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(71) Applicant(s)
Chevron U.S.A. Inc.

(72) Inventor(s)
James N. Ziemer; Dennis J. O'Rear; Donald S. Santilli

(74) Agent/Attorney
DAVIES COLLISON CAVE,1 Little Collins Street,MELBOURNE VIC 3000

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(71) Applicant: CHEVRON U.S.A. INC. [US/US]; 555 Market Street, San Francisco, CA 94105 (US).

(72) Inventors: ZIEMER, James, N.; 987 Calle Verde, Martinez, CA 94553 (US). O'REAR, Dennis, J.; 40 Upland Drive, Petaluma, CA 94952 (US). SANTILLI, Donald, S.; 260 Piedmont Road, Larkspur, CA 94939 (US).

(74) Agents: KLAASSEN, Alan, W. et al.; Chevron Corporation, Law Dept., P.O. Box 7141, San Francisco, CA 94120-7141 (US).

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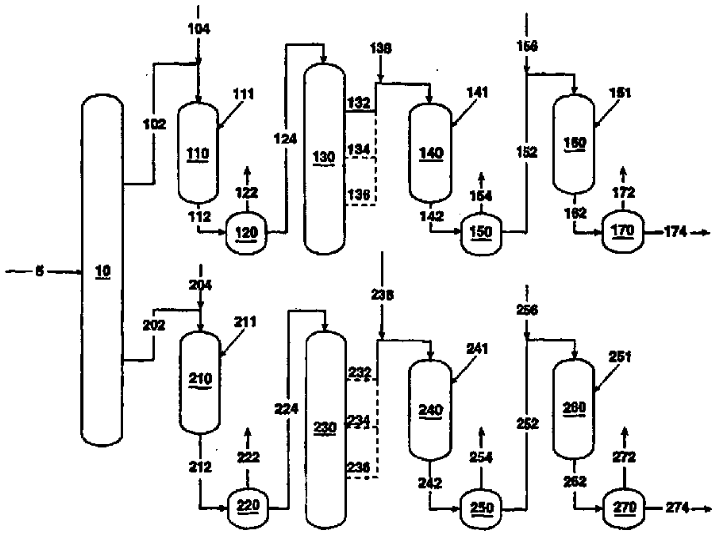

(57) Abstract

The invention provides for a layered catalyst system to effectively optimize and tailor the hydrocarbon processing of a hydrocarbon stream to maximize yield in the creation of a lube oil base stock process. In particular, the invention includes the surprising discovery that a layer of a first catalyst can be placed in contact and on top of the isodewaxing catalyst layer to achieve higher yields, increased catalyst lifetime and avoid VI reduction.

LAYERED CATALYST SYSTEM FOR LUBE OIL HYDROCONVERSION

FIELD OF THE INVENTION

This invention relates to catalytic hydroconversion of crude petroleum. More specifically, this invention relates to a layered catalyst system in lube oil based stock production.

BACKGROUND OF THE INVENTION

Non-synthetic lubricating oils are a major amount of a petroleum base oil and the additive package. The base oils are refined from crude oil through a plurality of processes such as distillation, hydrocracking, hydroprocessing, catalytic dewaxing, and the like. A pre-base oil from these processes needs to be further processed to create the finished base oil. In creating the base oil the refiner desires to obtain the highest possible yield while preserving the VI of the oil. Maintaining a high yield with a waxy crude oil is a particularly difficult problem. An approach is to solvent dewax the waxy fraction of the oil. However, this tends to lower yields at a given VI. This yield issue was addressed with catalytic dewaxing following the solvent extraction to create a lube oil base stock from a waxy base oil. However, the dewaxing step which removes the last traces of wax which effects pore point and cloud point causes a yield penalty. Thus, it would be highly desirable to have a process which optimizes the yield at a given VI.

In lube oil fabrication, the catalytic dewaxing or hydrotreating, or hydrocracking, is carried out in a reactor with discrete zones or discrete reactors. This procedure is costly, and adds to the complexity of the overall process or the internals of a given reactor. Thus, it would be highly desirable to have a catalyst layering system wherein one type or kind of catalyst is layered on top of a subsequent catalyst. Such an arrangement provides for faster sequential processing as well as more compact designs and simplified processes and reactor internals.

