

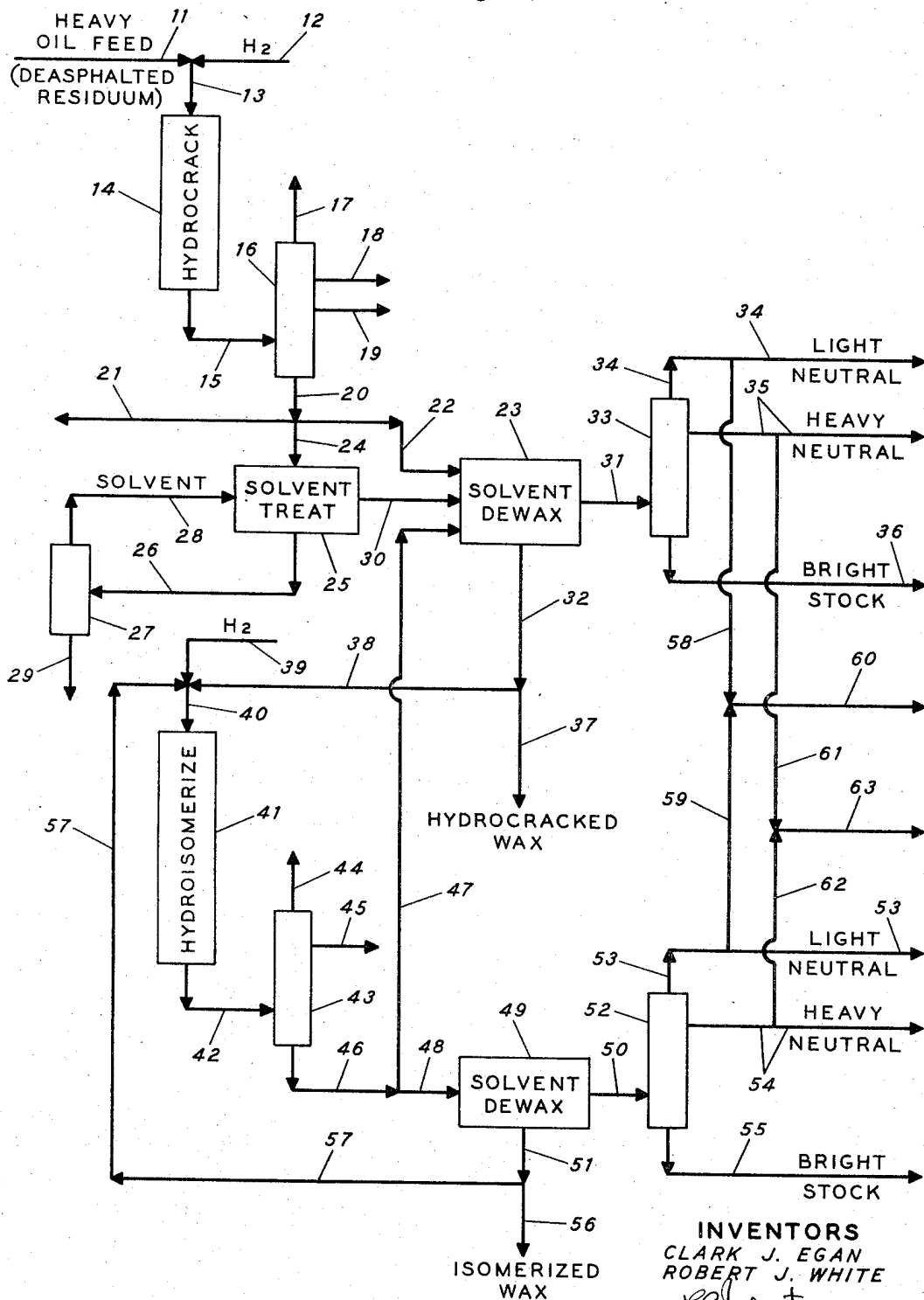
Jan. 23, 1968

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3,365,390

LUBRICATING OIL PRODUCTION

Filed Aug. 23, 1966



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3,365,390

LUBRICATING OIL PRODUCTION

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Continuation-in-part of applications Ser. No. 548,075, May 6, 1966, and Ser. No. 477,597, Aug. 5, 1965. This application Aug. 23, 1966, Ser. No. 574,353
6 Claims. (Cl. 208-60)

ABSTRACT OF THE DISCLOSURE

Lubricating oils are produced by hydrocracking a 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. An isomerized lubricating oil fraction so produced can be dewaxed separately, to recover ultrahigh VI isomerized lube oil, or in admixture with a hydrocracked lubricating oil portion. An additional hydrogenation step may precede and/or follow the hydroisomerization step.

Cross references

This application is a continuation-in-part of copending application Ser. No. 477,597, filed Aug. 5, 1965, and a continuation-in-part of copending application Ser. No. 548,075, filed May 6, 1966, in turn a continuation-in-part of said Ser. No. 477,597.

This invention relates to processes comprising catalytic hydroconversion of heavy oils to produce lubricating oils. More particularly, the invention provides a new process for producing lubricating oil of controllable quality as a byproduct of hydroconversion of heavy oils.

