PRODUCTION OF STABLE LUBRICATING OILS BY SEQUENTIAL HYDROCRACKING AND HYDROGENATION

Inventors: Bruce E. Stangeland, Berkeley; Clark J. Egan, Piedmont, both of Calif.

Assignee: Chevron Research Company, San Francisco, Calif.

Filed: Mar. 26, 1973

Appl. No.: 345,142

U.S. Cl.................. 208/58, 208/18, 208/264
Int. Cl.................... C10g 31/14, C10g 37/10
Field of Search............. 208/58, 18

References Cited
UNITED STATES PATENTS
2,960,458 11/1960 Beuther et al.................. 208/19
3,487,005 12/1969 Egan et al.................. 208/59
3,530,061 9/1970 Orkin et al.................. 208/60
3,629,096 12/1971 Divjak...................... 208/89
3,666,657 5/1972 Thompson et al................ 208/58
3,732,156 5/1973 Bennett et al................ 208/111

Primary Examiner—Delbert E. Gantz
Assistant Examiner—G. E. Schmitkons
Attorney, Agent, or Firm—G. F. Magdeburger; R. H. Davies; J. D. Foster

ABSTRACT

A process is disclosed for producing a lubricating oil having good UV stability from a hydrocarbon feedstock boiling in the range 700° to 1,200°F., which comprises:

A. catalytically hydrocracking in a hydrocracking zone said feedstock at a per pass conversion of at least 20 volume percent to materials boiling below the initial boiling point of said feedstock;

B. catalytically hydrogenating in a hydrogenating zone at least a substantial portion of the effluent from said hydrocracking zone boiling in the range 550°-1,200°F. at hydrogenation conditions, in the presence of a hydrogenation catalyst comprising
1. a refractory oxide, and
2. a hydrogenating component comprising a noble metal; and

C. recovering as a product of the hydrogenating step a lubricating oil having good UV stability.

10 Claims, No Drawings
PRODUCTION OF STABLE LUBRICATING OILS
BY SEQUENTIAL HYDROCRACKING AND
HYDROGENATION

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to the production of stabilized lubricating oils by a combination of catalytic hydrocracking and catalytic hydrogenation.

As high quality crude oils for use in preparing lubricating oils become more scarce, the economics and desirability of producing satisfactory lube stocks by hydrocracking processes become more attractive. This has been indicated by the increased research activities directed to producing lube oil stocks by various hydroconversion processes.

One of the major problems with lubricating oils prepared by hydrocracking processes is the instability of the oils in sunlight. This instability to ultraviolet light in the presence of air is evidenced by the formation of a precipitate after a short period of exposure. Such a precipitate is undesirable not only because it may prove detrimental to the lubricating function which the oil is designed to perform, but also because it reduces the aesthetic value of what would otherwise be a clear, premium quality oil. The latter is a true consideration; refiners have learned through experience that consumers will not buy lubricating oils which contain visible precipitates, even when those precipitates have no adverse effect on the performance qualities of the lubricating oil.

In the past, it has been known that certain types of lubricating oil instability, such as oxidation instability, could be prevented by treating the oil with any of a number of polar solvents such as phenol, furfural and sulfuric acid (see U.S. Pat. No. 3,463,724). While these treatments tend to remove the instability-causing components, they have the disadvantage of also removing a considerable portion of the desirable lubricating oil components. This indiscriminate removal, either by polar extraction or chemical reaction or both, is unsatisfactory since resulting low yields in most instances make the process uneconomical.

The present invention is directed to a process whereby the UV stability of lubricating oils produced by hydrocracking can be significantly improved by catalytic routes avoiding the reduced yields obtained in many solvent treating processes as well as providing oils with good oxidation stability.

2. Description of the Prior Art

Numerous patents have issued directed to the production of lubricating oils. Patents have also issued directed to stabilizing lubricating oils by hydrogenation treatment. For example, U.S. Pat. No. 3,666,657 teaches a process for improving the quality stability of hydrocracked oils by hydrogenating the oil subsequent to a hydrocracking treatment over a sulfided mixture of an iron group metal and a metal of Group VI.

U.S. Pat. No. 3,629,096 teaches preparation of technical grade white mineral oil by a series of steps comprising hydrorefining mineral lubricating oil distillate in a first zone, taking the hydrogenated oil from the first hydrogenation stage and contacting it with hydrogen in the presence of a hydrosorber-hydrocracking catalyst followed by hydrogenation over a catalyst comprising a platinum group metal on a support having no substantial cracking effect.