SUMMARY OF THE INVENTION

According to the present invention there is provided a refinery operation for producing a dewaxed oil and having at least one dewaxing reaction zone containing an isodewaxing catalyst, for reducing the pour point of a waxy oil, the process comprising:

a. including in the at least one dewaxing reaction zone a second catalyst layer on top of the isodewaxing catalyst in said reactor, the catalyst in said second catalyst layer selected from the group consisting of noble metal amorphous catalysts, noble metal hydrocracking catalysts or combinations thereof;

b. contacting said waxy oil with hydrogen over said second catalyst layer;

c. contacting the entire effluent from the second catalyst layer over the isodewaxing catalyst; and

d. recovering a dewaxed oil having a pour point which is reduced relative to that of the waxy oil.

There is also provided an integrated process for preparing a multiplicity of lubricating oil base stocks, which are differentiated from each other by viscosity, wherein the process of the immediately preceding paragraph is conducted simultaneously in at least two separate and parallel trains.

The present invention is directed to a process for preparing a lubricating oil base stock comprising dewaxing a waxy hydrocracked oil using a hydroisomerization dewaxing catalyst.

The present invention is further directed to a dewaxing process and a layered dewaxing catalyst system for preparing a lubricating oil base stock. The layered catalyst system comprises a catalyst having catalytic properties for hydrotreating reactions, including aromatic saturation and viscosity index increase, with minimum molecular weight reduction, and an isodewaxing catalyst having catalytic properties for pour point reduction by wax hydroisomerization.

More specifically, the invention provides for a layered catalyst system wherein a first layer of a catalyst pretreats the lube oil base stock while a second layer completes the dewaxing of a waxy feed to maintain high yields without VI penalties along with the ability to use higher catalytically active catalysts to either speed the process or run the reactor at energy saving lower temperatures. Thus, in a lube oil hydrocarbon processing process involving sequential steps of hydrotreating to remove heteroatoms and at least a portion of the aromatics followed by hydrotreating/hydrocracking for aromatic saturation, isomerization and VI upgrade, followed by hydroisomerization for wax removal and finally hydrofinishing for lube oil stability, the improved process for second stage hydrocracking which comprises:

a first catalyst in a reactor and on which a second catalyst is layered, said first catalyst comprising an isodewaxing catalyst; and

a second catalyst layer on top of a first catalyst layer in said reactor said second catalyst selected from the group consisting of noble metal amorphous catalysts, noble metal hydrocracking catalysts, or combinations thereof and wherein said first and second catalyst combination achieves a longer catalyst life with higher activity and higher yields at a constant VI for the base lube oil fabrication than solely a reactor charged with solely said first catalyst.

In the preferred process, the waxy oil is contacted with hydrogen over a hydrotreating catalyst comprising a noble metal hydrogenation component on an oxide support matrix. The effluent from the hydrotreating catalyst bed is then contacted with the isodewaxing catalyst.

The isodewaxing catalyst of the first layer comprises a medium pore molecular sieve, tailored for high yields of dewaxed oil in comparison to other types of dewaxing catalysts, and having pores of 7.1 Å most preferably 6.5 Å, or less in diameter, having at least one pore diameter greater than or equal to 4.8 Å and having a crystallite size of no more than about 0.5 micron. The catalyst is characterized in that it has sufficient acidity to convert at least 50% of hexadecane at 370°C. and exhibits a 40 or greater isomerization selectivity ratio as defined herein at 96% hexadecane conversion. The catalyst further includes at least one Group VIII metal.

The second catalyst, selected from the group consisting of noble metal amorphous catalysts, noble metal hydrocracking catalysts, or combinations thereof, comprises a noble metal selected from the platinum group metals, including platinum, palladium, rhodium, ruthenium, iridium and rhenium. The preferred platinum group metals are platinum, palladium, or combinations thereof.

Accordingly, in a preferred embodiment, the present process comprises contacting a waxy feedstock which contains less than about 100 ppm sulfur and less than about 50 ppm nitrogen with a hydrotreating catalyst in the presence of hydrogen at aromatics saturation conditions to produce a hydrotreated oil and a gaseous stream; and contacting the hydrotreated oil and the gaseous stream with an isodewaxing catalyst at isomerization conditions to produce a dewaxed oil having a pour point which is reduced relative to the pour point of the waxy feedstock, and wherein the hydrotreating conditions are preselected to maintain the liquid conversion in the hydrotreating reaction zone at less than about 25% by volume.