Hydrocarbon oils to be suitable for use as lubricants are generally required to be sufficiently high boiling to have low volatility and a high flash point. Superior lubricating properties are obtained if the oil is composed primarily of saturated hydrocarbons comprising paraffins and cycloparaffins, with a minimum content of aromatics. The oils are required to flow freely, and thus generally must have a pour point not in excess of about +35° F., and more usually pour points of +15° F., +5° F., or 0° F. or lower are specified. Many other oil products not designed for use as lubricants, spray oils for example, desirably have these same properties of low volatility, high flash point, high paraffin content, and low pour point.

High quality lubricating oils, for example high viscosity index oils, command a premium price in the market place, but demand is not great. It is known that high VI lube oils can be produced from lower VI heavy oils by hydrocracking directly. Heretofore, however, to obtain the desired high quality product it was necessary either to start with a high quality feedstock or else to accept a low yield of high quality product. Thus, methods of hydrocracking low VI oils to produce high VI oils require operating the hydrocracker at special conditions carefully tailored to the feed properties in order to obtain the particular desired properties in the lube oil, which is only a minor product. Such processes have not gained wide commercial acceptance for this reason. As a practical matter, a refiner has to operate his major facilities as needed to obtain the desired yields and properties of the major products.

In one aspect, the present invention provides a method, comprising a combination of treating steps including hydrocracking, whereby a wide selection of low, medium, high, and ultrahigh viscosity index lubricating oils can be produced as desired, while operating the hydrocracking step as needed or desired to obtain optimum economics

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with respect to conversion of unwanted heavy oils to those distillate fuel products for which demand is greatest.

In the aforementioned copending application Ser. No. 477,597, there is disclosed the catalytic hydrocracking of heavy oil to obtain low nitrogen content heavy oil which is catalytically hydroisomerized and hydrocracked to produce low pour point lubricating oil without dewaxing. In the aforementioned copending application Ser. No. 548,075, it is disclosed that the catalytic hydroisomerization of nitrogen-free waxy oils is made more selective for isomerization with less hydrocracking when the waxy oil is prehydrogenated. Although it is shown possible by these methods to make lubricating oils having pour points as low as those obtainable by a solvent dewaxing, the cloud points of the heaviest product oils were sometimes unsatisfactory. Also, stability problems were sometimes encountered in the product such that a mild finishing hydrogenation was needed. Conditions in the preparation of the feed had to be controlled so as to provide for the catalytic hydroisomerization step an oil having a low nitrogen content.

It has now been found that high quality lubricating oils can be prepared by catalytic hydroisomerization of wax separated from heavy hydrocracked oil. In accordance with the invention a heavy oil feed boiling at least partly above 900° F. is hydrocracked in a catalytic hydrocracking zone using a sulfactive hydrocracking catalyst, and the oil effluent thereof is separated into fractions including a distillate fuel and a higher boiling hydrocracked lube oil boiling range fraction. The said hydrocracked lubricating oil boiling range fraction is dewaxed to obtain a hydrocracked wax fraction of low nitrogen content. At least a portion of the hydrocracked wax fraction is hydroisomerized in a hydroisomerization zone using an active reforming catalyst, and the oil effluent thereof is separated into fractions including a distillate fuel and an isomerized lube oil boiling range fraction. Desirably, conversion of the wax to lubricating oil by hydroisomerization is incomplete, and at least a high boiling portion of the isomerized material is dewaxed, e.g. by the same techniques as used with the hydrocracked oil, to obtain additional dewaxed isomerized lube oil and an isomerized wax.

In the invention, the hydrocracking process from which the hydrocracked wax is derived can be operated to produce the desired yield and quality of distillate fuel products without trying to regulate the quality of lubricating oil obtainable by the hydrocracking step. For example, a relatively low viscosity index lubricating oil can be recovered from the dewaxing of the heavy hydrocracked oil, and the operation of the hydroisomerization step applied to the wax, involving treatment of a much smaller quantity of material than the hydrocracking step, can be controlled to produce a relatively higher viscosity index oil which can be blended with the low viscosity index oil to provide a lube oil of desired intermediate viscosity index.

A hydrocracked wax of low sulfur and nitrogen content is needed for the catalytic hydroisomerization step. However, it is not necessary to control the hydrocracking to get down to any particular low nitrogen content in the heavy hydrocracked oil. The dewaxing can include deoiling of the wax, if necessary, to remove most of the oil containing the nitrogen and sulfur compounds and provide hydrocracked wax of sufficient purity in most instances. Also, the oil to be dewaxed, or the wax, can be further treated to remove nitrogen and sulfur compounds more economically in a separate step as compared to attempting to obtain the required purity directly by hydrocracking. It is necessary, however, that the hydrocracked wax to be catalytically hydroisomerized be derived from hydrocracking of a heavy oil under conditions causing a large hydrogen consumption and substantial conversion

to lower boiling distillates. The wax present in the heavy hydrocracked oil, referred to herein as hydrocracked wax, differs substantially from wax separated by conventional solvent dewaxing of straight run lubricating oil fractions. In particular, the hydrocracked wax is of the micro-crystalline type and includes a much larger proportion of isoparaffins relative to normal paraffins as compared to straight run wax.

