure of 140 bar at a temperature of 360 °C and at a space velocity of 0.8 kg/kg.h over a commercially available fluorinated nickel-tungsten on aluminocatalyst. Naphthenic base oils were obtained containing less than 2.5 %w of polycyclic aromatic compounds whereas the amounts of sulphur were reduced to 0.06 %w and below and nitrogen to 73 ppm and below. The yield of the naphthenic base oils was 97%, calculated on unneutralized feedstock.

Example 3

An unneutralized naphthenic distillate of South American origin containing 1.73 %w of sulphur, a total nitrogen content of 315 ppm, an aromatics content of 49.8 %w, including 13.7 %w of polycyclic aromatic compounds and having a total acid number of 5.7 (mg KOH/g) was hydrotreated using the catalyst described in Example 1 at 378 °C using the same space velocity as described in said Example. A naphthenic base oil having an initial boiling point of 280 °C and a viscosity index of 45 was obtained in 59.2 %w yield, calculated on unneutralized starting material. The base oil obtained contained less than 5 ppm of nitrogen and less than 40 ppm of sulphur. The total aromatic content had been reduced to less than 7 %w, the amount of polycyclic aromatic compounds being even less than 1 %w.

Example 4

An unneutralized naphthenic distillate of South American origin containing 2.35% of sulphur and 1576 ppm of nitrogen, a total aromatics content of 63.9 %w, including 31.5 %w of polycyclic aromatic compounds and having a total acid number of 7.8 was hydrotreated at 380 °C and at a hydrogen partial pressure of 140 bar at a space velocity of 0.6 kg/kg.h. A naphthenic base oil having an initial boiling point of 400 °C and a viscosity index of 35.8 was obtained in 59.4% yield, calculated on unneutralized starting material. The base oil obtained contained less than 1 ppm of nitrogen and no detectable amounts of sulphur. The total aromatics content amounted to 21.8 %w, only 1.8 %w being attributed to polycyclic aromatic compounds.

Claims

1. Process for the manufacture of naphthenic base oils having a viscosity index of up to 100 by catalytically converting a naphthenic feedstock at

elevated temperature and pressure in the presence of hydrogen, characterized in that the process is carried out at a hydrogen partial pressure of at least 100 bar in the presence of a fluorided, nickel-containing catalyst also comprising tungsten and/or molybdenum.

2. Process according to claim 1, characterized in that an unneutralized naphthenic feedstock is used, in particular a naphthenic distillate.

3. Process according to claim 1 or 2, characterized in that the process is carried out at a hydrogen partial pressure in the range between 100 and 200 bar.

4. Process according to any one of claims 1-3, characterized in that a temperature is applied in the range between 280 and 425 °C, in particular between 325 and 400 °C.

5. Process according to any one of claims 1-4, characterized in that the catalyst applied contains between 2 and 20 %w of nickel, calculated as the oxide on total catalyst composition and between 10 and 40 %w of molybdenum and/or tungsten, calculated as the oxide(s) on total catalyst composition.

6. Process according to claim 5, characterized in that a catalyst is used comprising between 2 and 12 %w of nickel, calculated as the oxide on total catalyst composition, and between 10 and 30 %w of tungsten, calculated as the oxide on total catalyst composition.

7. Process according to any one of claims 1-6, characterized in that the catalyst applied contains between 0.5 and 10 %w, in particular between 2 and 8 %w of fluorine, calculated on total catalyst composition.

8. Process according to any one of claims 1-7, characterized in that the catalyst support contains silica, alumina, magnesia, zirconia or mixtures thereof, in particular alumina.

9. Process according to any one of claims 1-8, substantially as described hereinbefore with particular reference to the Examples.

10. Naphthenic base oil having a viscosity index of up to 100 whenever prepared according to a process as claimed in any one of claims 1-9.

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