In a separate embodiment, the present invention is directed to an integrated catalyst system for preparing a lubricating oil base stock. In the integrated process for producing a multiplicity of lubricating oil base stocks from a petroleum feedstock, the process comprises:

a) separating the petroleum feedstock into at least one light distillate stream and at least one heavy distillate stream;

b) producing at least one light lubricating oil base stock in a process comprising:

    i) contacting the at least one light distillate stream with hydrogen in a first hydrocracking reaction zone, at hydrocracking reaction conditions sufficient to remove at least a portion of the sulfur and at least a portion of the nitrogen from the light distillate stream, to produce at least one waxy light oil fraction having a viscosity index which is increased relative to the viscosity index of the light distillate stream;

ii) contacting the at least one waxy light oil fraction with hydrogen in a first dewaxing reaction zone containing a layered catalyst system comprising a first catalyst and on which a second catalyst is layered, the first catalyst comprising an isodewaxing catalyst; and the second catalyst selected from the group consisting of noble metal amorphous catalysts, noble metal hydrocracking catalysts, or combinations thereof; and

iii) contacting at least a portion of the first dewaxing reaction zone effluent in a hydrogenation reaction zone at conditions sufficient to produce a light lubricating oil base stock; and

c) producing at least one heavy lubricating oil base stock in a process comprising:

i) contacting the at least one heavy distillate stream with hydrogen in a second hydrocracking reaction zone at conditions sufficient to remove at least a portion of the sulfur and at least a portion of the nitrogen from the heavy distillate stream to produce at least one waxy heavy oil fraction having a viscosity index which is increased relative to the viscosity index of the heavy distillate stream;

ii) contacting the at least one waxy heavy oil fraction with hydrogen in a second dewaxing reaction zone containing a layered catalyst system comprising a third catalyst and on which a fourth catalyst is layered, the third catalyst comprising an isodewaxing catalyst; and the fourth catalyst selected from the group consisting of noble metal amorphous catalysts, noble metal hydrocracking catalysts, or combinations thereof; and

iii) contacting at least a portion of the second dewaxing reaction zone effluent in a hydrogenation reaction zone at conditions sufficient to produce a heavy lubricating oil base stock,

wherein the process for producing the at least one light lubricating oil base stock and the process for producing the at least one heavy lubricating oil base stock are conducted simultaneously in parallel reaction trains.

An advantage of the present system over conventional catalyst systems is the effectiveness with which the present process may be used to prepare such high quality base oils useful for manufacturing lubricating oils, and particularly with feedstocks which are not conventionally recognized as suitable sources for such base oils.

Among other factors, the present invention is based on the discovery that the performance of an isodewaxing catalyst, which is tailored for high yields of dewaxed oil, is improved if a portion of the isodewaxing catalyst is replaced in the dewaxing reaction zone with a hydrotreating catalyst comprising a noble metal hydrogenation component. The catalytic performance has been found to be particularly improved with a hydrotreating catalyst containing a platinum/palladium alloy hydrogenation component. More specifically, we have discovered, to our surprise, that adding a hydrotreating catalyst layer to the dewaxing reaction zone for aromatic saturation improves catalytic dewaxer operability, reduces the effect of uncontrollable exothermic reactions, and improves the properties of the dewaxed oil. Even more surprising is that including the layer of hydrotreating catalyst in the dewaxing reaction zone permits reducing the severity of the hydrocracking step prior to dewaxing, without affecting the properties of the high quality lubricating oil base stock produced in the process. The improved performance is believed to be due, at least in part, to the hydrotreating catalyst effectively removing sulfur and nitrogen, opening aromatic and cyclic structures, and otherwise increasing the viscosity index of the waxy oil prior to dewaxing, with little or no loss in lube yield.