The single figure in the attached drawing illustrates schematically flow paths and treating steps which can be used in carrying out the process of this invention. Briefly, as shown in the drawing, a heavy oil feed in line 11 and hydrogen in line 12 pass via line 13 to hydrocracking zone 14 wherein the oil is contacted with a sulfactive hydrocracking catalyst at hydrocracking conditions. At least the hydrocracked oil effluent in line 15 is separated as by distillation in zone 16 to obtain a light fraction in line 17, distillate fuel fractions in lines 18 and 19, and a bottoms hydrocracked fraction in line 20. A portion of the hydrocracked bottoms may be withdrawn through line 21. All or a portion of the hydrocracked bottoms fraction may pass via line 22 to solvent dewaxing zones 23. Alternately, all or a portion of the hydrocracked bottoms may pass via line 24 to further purification treatment such as solvent extraction in zone 25. Where solvent extraction is used, the solvent extract mixture in line 26 is separated in zone 27 into a solvent fraction for reuse in line 28 and an extract fraction in line 29. The solvent treated oil in line 30 then passes to the dewaxing zone 23. From the dewaxing there is obtained a dewaxed hydrocracked oil in line 31 and a hydrocracked wax fraction in line 32. The dewaxed hydrocracked oil of line 31 may be separated as by distillation in zone 33 into fractions such as a light neutral lube oil in line 34, a heavy neutral lube oil in line 35, and a bright stock in line 36 if the original heavy oil feed was sufficiently high boiling, such as a deasphalted residuum. A portion of the hydrocracked wax in line 32 may be withdrawn through line 37, but at least a portion thereof is passed via line 38 and line 40 with hydrogen added via line 39 into hydroisomerization zone 41. In hydroisomerization zone 41 the oil and hydrogen contact an active reforming catalyst at hydroisomerization conditions of elevated temperature and pressure. At least the oil effluent of the hydroisomerization in line 42 is separated as by distillation in zone 43 to obtain a light fraction in line 44, a distillate fuel fraction in line 45, and an isomerized bottoms fraction in line 46. All or a portion of the waxy isomerized oil in line 46 may be passed via line 47 to the solvent dewaxing zone 23. Alternately, all or a portion of the waxy isomerized oil may pass via line 48 to separate solvent dewaxing zone 49. From the dewaxing zone 49 there is obtained a dewaxed isomerized oil in line 50 and an isomerized wax fraction in line 51. The dewaxed isomerized oil may be separated as by distillation in zone 52 to obtain fractions such as a light neutral lube oil in line 53, a heavy neutral lube oil in line 54, and a bright stock in line 55. All or a portion of the isomerized wax fraction of line 51 may be withdrawn through line 56. All or a portion may instead be recycled via line 57 to the hydroisomerization zone 41.

More specifically, the heavy oil feed treated in accordance with the invention is a high pour point heavy oil boiling in the lubricating oil range, which must boil mostly above 700° F. More desirably, the oil feed boils mostly above 800° F. and at least partly above 900° F. A preferred feed is at least as heavy as a straight run vacuum gas oil, and the single most preferred feed is a deasphalted residual oil. The oil is required to be nonasphaltic because the asphaltenes, being polynuclear aromatic-type compounds, interfere with the conversion of paraffins in the process of the invention and also tend to rapidly deactivate the catalysts used. The deasphalting treatment applied in preparing the preferred feed may be the type of deasphalting used in preparing heavy catalytic cracked feedstocks, i.e., treatment with a light hydrocarbon solvent such as

propane, butane, pentane, or mixtures thereof, at or near the critical point of the solvent. The treatment may be such as to recover as feed the entire so-called maltene fraction, comprising oil and resins, rejecting only the asphaltenes. The deasphalted oil feed treated in accordance with the invention will have a high pour point of above +35° F., and more usually of at least 50° F. Thus, a deasphalted oil feed will contain sufficient high melting paraffins such that at least about 10 weight percent of the feed would have to be separated as wax to obtain a pour point of 0° F. by known solvent dewaxing methods.

In the hydrocracking step of the present invention the heavy oil feed and hydrogen are passed through a reaction zone to contact therein a sulfactive hydrocracking catalyst at elevated temperature and pressure at a space velocity providing sufficient contacting time to accomplish the desired conversion. Conditions used include temperatures of 650–900° F., more desirably 700–850° F., and pressure of at least about 1000 p.s.i.g., which may range upwards of 5000 p.s.i.g., the preferred range being 1500–4000 p.s.i.g. The throughput of hydrogen-rich gas, which may be recycled, should be at least 1,000 s.c.f./bbl. of feed, more usually 2,000–20,000 s.c.f./bbl. The space velocity is generally in the range 0.2–10 volumes of oil per volume of catalyst per hour (LHSV), usually 0.3–3 LHSV.

The catalyst used in the hydrocracking may be of the sulfactive hydrogenation type commonly used for desulfurization and denitrification. Suitable catalysts include combinations of the Group VI and Group VIII metals, oxides, or sulfides, associated with porous refractory oxide carriers. Most suitable metals are nickel or cobalt in combination with molybdenum or tungsten, as sulfides. The refractory oxide may be alumina, but usually, to provide more hydrocracking activity, there is employed a combination of alumina with silica, magnesia, titania, and like materials, or combinations of such other oxides, for example silica-magnesia. Such catalysts can be prepared in a variety of ways, including preparing the porous carrier first and then impregnating it with solutions of the metal compounds which are later converted to metal oxides by calcining. Particularly good catalysts for use in the hydrocracking step can be prepared by coprecipitation or cogelation techniques wherein all of the components are initially supplied as dissolved compounds in aqueous solutions, and coprecipitated together. The conditions in the hydrocracking step may be such as to substantially eliminate organic sulfur compounds by conversion to H₂S and to substantially eliminate organic nitrogen compounds by conversion to NH₃. The nitrogen conversion is the most difficult to accomplish, and accordingly if conditions are sufficiently severe to reduce the organic nitrogen content to about 10 p.p.m. or lower, the organic sulfur concentration will also have been reduced to about 50 parts per million or lower unless the impure oil feed has an unusually high sulfur content, and a substantial portion, at least about 30 volume percent, of the oil will be hydrocracked to distillates boiling below 900° F.

