United States Patent

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[54] SYNTHETIC LUBRICATING OIL STOCK PRODUCTION

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[51] Int. Cl. C10g 13/00

[58] Field of Search 208/18, 86, 92, 251, 309

[56] References Cited

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2,917,448	12/1959	Beuther et al.	208/86
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[57] ABSTRACT

A process for the production of a synthetic lubricating oil, which comprises:

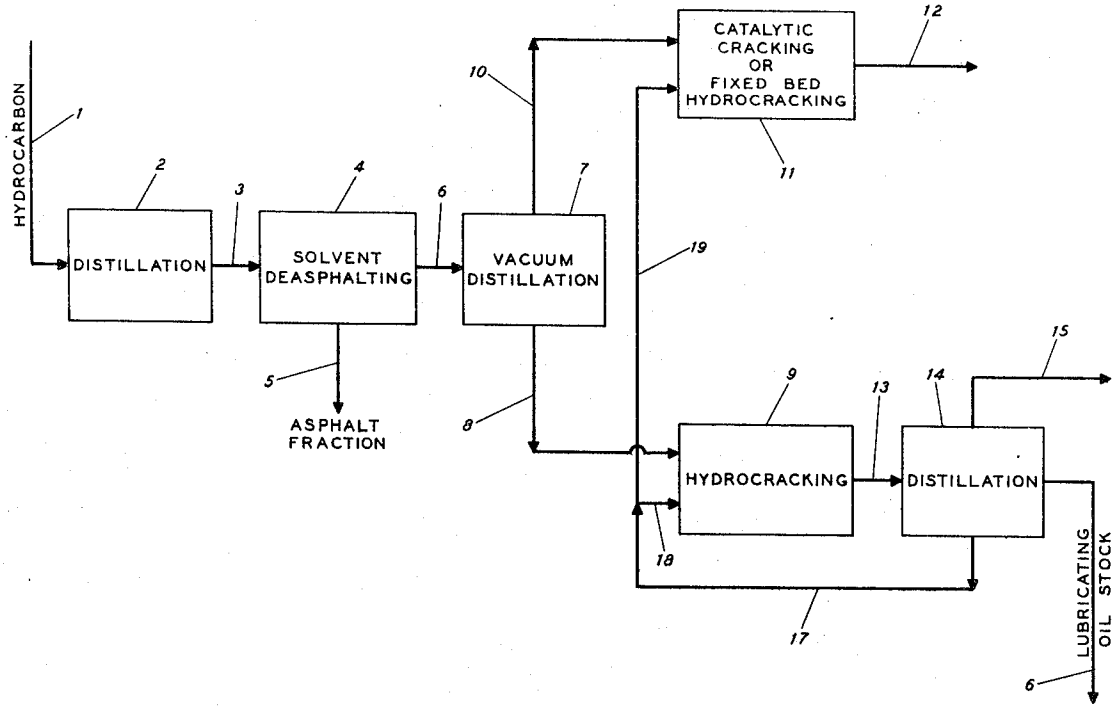
a. Solvent deasphalting a metals-contaminated heavy oil to obtain an asphalt-rich fraction and a raffinate oil of reduced metals content;