This invention further stems from the surprising discovery that a catalyst bed in the fabrication of a lube base oil can contain a plurality of different catalysts in regions within the catalyst bed to optimize a final and given base oil product stream. The combination system of the amorphous catalyst noble metal which provides the primary benefits of increased catalyst activity which leads to greater catalyst life whereas the underlying region catalytically dewaxes the waxy portion of the feed to provide both a VI boost and maximum yield to the overall product stream.

IN THE DRAWINGS

Figure 1 is a block diagram of a preferred integrated process of the present invention.

Figure 2 shows the benefit in yield with the present layered dewaxing catalyst system.

Figure 3 shows the benefit in viscosity index with the present layered dewaxing catalyst system.

Figure 4 shows the effect of the layered dewaxing catalyst system on observed catalytic activity.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a layered catalyst for dewaxing a waxy feedstock in the preparation of a lubricating oil base stock. The layered system provides a higher yield of high VI dewaxed oil when compared to conventional dewaxing processes employing a dewaxing catalyst alone. A second catalyst layer, comprising a noble metal hydrogenation component, provides hydrotreating for aromatic saturation and for paraffin hydroisomerization. At least a portion of the effluent from the second catalyst layer is contacted with hydrogen in a first catalyst layer comprising an isodewaxing catalyst, which reduces the pour point of the waxy oil by hydroisomerizing, cracking, and otherwise converting the waxy molecules in the oil to non-waxy forms.

The feedstocks which can be treated in accordance with the present invention include oils which generally have relatively high pour points which it is desired to reduce to relatively low pour points. Such petroleum feedstock suitable for use herein may be selected, for example, from crude oil, petroleum distillates having a normal boiling point above about 100°C, gas oils and vacuum gas oils, residuum fractions from an atmospheric pressure distillation process, solvent-deasphalted petroleum residua, shale oils, cycle oils, petroleum and slack wax, waxy petroleum feedstocks, NAO wax, and waxes produced in chemical plant processes. Straight chain n-paraffins either alone or with only slightly branched chain paraffins having 16 or more carbon atoms are sometimes referred to herein as waxes. Preferred petroleum distillates boil in the normal boiling point range 200°C to 700°C, more preferably in the range 260°C to 650°C. Suitable feedstocks include those heavy distillates normally defined as heavy straight-run gas oils and heavy cracked cycle oils, as well as conventional FCC fed and portions thereof. Cracked stocks may be obtained from thermal or catalytic cracking of various stocks. The feedstock may have been subjected to a hydrotreating and/or hydrocracking process before being supplied to the present process. Alternatively, or in addition, the feedstock may be treated in a solvent extraction process to remove aromatics and sulfur- and nitrogen-containing molecules before being dewaxed.

The typical feedstocks which are advantageously treated in accordance with the present invention will generally have an initial pour point above about 0°C., more usually above about 20°C. The resultant products after the process is completed generally have pour points which fall below -0°C., more preferably below about -10°C.

As used herein, the term "waxy petroleum feedstocks" includes petroleum waxes. The feedstock employed in the process of the invention can be a waxy feed which contains greater than about 50% wax, even greater than about 90% wax. Highly paraffinic feeds having high pour points, generally above about 0°C., more usually above about 10°C. are also suitable for use in the process of the invention. Such a feeds can contain greater than about 70% paraffinic carbon, even greater than about 90% paraffinic carbon.

Exemplary additional suitable feeds for use in the process of the invention include waxy distillate stocks such as gas oils, lubricating oil stocks, synthetic oils and waxes such as those by Fischer-Tropsch synthesis, high pour point polyalphaolefins, foots oils, synthetic waxes such as normal alphaolefin waxes, slack waxes, deoiled waxes and microcrystalline waxes. Foots oil is prepared by separating oil from the wax. The isolated oil is referred to as foots oil.

Slack wax can be obtained from either a hydrocracked lube oil or a solvent refined lube oil. Hydrocracking is preferred because that process can also reduce the nitrogen content to low values. With slack wax derived from solvent refined oils, deoiling can be used to reduce the nitrogen content. Optionally, hydrotreating of the slack wax can be carried out to lower the nitrogen content thereof. Slack waxes possess a very high viscosity index, normally in the range of from 140 to 200, depending on the oil content and the starting material from which the wax has been prepared. Slack waxes are therefore eminently suitable for the preparation of lubricating oils having very high viscosity indices, i.e., from about 120 to about 180.