In the present invention the hydrocracking step need not be regulated to obtain a particular low nitrogen or sulfur concentration in the hydrocracked lubricating oil boiling range fraction produced. Instead, the hydrocracking operation may be, and preferably is, regulated with reference to achieving a desired degree of hydrocracking conversion to distillate fuels. Thus, the operation can be controlled to obtain a desired API gravity in the whole liquid effluent of the hydrocracking which is higher than the API gravity of the heavy oil feed by a predetermined amount. Adjustment of the operating conditions with time onstream to compensate for gradual catalyst aging can be with reference to maintaining the desired product gravity, in which case the organic nitrogen and sulfur concentrations in the hydrocracked lubricating oil fraction produced may gradually increase with time onstream if

the catalyst activity for desulfurization and/or denitri-
fication declines more rapidly than the catalyst activity
for hydrocracking. Since the attaining of the desired re-
sults in the hydroisomerization of wax separated from
the hydrocracked lubricating oil boiling range fraction de-
pends in part on the wax having properties peculiar to a
hydrocracked wax fraction, it appears important that
there be substantial hydrocracking and hydrogen con-
sumption in the hydrocracking step. It appears that at least
about 20 percent conversion of the feed to distillates lower
boiling than the feed is needed to obtain the desired wax
properties. With residual oil feeds conversion should be
at least 30 volume percent to distillates boiling below
900° F. and may range upwards of 80 percent. The con-
version is accompanied by the consumption of substan-
tial amounts of hydrogen, amounting usually to above
500 standard cubic feet per barrel of oil and usually 750
s.c.f./bbl. or more.

Various forms of apparatus and manipulative tech-
niques which can be used in carrying out the hydro-
cracking step are well known in the art, and accordingly
no particular equipment arrangement is specified in the
hydrocracking step of the attached drawing. Most con-
veniently, the heavy oil and hydrogen-rich gas are passed
together downward through fixed beds of catalyst par-
ticles in a high pressure reactor at the reaction condi-
tions, the effluent is cooled to separate the normally liq-
uid portion of the oil from hydrogen-rich gas which is
recirculated, and the liquid oil portion represented by line
15 of the drawing is fractionated into various streams as
shown by zone 16. Distillate fuels produced boiling en-
tirely below the lubricating oil boiling range, i.e. below
about 650–750° F., are separated from a higher boiling
hydrocracked lubricating oil boiling range fraction, i.e.
boiling entirely above about 650–750° F. In accordance
with the invention at least a portion of such a lubricating
oil boiling range hydrocracked fraction is dewaxed to
obtain a hydrocracked wax fraction for subsequent treat-
ing in the process.

The dewaxing involves physically separating wax from
the oil, which may be done by a variety of known proce-
dures. Thus, the oils may be cooled to a low tempera-
ture sufficient to crystallize out the wax, and the wax can
then be physically separated by filtration, centrifugation,
or like methods. More commonly, solvent dewaxing is
employed wherein a solvent such as a mixture of methyl-
ethyl ketone and benzene is added, which preferentially
dissolves the nonwaxy hydrocarbons and lowers the oil
viscosity without appreciably lowering the crystallization
temperature of the wax. Other methods involving form-
ing complexes with the wax molecules, such as in the
urea adduction process, can also be used. In general, the
dewaxing is regulated to obtain a specified pour point in
the dewaxed oil usually of 20° F. or lower.

The dewaxed oil, in line 31 of the drawing, is usually
separated by vacuum distillation as in zone 33 into var-
ious grades of lubricating oil on the basis of viscosity
and boiling range. Thus, there may be obtained for ex-
ample in line 34 a light neutral lube oil base stock having
a viscosity of 150 SSU at 100° F., in line 35 a heavy
neutral with a viscosity of 380 SSU at 100° F., and in
line 36 a bright stock having a viscosity of 120 SSU
at 210° F. In some cases it may be desirable to separate
the broad boiling range hydrocracked lubricating oil frac-
tion into the various viscosity grades prior to dewaxing
if it is found advantageous to use different dewaxing
conditions to obtain the desired pour points. Lubricating
oil produced by either method may have a viscosity in-
dex ranging from low to high, depending on the hydro-
cracking conditions used, and may require further treat-
ment to improve color and stability, the hydrocracking
step not having been controlled with reference to obtain-
ing particular lubricating oil properties.