U.S. Pat. No. 3,530,061 teaches the production of stabilized lube oils by hydrocracking hydrocarbon feed material following by contacting the product from this hydrocracking step with a catalyst having hydrogenation activity provided by one or more elements from Groups IIb, VIb and VIII at hydrocarbon pressures in the range from atmospheric up to about 100 psig.

U.S. Pat. No. 3,420,768 teaches a method for reducing the pour point of a hydrocarbon middle distillate by hydrocracking the middle distillate followed by reducing the pour point by contacting the effluent from the hydrocracking zone with hydrogen and a noble metal on alumina.

SUMMARY OF THE INVENTION

The subject invention is directed to a process for producing a lubricating oil of improved sunlight (UV) and good oxidation stability from a hydrocarbon feedstock boiling in the range of from about 700° to 1,200°F. by a sequential process which comprises:

A. catalytically hydrocracking in a hydrocracking zone said feedstock at a per mass conversion of at least 20 volume percent to materials boiling below the initial boiling point of said feedstock;

B. catalytically hydrogenating in a hydrogenation zone at least a substantial portion of the effluent from said hydrocracking zone boiling in the range 550° to 1,200°F.; at hydrogenation conditions including:

- a temperature of from 400° to 700°F.,
- a pressure of from 1,500 to 5,000 psig,
- an LHSV of from 0.2 to 1.5, and
- a hydrogen supply rate of from 500 to 20,000 SCF/barrel of said effluent fed to said hydrogenation zone,

in the presence of a hydrogenation catalyst comprising

1. a refractory oxide, and
2. a hydrogenating component comprising a noble metal, and

C. recovering as a product of said hydrogenation a lubricating oil having good UV stability.

A preferred catalyst for use in the hydrogenation zone is a noble metal on silica-alumina support wherein the alumina content is at least about 40 percent and the composite catalyst has been subjected with the noble metal in the oxide state to a heat treatment in the range of 1,200° to 1,800°F. The preferred noble metal is palladium.

DETAILED DESCRIPTION OF THE INVENTION

Statement of the Invention

In accordance with the present invention, there is provided a process for producing a lubricating oil having good UV stability.

The process comprises the steps set forth above under the "SUMMARY OF THE INVENTION.

These steps, which will be described in detail hereinafter, briefly call for:

1. catalytically hydrocracking a hydrocarbon feedstock in a hydrocracking zone at hydrocracking conditions;

2. catalytically hydrogenating at least a substantial portion of the effluent from the hydrocracking zone boiling in the range 550° to 1,200°F. at hydrogenation conditions with a hydrogenation catalyst; and
3,852,207

3. recovering as a product of the hydrogenation zone lubricating oil having good UV stability.

Hydrocarbon Feedstock
The hydrocarbon feedstock to the hydrocracking zone may encompass a wide range of feedstocks boiling in the range of from about 700°F to about 1,200°F. It may be a heavy straight run gas oil, deasphalted oil, vacuum gas oils, atmospheric residua, or the like. Preferred feedstocks are vacuum gas oils boiling in the range of from about 700°F to about 1,050°F, and solvent deasphalted oils having boiling ranges of from about 900°F to about 1,200°F. Reduced topped crude oils as well as atmospheric residua and the like may also be used. Because of the poisoning effect on the catalyst caused by cracking of asphaltenes to coke, it is preferred that the hydrocarbon feedstocks to the hydrocracking zone contain less than about 5 percent by weight of asphaltenes, preferably less than 1 percent by weight. The hydrocarbon feedstock has a boiling range extending over at least about 100°F. While the sulfur and nitrogen content of the hydrocarbon feedstock to the hydrocracking zone is not critical, excessive quantities of either sulfur or nitrogen are not desirable. Preferred feedstocks contain less than about 3 percent of sulfur and less than about 1 percent of nitrogen by weight.

Operating Conditions in the Hydrocracking Zone
Process conditions in the hydrocracking zone are those typical of hydrocracking operations. A temperature of about 500°F to 900°F, preferably 650°F to 800°F, is used. A pressure of from about 500 to about 10,000 psig, preferably 500 to 3,000 psig, is used with a LHSV of from 0.2 to 5.0, preferably 0.5 to 2.0, more preferably 0.5 to 1.0. The hydrogen supply rate (makeup and recycle) to the hydrocracking zone is in the range of from about 500 to about 20,000 standard cubic feet per barrel of hydrocarbon feed, preferably about 2,000 to about 10,000 standard cubic feet per barrel.

It should be noted that while hydrocracking is the primary reaction being carried out, the feedstocks as noted above generally contain some hetero organic compounds of sulfur, nitrogen, oxygen, and even metals in some cases. Therefore, hydrosulfurization, hydrodenitification, etc., may also be occurring.