The layered catalyst comprises a first catalyst in a reactor and on which a second catalyst is layered, said first catalyst comprising an isodewaxing catalyst; and a second catalyst layer on top of a first catalyst layer in said reactor said second catalyst selected from the group consisting of noble metal amorphous catalysts, noble metal hydrocracking catalysts, or combinations thereof. The catalyst layer comprises from about 1 to about 70% by volume of the second catalyst layer and from about 99% to about 30% by volume of the first catalyst layer. From about 5% to about 50% by volume of the second catalyst layer is preferred, and from about 20 to about 30% by volume being most preferred, the remainder being the first catalyst layer.

The layered catalyst useful in the present dewaxing process comprises a hydrotreating catalyst selected from the group consisting of noble metal amorphous catalysts, noble metal hydrocracking catalysts, or combinations thereof. Useful noble metals include platinum, palladium, ruthenium, rhodium, osmium and iridium. While the hydrotreating catalysts utilized in the present invention will contain at least one metal, it is also possible to use combinations of two or more metals or their compounds, such as for example a combination of metals containing both platinum and palladium. A number of methods are known in the art to deposit platinum and palladium metal or their compounds onto the support, such as, for example, by ion exchange, impregnation, coprecipitation, etc.

The hydrotreating catalyst further comprises a matrix material, which is resistant to the temperatures and other conditions employed in the present process. Included in the matrix material is at least one binder, such as naturally occurring clays and inorganic oxides used to improve the crush strength of the catalyst. The oxide matrix material, which includes the binder, is selected from the oxides generally used in the art for preparing catalysts, including silica, alumina, magnesia, zirconia, titania. Clays may also be used. The preferred catalysts employed in the present invention contain a oxide matrix material that is generally prepared from silica-alumina base materials. The distribution of silica and alumina in the oxide matrix material may be either homogeneous or heterogeneous, but is preferably heterogeneous. A preferred form of the oxide matrix material consists of an alumina gel binder in which is dispersed the silica-alumina base material, which form is referred to herein as the "heterogeneous support". The support may also contain refractory materials other than alumina or silica, such as for example other inorganic oxides or clay particles, provided that such material does not adversely affect the hydrotreating activity of the final catalyst. Other inorganic oxides that may be present in the support may include, but are not necessarily limited to, titania, magnesia and zirconia or combinations thereof. Generally, silica-alumina will make up at least 90 weight percent and preferably up to 100 weight percent, of the matrix material exclusive of oxide binder, and the matrix material will comprise from about 5 weight percent to about 70 weight percent binder, and preferably from about 20 weight percent to about 50 weight percent binder. The binder materials may include the oxides of aluminum, silicon, magnesium, germanium, titanium and zirconium. Combinations of such oxides with other oxides are also useful. An alumina binder is preferred. The noble metal amorphous catalyst comprises a noble metal hydrogenation component and an amorphous (i.e. non-crystalline) matrix material. A preferred hydrocracking catalyst which is useful in the present invention is a noble metal catalyst such as a $Pd/SiO_2/Al_2O_3$ catalyst, which is described, for example, is U.S. Patent No. 5,393,408, the specification of which is completely incorporated herein by reference for all purposes.

A particularly preferred hydrotreating catalyst comprises a platinum-palladium alloy and an oxide matrix, wherein the molar ratio of platinum to palladium in the alloy is between about 2.5:1 and about 1:2.5, preferably between about 2:1 and about 1:1 and most preferably the platinum to palladium ratio is 1:1.5. The particularly preferred catalyst exhibits the activity of the palladium based catalyst while maintaining the sulfur tolerance of the normally less reactive platinum based catalyst, thus avoiding the need for higher reaction temperatures, which increase undesirable cracking reactions rates and produce products of low stability. This alloy material is a new catalyst species and different from a mixture of platinum and palladium metals on the catalyst acid support. The catalyst is preferably fabricated in accordance with the teachings of US 5,393,408, the specification of which is completely incorporated herein by reference for all purposes. In addition the complete specification of copendingly filed application entitled "Sulfur Resistant Hydroconversion Catalyst and Hydroprocess of Sulfur-containing Lube Feedstock", and having docket number T-5244A, is completely incorporated herein by reference for all purposes.