The hydrocracked wax of line 32 may comprise the so-
called "slack wax" containing entrained oil first separated

by filtration in the dewaxing of the oil, if the hydro-
cracking of the heavy oil feed was carried out at condi-
tions sufficiently eliminating organic nitrogen and sulfur
compounds from the oil such that the small amount re-
maining in the oil entrained with the slack wax does
not provide a nitrogen content above 10 p.p.m. If the
slack wax contains above about 10 p.p.m. nitrogen, or
above about 50 p.p.m. sulfur, it should be deoiled to re-
move the oil, which contains most of the organic sulfur
and nitrogen compounds, if this will provide a sufficiently
low concentration of these contaminants. In cases where
the heavy oil feed was highly contaminated with nitrogen
and/or sulfur and the hydrocracking conversion did not
sufficiently eliminate such compounds, it will be necessary
to further eliminate them from the wax. For example, a
portion of the waxy hydrocracked oil boiling in the lubri-
cating oil range, in line 24, may be treated with an acid
solvent such as sulfuric acid or HF in zone 25 to extract
the organic nitrogen compounds therefrom. Where HF is
used, the acid-oil sludge in line 26 may be separated into
a reusable HF fraction in line 28 and an extract oil frac-
tion rich in sulfur and nitrogen compounds in line 29,
which is withdrawn. Such a treatment is preferably ap-
plied to the portion of the whole hydrocracked bottoms
from which the hydrocracked wax and hydrocracked lubri-
cating oil are to be separated, as it also improves the
quality of the lubricating oil fraction besides purifying
the wax fraction.

A portion of the clean hydrocracked wax in line 32
may be withdrawn through line 37 if, for example, the
amount of hydrocracked lubricating oil of relatively low
viscosity index which is salable substantially exceeds the
need, either directly or as a blending stock, for higher
viscosity index lubricating oil which can be produced
from the hydrocracked wax by the subsequent hydro-
isomerization. At least a portion of the hydrocracked
wax is hydroisomerized in the hydroisomerization zone
to produce high viscosity index lubricating oil. In the hy-
droisomerization zone the hydrocracked wax is contacted
with a naphtha reforming catalyst at conditions including
temperatures of 700–900° F., preferably 750–850° F.;
pressures of 500–5000 p.s.i.g., more usually 1000–3000
p.s.i.g.; hydrogen-rich gas throughput rates greater than
1,000 standard cubic feet per barrel of oil, generally 2,000–
20,000 s.c.f./bbl.; and contact times in terms of liquid
hourly space velocity of from 0.2–10, preferably 0.3–3
LHSV. The conditions are such that at least about 10
weight percent of the wax entering the hydroisomeriza-
tion reaction zone is hydrocracked to lower boiling distil-
lates. It is desirable to minimize hydrocracking and to
favor hydroisomerization to produce high viscosity index
lubricating oil without unduly lowering the viscosity, but
it appears desirable at least with wax derived from residual
oil feeds that the conversion be at least about 20 percent
to distillates boiling below 750° F. to obtain a high per
pass yield of lubricating oil after dewaxing. If it is de-
sired to dispense with solvent dewaxing of the hydroisom-
erized oil produced from the hydrocracked wax, sub-
stantially more severe conditions with attendant hydro-
cracking conversion are needed.

The catalyst employed in the hydroisomerization zone
is described as a naphtha reforming catalyst, which typi-
cally comprises a Group VI metal oxide or a Group VIII
metal hydrogenation-dehydrogenation component, desir-
ably a noble metal, preferably platinum or palladium,
associated with a porous refractory oxide carrier such
as alumina, and which may be moderately acidic or acidif-
ied with a halide. Thus, a typical preferred catalyst com-
prises essentially alumina promoted with a small amount,
0.1–2 percent, of platinum metal and a small amount,
less than 1 percent, of chloride and/or fluoride. This in-
cludes well-known platinum reforming catalysts, but their
action is quite different at the conditions used in the hy-
droisomerization zone. There is a net consumption of hy-
drogen, and instead of forming aromatics from naph-
thenes, the essential reaction occurring appears to be one

of isomerizing moderately branched isoparaffins to highly branched isoparaffins. The reforming catalyst is an active isomerization catalyst. Nitrogen and sulfur compounds may deactivate such a catalyst, and accordingly these hetero-organic compounds are substantially excluded from the hydrocracked wax feed. Instead of pure alumina or halided alumina as the carrier or support, there may be used a moderately acidic alumina-silica cogel or coprecipitate containing more alumina than silica. For example, good results have been obtained using a 2 percent palladium catalyst on 82 percent alumina-18 percent silica. Other analogous carriers and supports suitable for use will suggest themselves to those skilled in the art. The silica-alumina materials containing more silica than alumina, such as active cracking catalysts, do not appear to be good supports for the catalysts because they are too strongly acidic and adversely affect selectivity for the isomerization of isoparaffins.

Good results have been obtained in the hydroisomerization step using a platinum-alumina reforming catalyst containing only a small amount of halides, from 0 to 1 weight percent total. The known noble metal isomerization catalysts containing upwards of 2 weight percent halide appear to be too acidic and have low selectivity at the conditions employed within the process of this invention, accomplishing less isomerization and more hydrocracking and tending to become deactivated more rapidly. Improved results are obtained if the platinum reforming catalysts are prerduced before use in the hydroisomerization, which can be done by flowing hydrogen through the catalyst bed at 700–1100° F., especially at about 1000° F., for a few hours. Such a hydrogen treatment can also be used intermittently in the process to extend the catalysts' active life.

To improve selectivity for hydroisomerization in hydroisomerization zone 41, there may be incorporated a prehydrogenation step in the manner specified in the aforementioned copending application Ser. No. 548,075. Similarly, to improve the quality of the isomerized lubricating oil and isomerized wax produced, there may be incorporated a post-hydrogenation step at below 600° F. following the hydroisomerization.