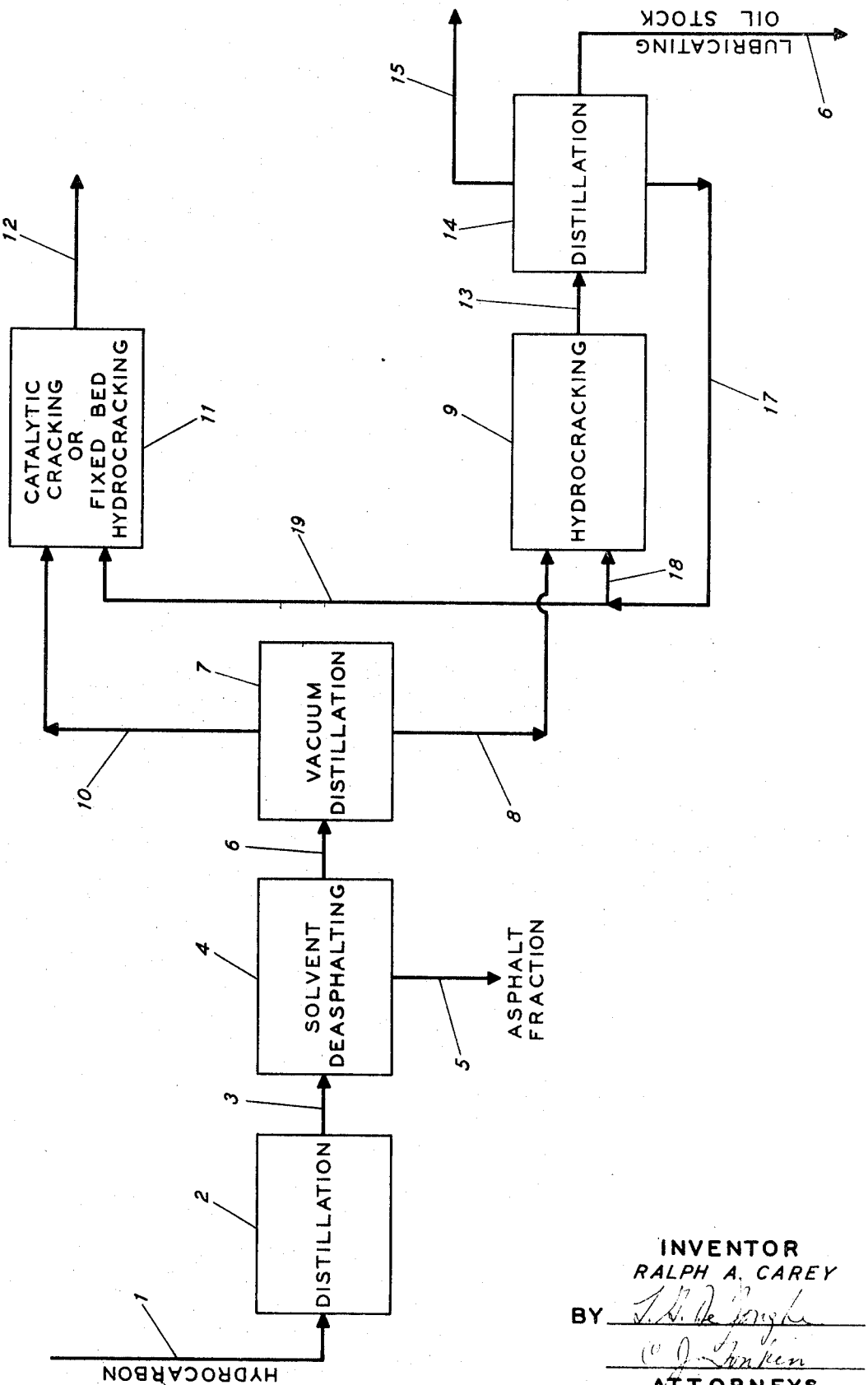
b. Vacuum distilling the raffinate oil to obtain at least a light oil fraction and a bottoms fraction;

c. Hydrocracking at least a portion of the bottoms fraction in a hydrocracking zone; and

d. Separating an all-synthetic lubricating oil stock from an effluent stream from the hydrocracking zone.

6 Claims, 1 Drawing Figure





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SYNTHETIC LUBRICATING OIL STOCK PRODUCTION

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to the production of lubricating oil by a process combination involving hydrocracking. More particularly, the present invention relates to producing a lubricating oil stock from a heavy hydrocarbon oil which is contaminated with metals such as organometallic compounds.

2. Prior Art

It has previously been proposed to prepare high-viscosity index lubricating oils by hydrocracking heavy oils such as residuum.