The most preferred hydrotreating catalyst has a total pore volume greater than about 0.45 cm^3/g, preferably greater than about 0.55 cm^3/g, with at least about 1%, and preferably at least about 3%, of the total pore volume being in macropores of diameter of greater than about 1000 angstroms, with the minimum amount of macropore volume preferably being greater than 0.07 cm^3/g. As used herein, the term "macroporous" refers to a catalyst having a relatively large amount of pore volume, i.e., at least 1%, in pores of diameter greater than about 1000 Angstroms, with a minimum macropore volume preferably being greater than 0.07 cm^3/g.

Pore size distribution for the catalysts employed in the present invention is determined using mercury intrusion porosimetry as described, for example, in ASTM D4284, "Pore Volume Distribution of Catalysts by Mercury Intrusion Porosimetry." According to this procedure, a catalyst is heated at 450°C in a vacuum for 30 minutes to remove water vapor and other volatiles. A weighed portion of sample (0.3-0.5 g, depending on the total pore volume estimate) is placed in a volume-calibrated sample tube. The tube is filled with mercury and inserted into the pressurization chamber of a Quantachrome Auto-Scan Porosimeter. The pressure in the chamber is increased from 0 to 60,000 psig. As the pressure increases, the volume of mercury in the sample tube appears to decrease as the mercury intrudes into the pores of the sample. Apparent mercury volume is obtained as a function of the applied pressure. Apparent mercury volume and applied pressure are then related to pore volume (V) and pore diameter (D), respectively. Results are reported as plots of pore volume (in cm^3) and cumulative pore volume (cm^3) as a function of pore diameter (in angstroms). Analysis of the data gives the percent macropore volume according to the formula: Percent Macropore Volume = (macropore volume/total pore volume) X 100.

The amount of platinum-palladium alloy placed on the support must be sufficient to act as an effective catalyst in the hydrogenation of the lubricating oil base stock. Generally, the amount of alloy on the support used to catalyze a hydrogenation process within the scope of the present invention will be within the range of from about 0.01 weight percent to about 5 weight percent, preferably the range is from about 0.1 weight percent to about 1 weight percent. Generally, adding greater than about 1 weight percent of the alloy does not significantly improve on the activity of the catalyst and is therefore economically disadvantageous. However, amounts in excess of 1 weight percent are usually not harmful to the performance of the catalyst.

A number of methods are known in the art to deposit platinum and palladium metal or their compounds onto the support, such as, for example, by ion exchange, impregnation, coprecipitation, etc. It has been found that depositing platinum and palladium on the supports used in the catalyst of the present invention is particularly advantageous when using a contacting solution containing active compounds of both platinum and palladium under a controlled pH. The contacting solution preferably will be buffered to maintain a pH within the range of from about 9 to about 10. Values outside of this pH range may be used to deposit platinum and palladium jointly on the support, but the final distribution of the alloy on the support may not be as favorable as those obtained within this pH range.

In addition to the hydrogenation component and matrix material already described, a noble metal hydrocracking catalyst may further comprise an active matrix cracking component, such as one or more molecular sieves, including non-zeolitic molecular sieves and aluminosilicate zeolites, added in some cases to increase the reactivity and/or life of the catalyst. Zeolite-containing hydrotreating catalysts for the present process generally contain between about 0.1 and about 20 weight percent zeolite, and preferably between about 1 and about 10 weight percent zeolite. Preferred zeolites for the hydrotreating catalyst include zeolites Y, X, and ultrastable Y. Particularly preferred are the zeolites having a framework SiO_2/Al_2O_3 ratio of greater than about 10, and preferably greater than about 20. Use of other active materials in association with the zeolite to improve conversion or catalyst selectivity is also within the scope of the present invention. However, while the cracking activity of the hydrotreating catalyst may be further increased by adding a halogen, such as fluorine, to the catalyst, a catalyst which is substantially free of fluorine is preferred.