Hydrocracking Catalyst
The catalysts employed in the hydrocracking zone are comprised of materials having hydrogenation-dehydrogenation activity, together with an active cracking component support. These catalysts are well known in the art as evidenced by the wide range of patent and literature references. Exemplary cracking component supports include silica-alumina, silica-alumina-zirconia composites, acid-treated clays, crystalline aluminosilicate zeolitic molecular sieves such as zeolite A, faujasite, zeolite X, and zeolite Y, and combinations of the above. Hydrogenation-dehydrogenation components of the catalyst preferably comprise at least selected from Group VIII metals and compounds thereof and Group VIB metals and compounds thereof. Preferred Group VIII components include cobalt and nickel, particularly the oxides and sulfides thereof. Preferred Group VIB components are the oxides and sulfides of molybdenum and tungsten. Thus, examples of a hydrocracking catalyst which would be preferred for use in the hydrocracking process step are the combinations of nickel-tungsten-silica-alumina, nickel-molybdenum-silica-alumina, and cobalt-molybdenum-silica-alumina. Such catalysts may vary in their activities for hydrogenation and for cracking and in their ability to sustain high activity during long periods of use depending on their compositions and methods of preparation. Obviously, the best proven catalysts available are selected, taking into consideration the above factors and cost.

A particularly preferred hydrocracking catalyst is a nickel sulfide-tungsten sulfide catalyst on a silica-alumina-titania support.

Conditions in the Hydrogenation Zone
The process conditions in the hydrogenation zone include a temperature in the range of from about 400°F to 700°F, preferably 500°F to 600°F, a pressure of from about 1,500 to 5,000 psig, preferably 2,000 to 3,000 psig, an LHSV in the range of from about 0.2 to 1.5, preferably 0.2 to 1.0, more preferably 0.3 to 0.7, and a hydrogen supply rate (makeup and recycle) in the range of from about 500 to about 20,000 standard cubic feet per barrel of hydrocarbon feed, preferably from about 2,000 to about 10,000.

Preferred operating conditions are a temperature in the range of from about 500°F to 600°F, a pressure in the range of from about 2,000 to 3,000 psig, an LHSV of from about 0.3 to about 0.7, and a hydrogen supply rate of about 2,000 to about 10,000 standard cubic feet per barrel of hydrocarbon feed.

Particularly preferred conditions are a temperature of about 550°F, a pressure of about 2,400 psig, an LHSV of about 0.5, and a hydrogen supply rate of about 8,000.

Hydrogenation Catalyst
The hydrogenation catalysts contemplated as useful herein for stabilizing the lube oil product obtained from the hydrocracking zone are those having a Group VIII noble metal component together with a refractory oxide support. Metals contemplated as useful include ruthenium, rhodium, and palladium, as well as osmium, iridium, and platinum. Preferred metals are platinum and palladium, more preferably palladium. The refractory oxide supports may include silica-alumina, silica-alumina-zirconia, etc.

A preferred hydrogenation catalyst is palladium or platinum deposited on a silica-alumina support having an alumina content of from 40 to 95 weight percent, preferably 50 to 80 percent. That is, the alumina/silica weight ratio is 40/60 to 95/5, preferably 50/50 to 80/20. The palladium or platinum is present in an amount of from about 0.2 to about 10.0 weight percent, preferably 0.2 to 1.0 percent of the composite. The catalyst with the palladium or platinum in the oxide form is subjected to a heat treatment in a dry nonreducing gas at a temperature in the range from 1,200°F to 1,800°F. Palladium is particularly preferred as the hydrogenation component. The silica-alumina support is preferably prepared by cogellation of the silica and alumina with the palladium or platinum impregnated on the dried or undried cogel.

The effluent from the hydrocracking zone which is fed to the hydrogenation zone preferably contains no more than about 50 ppm by weight of nitrogen and no more than about 50 ppm by weight of sulfur. Preferably, less than 10 ppm by weight of nitrogen and less than 10 ppm by weight sulfur is present. Low levels of nitrogen and sulfur are preferred since the noble metal containing catalyst in the hydrogenation zone is susceptible to poisoning by these components in the feed.
A range of lubricating oils is obtained from the subject process. As indicated above, the feedstock to the hydrocracking zone boils over a range which may extend from about 700°F to 1,200°F, and must extend over a range of at least about 100°F. The product obtained from the hydrogenation zone covers a range of lube stocks boiling over a range of at least about 100°F. These may range from light neutrals having SUS viscosities at 100°F, of from about 100 to 200 and boiling in the range of 700°F to 900°F, through medium neutral lubricating oils having boiling ranges in the range of from about 850°F to 1,050°F, up to and including bright stocks boiling in the range of from about 1,000°F to 1,200°F.