Also, processes for producing lubricating oils by hydrocracking solvent deasphalted oils have been disclosed. For example, according to the process disclosed in U.S. Pat. No. 3,365,390, lubricating oils are produced by hydrocracking a solvent deasphalted heavy oil feed, separating hydrocracked wax from a hydrocracked lubricating oil portion of the products, and hydroisomerizing the hydrocracked wax using an active reforming catalyst.

U.S. Pat. No. 3,308,055, also proposes a process to produce a lube oil from a heavy oil. According to example 2 in that patent, deasphalted residual oil is blended with a recycle oil and is then hydrocracked. The effluent from the hydrocracking step is distilled to obtain relatively light products, such as gasoline, and heavy products, including lubricating oil stock. The lubricating oil stock is dewaxed to obtain a relatively high-viscosity index lubricant oil.

Prior art processes involving solvent deasphalting have been disclosed in connection with vacuum distillation of heavy oils, but in this connection the vacuum distillation has been applied only to the feed stock to the solvent deasphalting step.

SUMMARY OF THE INVENTION

According to the present invention, a process is provided for the production of a synthetic lubricating oil, which comprises:

a. Solvent deasphalting a metals-contaminated heavy oil to obtain an asphalt-rich fraction and a raffinate oil of reduced metals content;

b. Vacuum distilling the raffinate oil to obtain at least a light oil fraction and a bottoms fraction;

c. Hydrocracking at least a portion of the bottoms fraction in a hydrocracking zone; and

d. Separating an all-synthetic lubricating oil stock from an effluent stream from the hydrocracking zone.

In present specification, the term "synthetic" lubricating oil stock is used to mean a lubricating oil stock which has an upper boiling point cut point which is no higher than the lower boiling point cut point of the hydrocarbon feed stock fed to the hydrocracking step of the present invention.

It is to be understood that boiling point "cut points" generally do not coincide exactly with initial boiling points and end boiling points, because when an oil is fractionated, it is not cut surgically sharp into various boiling ranges. However, the term boiling point cut point is used herein to mean that no more than 5 volume percent of the particular oils boil below boiling point cut point and no more than 5 volume percent of the subject oil boil above the upper boiling point cut point.

The term "lubricating oil stock" is used herein as indicating that in some cases it will be desirable to further treat the oil, as by solvent extraction and/or dewaxing, in order to take maximum advantage of the improved oil qualities and produce superior lube oil.

In accordance with a preferred embodiment of the present invention, the feed heavy oil to the solvent deasphalting step is a bottoms product obtained from the distillation of a metals-contaminated hydrocarbon feed stock. The distillation of the feed oil can be in a conventional crude oil atmospheric distillation column, or a vacuum distillation column, or in a series combination of these two types of distillation units. Thus, although vacuum distillation subsequent to solvent deasphalting is a critical requirement of the present combination process, according to a preferred embodiment of the present invention, a vacuum distillation step also precedes the solvent deasphalting step.

The vacuum distillation step subsequent to solvent deasphalting of the metals-contaminated heavy oil feed, is operated so as to split the raffinate oil from the deasphalting step into at least a light fraction and a vacuum distillation bottoms fraction. Preferably, at least a portion of the light fraction from the vacuum distillation is converted to valuable hydrocarbon products by a fixed bed hydrocracking process or a catalytic cracking process. The light fraction is a particularly attractive feed stock for either of these processes, as the light fraction, although it is a fairly heavy oil, has a relatively low-metals content because it has been subjected to at least two metals-removing steps, that is, solvent deasphalting and vacuum distillation. When vacuum distillation is applied to a metals-containing heavy oil, a substantial amount of organic metallic compounds will be found to have entrained into the light fractions or side cuts withdrawn from the vacuum distillation column above the flash zone. This is largely because of the fact that it is extremely difficult to avoid entrainment of heavy organometallic compounds into the side cuts withdrawn from a vacuum distillation column when there is a substantial quantity of organometallic compounds in the feed to the vacuum distillation column. However, in the present invention, solvent deasphalting is applied to the metals-containing heavy oil feed prior to vacuum distillation and the deasphalting step serves to greatly reduce the amount of organometallic compounds contained in the metals-contaminated heavy oil feed. The asphaltic portion, which is separated from the raffinate the deasphalting step contains the bulk of the metals present in the metals-containing heavy oil feed stock the deasphalting step.