The contacting of the hydrocracked wax and hydrogen with the hydroisomerization catalyst may be carried out manipulatively in the manners previously described with respect to the hydrocracking step. In a similar manner, there is obtained a liquid oil effluent of the hydroisomerization zone in line 42, which is distilled in facilities 43 to remove the distillate fuel fractions produced boiling below about 650–750° F., and to recover an isomerized lubricating oil boiling range fraction in line 46, i.e. boiling entirely above about 650–750° F. This oil is then dewaxed to recover dewaxed isomerized lubricating oil and an isomerized wax fraction.

The dewaxing of the isomerized lubricating oil boiling range fraction may be carried out in the same manner as used for dewaxing the hydrocracked lubricating oil boiling range fraction. In fact, all or a portion of the isomerized lubricating oil boiling range fraction in line 46 may be passed via line 47 for dewaxing in admixture with all or a portion of the hydrocracked lubricating oil fraction in dewaxing zone 23. The wax obtained in line 32 then may comprise a mixture of hydrocracked wax and isomerized wax, and the properties including viscosity index of the lubricating oil fractions obtained by distillation of the dewaxed oil will be upgraded due to the inclusion therein of the dewaxed isomerized oil. Preferably, at least a portion of the isomerized lubricating oil boiling range fraction is separately dewaxed by passing through line 48 to dewaxing zone 49 in order to recover a dewaxed isomerized oil of ultrahigh viscosity index. The dewaxing is controlled with reference to the pour point desired in the product lubricating oils, and there is thus obtained isomerized wax which can be withdrawn as a product wholly or in part, or recycled wholly or in part

to the hydroisomerization reaction zone. Recycling of at least a portion of the isomerized wax to the hydroisomerization zone, controlling the relative proportions of fresh hydrocracked wax feed and recycled isomerized wax, can provide a method of adjusting the VI of the dewaxed isomerized lube oil fraction, for example to insure reaching an ultrahigh VI of at least 130.

The dewaxed isomerized oil may be separated as by distillation into various grades of lubricating oil on the basis of viscosity and boiling range. The dewaxed isomerized lubricating oil fractions so obtained characteristically have much higher viscosity index than the dewaxed hydrocracked lubricating oils, but it is found that appropriate fractions of the isomerized lube oil and the hydrocracked lube oil can be blended to obtain nearly any desired intermediate combinations of viscosity and viscosity index. Also, the isomerized lube oil can be blended with straight run lube oil fractions to obtain upgraded products.

In the marketing of lubricating oils, it is frequently desired to offer a slate of oils in various viscosity ranges having the same viscosity index, for example to offer a 120 neutral, a 400 neutral, and a 120 bright stock all having a viscosity index of 110. Such a situation is rarely obtainable directly by the hydrocracking, as it is more frequently found that the lower viscosity light lubricating oil produced has a lower viscosity index than the heavier high boiling lubricating oil fraction, or vice versa. By the present invention it has been found possible to produce a slate of lubricating oils of a constant viscosity index in the various viscosity grades. Thus, in cases where one or more of the hydrocracked dewaxed lube oil fractions if recovered separately would have too low a viscosity index to be readily salable, a portion of the isomerized lubricating oil boiling range fraction may be dewaxed in admixture with the hydrocracked lubricating oil fraction sufficient to provide a desired minimum viscosity index in the resulting blend of dewaxed hydrocracked and isomerized oil. Another portion of the isomerized lubricating oil boiling range fraction may be dewaxed separately to obtain an ultrahigh viscosity index dewaxed oil, and a portion of the dewaxed isomerized oil may be blended with a portion of the combined dewaxed isomerized and hydrocracked oil, thereby providing a minimum viscosity index product, an intermediate viscosity index product, and a high viscosity index product.

The possibility of distilling the hydrocracked lubricating oil boiling range fraction and the isomerized lubricating oil boiling range fraction prior to solvent dewaxing the resulting cuts separately has already been mentioned. In this context obviously portions of one or more distillation cuts from the isomerized lubricating oil fraction could then be blended with corresponding distillation cuts of the hydrocracked lubricating oil fraction for dewaxing in admixture. The possibility of combining the entire liquid oil effluent of the hydroisomerization zone in line 42 with the entire liquid oil effluent of the hydrocracking zone 14 in line 15 for distillation in common facilities to recover a mixture of hydrocracked and isomerized lubricating oil boiling range bottoms, has also been considered. This is feasible only if the entire bottoms fraction, or substantially all of it, would be dewaxed for recovery of lubricating oil fractions. If a substantial portion of the hydrocracked lubricating oil boiling range fraction is withdrawn as by line 21 of the drawing, there would be substantial loss of the hydroisomerized oil therein.

The following example is illustrative of the practice of the invention and further shows the unusual nature of the products obtainable thereby.

Example

From propane-butane deasphalting of vacuum residua of mixed crude oils there was obtained a deasphalted residual oil of 16° API gravity, containing 6000 p.p.m. nitrogen and 1.2 weight percent sulfur with a pour point of

+105° F. Over 90 percent of the oil boiled above 800° F. and over 80 percent of the oil boiled above 900° F. This oil was hydrocracked severely as needed to obtain a gravity of 34° API in the whole normally liquid oil effluent

Table II presents inspections of the deasphalted oil, the hydrocracked oil, the hydrocracked slack wax separated from the hydrocracked oil, the hydroisomerized oil, and the isomerized wax separated from the isomerized oil.