It is recognized that lubricating oils are not normally specified on the basis of boiling range, the primary criteria being viscosity and viscosity index. Generally, however, lubricating oils boil essentially entirely above 550°F, and more generally above 650°F, or even 700°F, and as high as about 1,200°F.

The term "lube oil" or alternatively "lubricating oil" has been used herein. It should be recognized that the process of the subject invention produces material which might also be referred to as lube oil base stock. Lubricating oils in use today are generally complex compositions formulated with a range of additives such as antioxidants, extreme pressure agents, VI improvers, corrosion inhibitors, detergents, dispersants, and the like.

The term "good UV stability" means that before a level of floc appears in the hydrocracked oil which is unsatisfactory (moderate floc of the level found in mid-Continent solvent refined 100 neutral oil after about 11 hours when the oil is exposed to UV light, as described in the example) will be at least about 6 hours. These UV stability values for the lube oils of this invention compare favorably with a commercial West Coast solvent-refined 126 neutral oil having 5.1 hours of stability before a fine light flocc appears and 7.0 hours of stability before a moderate floc appears. The oxidation stability, as measured by the test also described in the example, will be at least about 6 hours, preferably at least 10 hours. It should be noted that the hydrocracked stabilized lube oils of the subject invention may be dewaxed using conventional techniques, if required. Such dewaxing may be carried out by either catalytic means or by solvent extraction processes.

This invention will be better understood by reference to the following example, which is offered by way of illustration and not by way of limitation. This example compares lube oils prepared by a process of the general type described by the prior art and lube oils prepared by the process of the subject invention.

EXAMPLE 1

California deasphalted oil having the inspection data shown in Table I below was hydrocracked under the conditions shown in Table I.

<table>
<thead>
<tr>
<th>Feed Inspection</th>
<th>Hydrocracking Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sp. Gr. API</td>
<td>15°</td>
</tr>
<tr>
<td>S Content (wt. %)</td>
<td>1.37</td>
</tr>
<tr>
<td>N Content (wt. %)</td>
<td>0.48</td>
</tr>
<tr>
<td>Viscosity Index</td>
<td>6</td>
</tr>
<tr>
<td>D-1160</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>800°F</td>
</tr>
<tr>
<td>LHSV</td>
<td>0.47</td>
</tr>
<tr>
<td>Pressure</td>
<td>2400 psig</td>
</tr>
<tr>
<td>H₂ Supply Rate</td>
<td>5400 SCF/Barrel Feed</td>
</tr>
</tbody>
</table>

The 700°F.+ portion of the effluent from the hydrocracking zone was separated. The 700°F.+ portion had after dewaxing an oxidizer BN value of 4.7 hours and a viscosity index of 102.5. The UV stability of the 700°F.+ product from the hydrocracker was very poor (after 1 hour it formed a ring).


 Normally, the conditions are one atmosphere of pure oxygen at 340°F, and one reports the hours to absorption of 1000 ml of O₂ by 100 g of oil. In the Oxidizer BN test, 0.8 ml of catalyst is used per 100 grams of oil and an additive package is included in the oil. The catalyst is a mixture of soluble metal-naphthenates simulating the average metal analysis of used crankcase oils. The additive package is 820 milligrams of zinc bis-propylene phenyl dithio phosphate per 100 grams of oil. The oxidizer BN measures the response of a lubricating oil in a simulated application.

The UV stability of the lube oil is measured by placing the oil samples in glass bottles 16 mm in diameter, 50 mm high and having a wall thickness of about 1 mm.

The caps are loosened and the bottles are placed in a circular rack surrounding a 450 watt cylindrical Hanovia Mercury vapor lamp (Product of Conrad Precision Industries, Inc.) mounted in a vertical position. The distance along a line perpendicular to the longitudinal axis of the lamp extending from the longitudinal axis of the lamp to the longitudinal axis of the bottle is 2½ inches. The sample is observed over a period of time. At the first appearance of a light fine flocc (small particles suspended in the oil), the time to formation of the flocc is noted. The additional time until a moderate flocc or heavy flocc is also noted. In some cases of poor stability a ring of precipitated particles is observed clinging to the walls of the bottle.

A portion of the 700°F.+ product described above was hydrogenated over a noble metal hydrogenation catalyst containing 0.4 percent palladium on a silicacarbons (40-60 weight ratio of silica to alumina) support wherein the catalyst had been heat treated in substantially dry nonreducing gas at a temperature of about 1,400°F. Run conditions and inspections of the resulting product are shown in Table II below.