The process combination of the present invention is also particularly advantageous in that a very heavy feed is provided for the hydrocracking step so that an all-synthetic lubricating oil stock can be produced, but without large quantities of metals fouling the hydrocracking catalyst. Thus, the metals-contaminate heavy oil feed to the solvent deasphalting step of the present invention may contain more than 10 p.p.m. or even more than 50 p.p.m. or organometallic compounds (calculated by weight as the pure metal), but the solvent deasphalting step will reduce the metals content to below about 5 p.p.m. metals in most instances and usually at least below 15 p.p.m. metals.

In obtaining the desired heavy feed for the production of the all-synthetic lubricating oil stock in the hydrocracking zone, the vacuum distillation step immediately prior to the hydrocracking step will tend to concentrate the metals present in the solvent deasphalted oil into the bottoms withdrawn from the vacuum distillation step. However, the bottoms withdrawn from the vacuum distillation step usually will not contain more than about two times the metals concentration present in the solvent deasphalted oil, and, preferably, the combined deasphalting and vacuum distillation steps are operated so that less than 7 p.p.m. metals is present in the vacuum bottoms which is fed to the hydrocracking step.

Because the hydrocracking step of the present invention is fed a relatively heavy feed, a substantial to hydrocracking and hydrogenation must necessarily take place in the hydrocracking zone in order to convert the feed to the hydrocracking zone to a lower-boiling lubricating oil stock. For example, in accordance with a preferred embodiment of the present invention, a metals-contaminated heavy oil is solvent deasphalted to obtain an asphalt-rich fraction and a raffinate which boils from above at least about 600° F. up to a least about 1,200° F. The raffinate is vacuum distilled to obtain at least a light oil fraction which has an upper boiling point cut point below about 1,000° F. and a bottoms fraction which has a lower boiling point cut point above at least 900° F. and, preferably, above about 1,000° F. In short, the light oil

fraction boil below about 1,000° F. and the bottoms fraction boils about 1,000° F. The bottoms fraction, or at least a portion of the bottoms fraction is the feed to the hydrocracking step of the present process invention. Thus, it can be seen that the feed to the hydrocracking step is a very heavy oil. However, as explained above, even though this heavy oil is derived from a metals-contaminated heavy oil, the heavy oil feed stock to the hydrocracking step will contain only a relatively low amount of metals contaminants and thus the hydrocracking step can be more successfully conducted, because of less metals fouling of the hydrocracking catalyst and less plugging of the catalyst beds in that instance where fixed beds are used in this hydrocracking step. In converting the vacuum bottoms fraction to an all-synthetic lubricating oil stock, substantial saturation of aromatics to naphthenes will occur and, in general, considerable amounts of hydrogen will be added to the vacuum bottoms feed in converting the vacuum bottoms feed to material boiling below the upper boiling point of the vacuum bottoms feed. Both of these factors will operate in the direction of producing a good lubricating oil stock.

Preferably, the effluent stream from the hydrocracking zone is vacuum distilled to obtain a lubricating oil stock which boils within the range of 600° F. to 1,000° F. These boiling points, and any other specific boiling points specified in this specification, are used in the sense of boiling cut points, as explained previously. Also, by the term "at least within the range" is meant that the lubricating oil stock obtained by the vacuum distillation of the hydrocracking zone effluent, boils over a range no greater than 600° to 1,000° F. In any case, the upper boiling cut point of the lubricating oil stock is below the lower boiling point cut point of the vacuum bottoms feed stock to the hydrocracking step.