TABLE II

	Gravity, ° API	Weight Percent			
		Below 750° F.	750- 900° F.	900- 1,000° F.	Above 1,000° F.
Deasphalted Oil Fed to Hydrocracker	16	2	18	20	60
Hydrocracked Oil from Hydrocracker	34	60	15	15	10
Slack Wax from Hydrocracked Oil	35.2		15.7	13.9	65.4
Hydroisomerized Oil After Hydrogenation	40.5	28.7	34.2	16.6	21.4
Hydroisomerized Wax		6.3	26.0	21.9	45.8

by contacting with a 15% nickel sulfide-20% tungsten sulfide (60% alumina-40% silica) catalyst at 815° F., 2400 p.s.i.g., 0.67 LHSV, with about 5,000 s.c.f. H₂/bbl. The effluent oil was freed of NH₃ and H₂S and distilled to recover a distillate fraction and a bottoms fraction, the latter boiling entirely above 750° F. and amounting to 40 percent yield from the deasphalted oil. The bottoms fraction had a pour point of +105° F. and contained 20 p.p.m. nitrogen. This lubricating oil boiling range hydrocracked bottoms fraction was dewaxed to a pour point of 0° F. using a methylethyl ketone/benzene solvent. The slack wax thereby obtained had a gravity of 35.2° API and contained 4 p.p.m. nitrogen and 15 p.p.m. sulfur. This slack wax was hydroisomerized by contacting with a 0.5 weight percent platinum on alumina catalyst at 770° F., 2600 p.s.i.g., 0.35 LHSV, with 10,000 s.c.f. H₂/bbl. In the same reactor, the effluent of the hydroisomerization after contacting the platinum catalyst is then passed through a bed of 1 percent palladium on 80% alumina-20% silica catalyst at a lower temperature of 500° F. and higher space velocity of 0.7 LHSV as a mild finishing hydrogenation treatment. Conditions in the hydroisomerization step were selected so as to obtain constant gravity in the product of 40° API. This corresponded to conversion of from 80 to 86 percent of the hydrocracked wax to nonwaxy hydrocarbons. The waxy oil from the hydroisomerization and hydrogenation treatment was distilled to remove the approximately 25-30 volume percent distillates boiling below 750° F., and the isomerized lubricating oil boiling range fraction boiling above 750° F. was then solvent dewaxed to a pour point of -5° F. using a methylethyl ketone/benzene solvent. The dewaxed isomerized oil was then distilled into several narrow boiling range cuts for determination of lubricating oil inspections. The conditions used in the example and the results obtained are summarized in the following tables.

Table I presents the conditions used in the hydrocracking of the deasphalted oil and in the hydroisomerization and hydrogenation of the hydrocracked wax.

TABLE I

	Hydrocracking of Deasphalted Oil	Hydroisomerization of Hydrocracked Wax	Hydrogenation Finishing
Catalyst	NiS=WS ₂ /SiO ₂ -Al ₂ O ₃	Pt/Al ₂ O ₃	Pd/Al ₂ O ₃ -SiO ₂
Temperature, ° F.	815	770	500
Pressure, p.s.i.g.	2,400	2,600	2,600
Space Rate, LHSV	0.67	0.35	0.7
H ₂ Gas, s.c.f./bbl.	6,000-10,000	10,000	10,000
Gravity, ° API:			
Feed	16	35.2	40
Whole Product	34	40	40

Table III presents inspections of typical dewaxed lubricating oil fractions A and C recovered from the hydrocracked oil, typical dewaxed isomerized lube oil fractions B, D, and F recovered from the isomerized oil, and representative blended oils obtainable therefrom. Also shown is a hydrocracked lube oil, E, obtained by separately hydrocracking a heavy overhead gas oil from a residuum stripping operation, having a very low VI, and the improved VI blend obtainable using the isomerized oil.

TABLE III

	Dewaxed Hydrocracked Lube Oil	Dewaxed Hydroisomerized Lube Oil	Blended Lube Oil
	A	B	3 vols. A plus 1 vol. B
Viscosity, SSU at—			
100° F.	144	81.5	120
210° F.	42.3	38.5	40
Viscosity Index	85	135	99
	C	D	9 vols. C plus 1 vol. D
Viscosity, SSU at—			
100° F.	436	184.6	363.9
210° F.	59.9	48.4	58.4
Viscosity Index	97	133	101
	E	F	7 vols. E plus 3 vols. F
Viscosity, SSU at—			
100° F.	120.7	103.8	118.4
210° F.	40.88	41.02	40.89
Viscosity Index	67.5	140	98.5
Oxidation Stability, Hours	5.8	11.6	7.65

Table IV presents additional inspections of dewaxed hydroisomerized lube oils obtained from the hydroisomerization of hydrocracked wax in the foregoing example, prepared by blending appropriate cuts of the dewaxed oils boiling above 750° F. to obtain fractions having specified viscosities of 70, 100, and 200 SSU at 100° F.

TABLE IV

	750-800	800-875	875-1,000	1,000+
Boiling Range, ° F.	41.1	39.6	37.8	35.9
Gravity, ° API	71.9	103.8	206.7	659
Viscosity at 100° F.	37.24	41.02	50.4	85.8
Viscosity at 210° F.	130	140	132	124
Viscosity Index, "VI"	124	137	142	140
Viscosity Index, Extended, "VIE"	-10			-5
Pour Point, ° F.	+6			+4
Cloud Point, ° F.	236	246	262	292
Aniline Point, ° F.	12.2	11.6	11.2	11.2
Oxidation Stability, Hrs.	>100	>100	>100	>100
UV Lamp Test, Hr.				