<table>
<thead>
<tr>
<th>Hydrogenation Conditions</th>
<th>Product Inspection (After Dewaxing)</th>
</tr>
</thead>
<tbody>
<tr>
<td>552°F, 0.57 LHSV</td>
<td>Oxidizer BN 11.9 Hours</td>
</tr>
<tr>
<td>8000 SCF/Barrel Feed 2400 psig</td>
<td>UV Stability 9.1 Hours Light Flocc</td>
</tr>
</tbody>
</table>

A second portion of the 700°F.+ product described above was hydrogenated over a prior art catalyst hav-
ing the properties set forth in Table III below. The properties of the resulting products as well as operating conditions are also shown in Table III.

### TABLE III

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Hydrogenation Conditions</th>
<th>Product Inspection (After Dewaxing)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.5% NiO (by weight)</td>
<td>550°F.</td>
<td>Oxidizer BN 4.9 Hours</td>
</tr>
<tr>
<td>24.5% WO₃</td>
<td>0.60 LHSV</td>
<td>UV Stability 1.3 Hr. to Moderate Flocculation</td>
</tr>
<tr>
<td>27.0% SiO₂</td>
<td>8000</td>
<td></td>
</tr>
<tr>
<td>30.0% Al₂O₃</td>
<td>2400 psig</td>
<td>VI 109</td>
</tr>
<tr>
<td>8.0% TiO₂</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As can be seen from the data set forth above, use of the noble metal catalyst in the hydrogenation step resulted in a product having significantly improved UV stabilization and oxidizer BN stabilization. Stable oil was still being produced with this noble metal catalyst when the 2,400 psig test run was ended at 850 hours.

It is apparent that many widely different embodiments of the invention may be made without departing from the scope and spirit thereof; and, therefore, it is not intended to be limited except as indicated in the appended claims.

What is claimed is:

1. A two-stage process for producing a lubricating oil having good UV stability from a hydrocarbon feedstock boiling in the range 700°F to 1,200°F, which comprises:
   A. catalytically hydrocracking said feedstock in a hydrocracking zone at hydrocracking conditions at a per pass conversion of at least 20 volume percent to materials boiling below the initial boiling point of said feedstock; and
   B. catalytically hydrogenating in a hydrogenating zone at least a substantial portion of the effluent from said hydrocracking zone boiling in the range 550°F to 1,200°F. at hydrogenation conditions including:
      a temperature of from 400°F to 700°F, a pressure of from 1,500 to 5,000 psig, an LHSV of from 0.2 to 1.5, and a hydrogen supply rate of from 500 to 20,000 SCF/barrel of said effluent fed to said hydrogenating zone,
      in the presence of a hydrogenation catalyst comprising
      1. a refractory oxide, and

2. The process of claim 1 wherein said hydrogenation conditions include a temperature of from 500°F to 600°F, a pressure of from 2,000 to 3,000 psig, an LHSV of from 0.2 to 1.0, and a hydrogen supply rate of from 2,000 to 10,000 SCF/barrel of said effluent fed to said hydrogenating zone.

3. The process of claim 1 wherein said hydrocarbon feedstock is selected from the class consisting of heavy run gas oil, deasphaltered oil, vacuum gas oil and atmospheric residua.

4. The process of claim 1 wherein said hydrogenation catalyst comprises palladium on an alumina-silica support.

5. The process of claim 4 wherein said hydrogenation catalyst has an alumina to silica weight ratio of 40–60 to 95–5 and said noble metal is palladium present in an amount of from 0.2 to 10 weight percent.

6. The process of claim 5 wherein said hydrogenation conditions include a temperature in the range of 500°F to 600°F, a pressure in the range of from about 2,000 to 3,000 psig, an LHSV of from about 0.2 to about 1.0, and a hydrogen supply rate of from about 2,000 to 10,000 SCF/barrel of hydrocarbon feed to said hydrogenation zone.

7. The process of claim 6 wherein said hydrogenation catalyst has a silica to alumina weight ratio of 40 to 60 and contains 0.4 weight percent palladium.

8. The process of claim 7 wherein said lubricating oil has, after dewaxing, a UV stability of at least 9 hours.

9. The process of claim 6 wherein said hydrogenation catalyst was subjected to said heat treatment at a temperature in the range of 1,200°F to 1,800°F.

10. The process of claim 7 wherein said hydrogenation catalyst was subjected to said heat treatment at about 1,400°F.