In accordance with a particularly preferred embodiment of the present invention, all of the bottoms fraction from the vacuum distillation immediately prior to the hydrocracking step is hydroconverted to synthetic lubricating oil stock and lower boiling hydrocarbons. That is, in the general process of the present invention, typically, the effluent from the hydrocracking zone will be distilled into various fractions, including a small heavy fraction boiling above the lower boiling point cut point of the feed to hydrocracking zone and this material can be sent to other processing, such as fluid catalytic cracking, but according to the particularly preferred embodiment to which reference is now made, this heavy material which, at least from the standpoint of boiling point, contains material which has not been hydroconverted, is recycle of to the hydrocracking step of the present invention. Using the recycle operation, all of the bottoms fraction feed to the hydrocracking zone is hydroconverted to synthetic lubricating oil stock and lower boiling hydrocarbons such as gasoline or jet fuel. Although the heavy recycle stream can be obtained by distillation subsequent to the hydrocracking zone, in one preferred embodiment of the present invention, the heavy oil recycle portion is obtained by a hot flash subsequent to the hydrocracking reactor, such as is described in U.S. Pat. No. 3,463,611.

BRIEF DESCRIPTION OF THE DRAWING

The drawing is a schematic process flow diagram illustrating a preferred embodiment of the prevent invention.

DETAILED DESCRIPTION OF THE DRAWING

Referring now in more detail to the drawing, metals-contaminated hydrocarbon feed stock is fed via line **1** to distillation zone **2**. The hydrocarbon feed stock may be a crude petroleum oil or a reduced crude obtained by distillation of crude oil. Distillation zone **2** is operated in a conventional manner per se. In that instance where the hydrocarbon feed stock is a whole crude oil, distillation zone **2** can consist of an atmospheric distillation column and a vacuum distillation column receiving reduced crude from the bottom of the atmospheric distillation column.

A metals-contaminated heavy oil is withdrawn from distillation zone **2** via line **3** and fed to solvent deasphalting zone **4**. The feed to the solvent deasphalting step can be any high-boiling hydrocarbon oil containing metal contaminants, principally oils boiling above about 600° F. The original source of the oil may be any hydrocarbonaceous deposit of ancient origin, including, besides crude petroleum, such materials as gilsonite, shale oil, oil sands, and the like. Metal contaminants are found in increasing concentrations in the higher boiling portions of these hydrocarbonaceous materials, probably as organometallic compounds having condensed ring structures. The most common metals, and the most troublesome, are sodium, iron, vanadium, nickel and copper.

Light and medium boiling range gas oils distilled from crude petroleum rarely contain more than very small amounts of metal contaminants, and these stocks can be successfully hydrocracked by known processes. Metal contamination may appear in the heavy gas oils; for example, vacuum gas oils from reduced crude. The depth of distillation of crude oils is often controlled with respect to the cut point at which metal contamination of the distillate appears, so that the metals are concentrated in the residuum. Metal contamination may then appear in the heavy gas oils produced by coking, resid stripping, vis-breaking, and other residuum conversion processes. Hence the preferred feed stock for the solvent deasphalting step of this invention are reduced crude, heavy gas oils, the residuum itself, and portions thereof.

Heavy oils such as crude residuum contain asphaltic material including pitch or tar, within which material the bulk of the organometallic compounds is located. These asphaltic materials are very difficult to process in a hydrocracking step. Accordingly, it is desirable to deasphalt heavy oils before hydrocracking and, more important for purposes of the present invention, the deasphalting step serves as a substantial metal-removal step, because a large portion of the metal contaminants are present in structures contained in the asphaltic material removed by solvent deasphalting.