In the above Table IV, "VIE" refers to viscosity index determined in the extended range, above 100, by the new method of ASTM D-2270. This is considered to indicate more accurately the suitability of the oils as ultrahigh VI multi-grade base oils as compared to the old method of ASTM D-567, reported as "VI." Particularly to be noted in the above data are the very high viscosity indices in the isomerized lubricating oils and the nearly constant viscosity index of about 140 VIE in all the isomerized lube oil cuts boiling above 800° F. The pour points and cloud points are good and the oils have excellent oxidation stability and ultraviolet light stability. In the foregoing Tables III and IV, Oxidation Stability is a measure of additive response, and refers to the time required for a given volume of oil to absorb one liter of oxygen from air bubbled through it at 340° F., when the oil contains both a commercial oxidation inhibitor and oxidation catalyzers. A time of seven hours is considered excellent. The UV Lamp Test is a controlled sunlight simulator measuring the time for formation of a haze, cloud, or sediment in the oil, as is, as an indication of light stability. A value of 20 hours is considered very good in a typical commercial mid-content 150 neutral lube oil.

In a large installation processing 25,000 barrels of the deasphalted oil feed as in the foregoing example, modified by including acid extraction of nitrogen compounds and recycling of isomerized wax, there would be obtained from the hydrocracking step about 18,000 barrels per day of distillate fuels and 8,000 barrels per day of hydrocracked oil boiling above 750° F. About 4,000 barrels of this oil is withdrawn and passed to another hydrocracker, or a catalytic cracker, or a thermal cracker, or blended into heavy fuel oil. The remaining 4,000 barrels is treated with hydrofluoric acid to lower the nitrogen content of the oil, leaving about 3,900 barrels of clean waxy oil. Solvent dewaxing yields 1,200 barrels of slack wax, and 2,700 barrels of dewaxed oil which is separated into 900 barrels of 95 VI light neutral, 1,200 barrels of 98 VI heavy neutral, and 600 barrels of 100 VI bright stock. The 1,200 barrels of hydrocracked slack wax is catalytically isomerized with 210 barrels of recycle isomerized wax, distilled and dewaxed, yielding 430 barrels of distillates boiling below 750° F., 770 barrels of dewaxed isomerized 130-140 VI lubricating oil, and the 210 barrels of isomerized wax which is recycled. The dewaxed isomerized oils comprise 230 barrels of 100 SSU neutral, 290 barrels of 200 SSU neutral, and 250 barrels of 85 bright stock.

When the catalytic hydrocracking is operated at higher severity to obtain greater yield of distillate fuels, a higher viscosity index is obtained in the hydrocracked lubricating oil boiling range fractions and the hydrocracked wax is more amenable to treatment in the hydroisomerization zone. Accordingly, less severe conditions can be used in the hydroisomerization to obtain a high yield of isomerized lubricating oil with less production of distillate fuels therein.

Various alternatives and obvious modifications in the process of the invention as exemplified herein will be ap-

parent to those skilled in the art, and accordingly the appended claims are intended to include all such modifications as are embraced thereby.

We claim:

1. Process for producing lube oil which comprises: hydrocracking a deasphalted petroleum residuum boiling mostly above 800° F. and at least partially above 900° F. by contacting said residuum and hydrogen with a sulfactive hydrocracking catalyst in a hydrocracking zone under conditions to convert at least 20 percent of said residuum to distillates boiling lower than the feed and at least 30 percent of the portion of said residuum boiling above 900° to distillates boiling below 900° and with a hydrogen consumption of at least 500 s.c.f. per barrel of residuum; separating the oil effluent from said hydrocracking zone into fractions including a distillate fuel and a hydrocracked lube oil boiling range fraction; dewaxing a said hydrocracked lube oil boiling range fraction, thereby obtaining a hydrocracked wax fraction of low nitrogen content; hydroisomerizing at least a portion of said hydrocracked wax fraction by contacting said wax fraction with an active reforming catalyst containing 0-2 weight percent halide in a hydroisomerization zone under conditions to convert at least 20 percent of said wax fraction to distillates boiling below 750° F.; and separating the oil effluent from said hydroisomerization zone into fractions including a distillate fuel and a hydroisomerized lube oil boiling range fraction.

2. The process of claim 1 wherein said dewaxing is accomplished by a conventional solvent dewaxing procedure.

3. Process according to claim 1 wherein at least a portion of a said isomerized lube oil boiling range fraction is dewaxed in admixture with at least a portion of a said hydrocracked lube oil boiling range fraction.

4. Process according to claim 1 wherein said hydrocracked lube oil boiling range fraction is further treated to remove organic nitrogen compounds before dewaxing said fraction.

5. Process according to claim 1 wherein said reforming catalyst comprises platinum supported on alumina and contains no more than 1 weight percent halide.

6. Process according to claim 5 wherein said hydrocracked lube oil boiling range fraction is further treated to remove organic nitrogen compounds prior to dewaxing said fraction, whereby said hydrocracked wax fraction contains less than 10 p.p.m. nitrogen.

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Disclaimer

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Hereby enters this disclaimer to claim 6 of said patent.
[*Official Gazette April 29, 1969.*]