The solvent deasphalting step in zone **4** may be any solvent decarbonizing procedure whereby compounds such as asphaltenes, pitches, resins, or tars are caused to separate from the bulk of the oil on the basis of their molecular weight, configuration, or size. The preferred process is propane deasphalting, but other light paraffins having two to five carbon atoms per molecule may be used instead of or with the propane. The deasphalted oil forms an extract phase with the light paraffin solvent, which separates from the tarry material or asphalt. The deasphalted oil is then recovered from the solvent which is reused. How completely the asphaltic materials are removed depends on the nature of the residuum, the relative proportions of solvent and residuum, the nature of the solvent, and the efficiency of the process itself. Since the separation is not based strictly on the boiling point of the materials removed, the deasphalted oil may still contain very high-boiling oils and some contaminating compounds.

As is schematically indicated on the drawing, an asphaltic fraction is removed via line **5** from the solvent deasphalting zone **4**. The raffinate is removed via line **6** and is fed to vacuum distillation zone **7**.

The vacuum distillation zone **7** can comprise one or more vacuum flash towers, vacuum distillation columns, or vacuum stripping operations such as a residuum stripper employing steam to reduce the hydrocarbon partial pressure. The vacuum distillation is carried out in a manner which is per se conventional. However, the process sequence of the present invention is unique and the feed to the vacuum distillation zone **7** can be considered unconventional in the sense that it is a heavy oil obtained by solvent deasphalting of a metals-containing heavy oil. Also, vacuum distillation operation in zone **7** is, to a degree, unconventional in that, according to a preferred embodiment of the present invention, the vacuum cut into the heavy oil fed to the vacuum distillation zone is quite deep, preferably down to about 900° F. normal boiling point and, still more preferably down to about 1000° F. cut

point. In order to cut this deeply into the heavy feed to the vacuum distillation zone 7, in certain instances (depending upon an economic analysis based on capital investment, utilities expense and the particular characteristics of the feed) it is preferable to use two vacuum distillation columns in series, with the first vacuum distillation column operating at a moderately low vacuum and the second one at a very low vacuum. Usually, however, it is preferred to carry out the vacuum distillation step using only one vacuum distillation column operated at a relatively low (about 20–40 mm. mercury absolute pressure) pressure and with a considerable amount of stripping steam used to lower the effective hydrocarbon partial pressure in the flash zone of the vacuum distillation column and with multistage steam jet ejectors used to draw the relatively low vacuum in the vacuum distillation column.

To better illustrate operation under the process of the present invention, brief reference is now made to an example based partly on calculation and partly on operating data. A solvent deasphalted oil is fed in the amount of about 30,000 barrels per day to a vacuum distillation column. The solvent deasphalted oil contains about 5 p.p.m. metals, mostly in the form of organometallic compounds or porphyrins or iron, nickel and vanadium. The solvent deasphalted oil is derived from residuum containing approximately 20 p.p.m. metals. The solvent deasphalted oil, i.e., the raffinate from the solvent deasphalted step, is fractionated in a vacuum distillation column to yield an upper product of about 10,000 barrels per day, and having a boiling range of about 800° F. to 1,000° F. A bottoms fraction in the amount of about 20,000 barrels per day is withdrawn from the lower part of the vacuum distillation column and this bottoms portion has a boiling range of about 1,000° F. up to about 1,400° F. or higher, the upper boiling point being estimated by extrapolation. The metals content of the light fraction from the vacuum distillation column is about 1 or 20 p.p.m. Thus, this light fraction forms a particularly attractive feed for fluid catalytic cracking or hydrocracking, particularly fixed bed hydrocracking; as in all of these processes operation is improved by using a low-metals content feedstock. The bottoms from the vacuum column does not contain a prohibitively large amount of organometallic compounds for hydrocracking feed because of the solvent deasphalting step which preceded the vacuum distillation step.

The metals content of the 1,000° F.+ boiling point material is about 8 p.p.m. Because this material has a relatively high-initial boiling point, it is particularly attractive feedstock for conversion in a hydrocracking zone to all-synthetic lubricating oil stock.

Twenty thousand barrels per day of the 1,000° F.+ vacuum bottoms is fed to a hydrocracking step, as indicated by zone 9 in the schematic drawing. The effluent from the hydrocracking zone is fractionated by a pressurized column and a vacuum distillation column in series to obtain various lower boiling hydrocarbon cuts which boil below about 650° F., as well as to obtain about 8,000 barrels per day of synthetic lubricating oil stock boiling between 650° F. and 1,000° F. and a 1,000° F.+ vacuum bottoms material which is recycled to the hydrocracking step. The synthetic lubricating oil stock is then solvent extracted and dewaxed to form about 4,000 barrels per day of refined synthetic lubricating oil.

Referring now again more specifically to the drawing, a light fraction which may be more conventionally referred to as a heavy vacuum gas oil is withdrawn via line 10 from distillation zone 7 and fed to zone 11 for catalytic hydrocracking or fixed bed hydrocracking. Catalytic cracking, in zone 11, can comprise any of the well-known conventional catalytic cracking processes such as those employing fluidized catalyst powder, or gravitating catalyst particles. Generally, a natural or synthetic silica-alumina catalyst is employed and passed continuously in a cycle from a reaction stage to a regeneration stage, wherein coke is burned off the catalyst, and back to the reaction stage. In the catalytic cracking operation, the vacuum gas oil is converted to light hydrocarbon products such as gasoline (and middle distillates in the jet fuel boiling range) and these light products are withdrawn via line 12.

Alternately, zone 11 can comprise hydrocracking operation of any of the various conventional types. Although an ebullated bed, for example, can be used, it is preferred to take advantage of the higher efficiency and other advantageous characteristics of fixed bed hydrocracking, because the feed via line 10 to the hydrocracking process, although a heavy feed, contains only a relatively low amount of metallic contaminants.

The heavy portion withdrawn from vacuum distillation zone 7 is passed via line 8 to hydrocracking zone 9. Hydrocracking zone 9 is operated in a manner which is conventional, per se, but, as is the case with vacuum distillation zone 7, hydrocracking zone 9 has certain features which can be considered unconventional because of the particular service of hydrocracking zone 9 and the feed which hydrocracking zone 9 receives. Thus, it is preferred to hydrocracking zone 9 under relatively severe conditions so as to convert the feed to hydrocracking zone 9 to an all-synthetic lubricating oil stock.

In particular, preferably the pressure is at least 1,000 p.s.i.a. hydrogen partial pressure and, more preferably, at least 2,000 p.s.i.a. hydrogen partial pressure. Although pressures within the range of 500–10,000 p.s.i.a. hydrogen are operable, generally, pressures of 2,000 to 3,500 p.s.i.a. hydrogen partial pressure are preferred.

The temperature should be in the range 650°–850° F., extremely high temperatures being avoided in order to favor hydrogenation, and the space velocity should be less than 2.0, preferably in the range 0.2–1.0 liquid hourly space velocity (LHSV) so as to provide sufficient time for the conversion without using excessively high temperatures. The hydrogen-to-oil ratio is generally between 2,000 and 10,000 standard cubic feet per barrel (s.c.f./bbl.). Because of the difficulty of hydrogenating the aromatic and contaminated oil, there is preferably used a highly active catalyst containing Group VI and/or Group VIII metals, such as a sulfided high-metal content nickel-molybdenum catalyst. As a guide in determining the suitability of a particular catalyst, it should be capable of removing a least 95 percent of the nitrogen compounds contained in the extract by hydrogenation to ammonia at conditions in the aforementioned ranges. The obtaining of greater than 95 percent nitrogen removal is used as a guide or criterion for determining that sufficient hydrogenation is being accomplished. At the conditions necessarily employed, at least a portion of the feed will be converted to distillate fuel comprising hydrocarbons boiling in the range of gasoline, kerosene, and middle distillates lower boiling than generally included in lubricating oil. Accordingly, such distillate fuels are separated from the products of the hydrocracking zone to recover a heavier portion comprising hydrogenated oil suitable for incorporating into lubricating oil.

In carrying out the catalytic hydrogenation in zone 9, any suitable equipment may be used for contacting the oil with the catalyst in the presence of excess hydrogen, For example the catalyst may be maintained as one or more fluidized beds, gravitating beds, or fixed beds of small particles, through which the oil and hydrogen are passed, upflow or downflow, concurrent or countercurrent. A slurry of catalyst in oil may also be used. Usually, the catalyst is in the form of small pellets or rodlike extrusions contained in a reactor as several fixed beds, and the oil and hydrogen are passed together downflow through the bed at controlled temperature, pressure and flow rate. The effluent is cooled to separate product oil from hydrogen-rich gas which is recycled.

The oil thus obtained in hydrocracking zone 9 is passed via line 13 to distillation zone 14, wherein the products of the hydrocracking operation are separated into distillate fuels and lighter hydrocarbons withdrawn via line 15 and the primary lubricating oil stock withdrawn via line 16. An unconverted heavy oil fraction is withdrawn via line 17 and preferably is recycled to hydrocracking zone 9, as discussed under "Summary of the Invention." This heavy oil can be recycled and fed entirely to hydrocracking zone 9 via line 18, or a portion or all of this oil may be fed to zone 11 via line 19. As discussed under the "Summary of the Invention," according to a

preferred embodiment of the present invention, the recycle oil to hydrocracking zone 9 is obtained internal to zone 9 by use of a hot flash following the hydrocracker reactor in zone 9.

Although various specific embodiments of the invention have been described and shown, it is to be understood that they are meant to be illustrative only and not limiting. Certain features may be changed without departing from the spirit or essence of the invention. It is apparent that the present invention has broad application to the production of an all-synthetic lubricating oil stock by a process involving solvent deasphalting of a metals-containing oil, followed by vacuum distillation and then hydrocracking of the bottoms from the vacuums distillation step. Accordingly, the invention is not to be construed as limited to the specific embodiments illustrated, but only as defined in the appended claims.

I claim:

1. A process for the production of a synthetic lubricating oil stock from a metals-contaminated heavy oil which comprises:

a. Deasphalting the heavy oil to obtain an asphalt-rich fraction and a raffinate which boils from above at least about 600° F. and up to at least about 1200° F.;

b. Vacuum distilling, in a vacuum distillation column or a vacuum stripping column, the raffinate to obtain at least a light oil fraction which has an upper boiling point cut point below about 1,000° F. and a bottoms fraction which has a lower boiling point cut point above at least about 900° F.;

c. Hydrocracking at least a portion of the bottoms fraction in a hydrocracking zone; and

d. Separating from an effluent stream from the hydrocracking zone a lubricating oil stock which boils below the lower boiling point of the bottoms fraction.

2. A process in accordance with claim 1 wherein the feed heavy oil to the solvent deasphalting step contains at least 10 p.p.m. metals and is a bottoms product obtained from distillation of a metals-contaminated feedstock.

3. A process in accordance with claim 1 wherein all of the bottoms fraction is hydroconverted to synthetic lubricating oil stock and lower boiling hydrocarbons.

4. A process in accordance with claim 1 wherein said effluent stream from the hydrocracking zone is vacuum-distilled to obtain a lubricating oil stock which boils at least within the range of about 600° F. to 1,000° F.

5. A process in accordance with claim 4 wherein all of a bottoms stream from the vacuum distillation of the hydrocracking zone effluent is recycled to the hydrocracking zone so that all of the bottoms fraction is converted to synthetic lubricating oil stock and lower boiling hydrocarbons.

6. A process in accordance with claim 5 wherein the lubricating oil stock is dewaxed to obtain a high-viscosity index lubricating oil.

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