At least a portion of the effluent from the layer of hydrotreating catalyst in the dewaxing reaction zone is contacted with hydrogen over a catalyst layer comprising an isodewaxing catalyst. The conditions under which the hydrotreating/dewaxing process of the present invention is carried out generally include a temperature which falls within a range from about 550°F. to about 850, preferably from about 600°F. to about 800°F, the pressure ranges from about 15 to about 3500 psig, preferably from about 200 to about 3000 psig, and more preferably from about 1000 to about 3000 psig. The liquid hourly space velocity (LHSV) during contacting is generally from about 0.1 to about 20 hr^{-1}, more preferably from about 0.2 to about 10 hr^{-1}. The contacting is preferably carried out in the presence of hydrogen. The hydrogen to hydrocarbon ratio preferably falls within a range from about 1.0 to about 50 moles H_2 per mole hydrocarbon, more preferably from about 10 to about 30 moles H_2 per more hydrocarbon. As used herein, LHSV is expressed as volumes of oil per hour, per volume of catalyst, in units of hr^{-1}. While minimizing conversion during hydrotreating is desirable during the present hydrotreating process prior to dewaxing, some measure of conversion, of the lubricating oil base stock, for example up to about 25%, may occur. As used herein, the cracking conversion is a measure, in volume percent, of the petroleum feedstock which is converted during hydrotreating into reaction products having a normal boiling point less than a reference temperature T_{ref}, wherein:

$$T_{ref} = T_{50} - 2.5(T_{50} - T_{30}),$$

and wherein T_{50} and T_{30} are equal to the normal boiling point temperature of 50% and 30% by volume, respectively, according to a D2887 simulated distillation, of the petroleum feedstock to the hydrotreating reaction zone

The isodewaxing catalyst comprises a molecular sieve having pores of 7.1 Å, most preferably 6.5. Å, or less in diameter, having at least one pore diameter greater than or equal to 4.8 Å and having a crystallite size of no more than about 0.5 micron. The catalyst is characterized in that it has sufficient acidity to convert at least 50% of hexadecane at 370°C and exhibits a 40 or greater isomerization selectivity ratio as defined herein at 96% hexadecane conversion. The catalyst further includes at least one Group VIII metal. A dewaxing process employing the isodewaxing catalyst is described in U.S. Patent No. 5,282,957, the entire disclosure of which is incorporated herein by reference for all purposes.

The molecular sieve is of the 10- or 12- member ring variety and has a maximum pore diameter of no more than 7.1 Å across. Specific molecular sieves which are useful in the process of the present invention include the zeolites ZSM-12, ZSM-21, ZSM-22, ZSM-23, ZSM-35, ZSM-38, ZSM-48, ZSM-57, offretite, ferrierite, L, SSZ-31, SSZ-32, SSZ-36, SSZ-41 and SUZ-4 and other molecular sieve materials based upon aluminum phosphates such as SAPO-11, SAPO-31, SAPO-41, MAPO-11 and MAPO-31. Such molecular sieves are described in the following publications, each of which is incorporated herein by reference: U.S. Pat. Nos. 3,702,886; 3,709,979; 3,832,449; 3,950,496; 3,972,983; 4,076,842; 4,016,245; 4,046,859; 4,234,231; 4,440,871; 5,053,373; 5,106,801; and 5,591,421 and U.S. Provisional Patent Application Serial No. 60/034,252 filed Dec. 31, 1996. While ZSM-5 does not meet the pore size limitations specified for the isodewaxing catalyst, a ZSM-5 having a crystallite size of less than about 0.5 μ has been found to be suitable as a hydroisomerization catalyst for the present dewaxing process.

The molecular sieves of the invention are optimized to allow the initially formed branched species to escape the pore systems of the catalysts before cracking occurs. This is done by using small crystallite size molecular sieves and/or by modifying the number, location and/or strength of the acid sites in the molecular sieves. The greater the number of acid sites of the molecular sieves, the smaller must be the crystallite size in order to provide optimum dewaxing by isomerization with minimized cracking. Those molecular sieves which have few and/or weak acid sites may have relatively large crystallite size, while those molecular sieves which have many and/or relatively strong acid sites must be smaller in crystallite size.

The length of the crystallite in the direction of the pores is the critical dimension. X-ray diffraction (XRD) can be used to measure the crystallite length by line broadening measurements. The preferred size crystallites in this invention are $\leq$ 0.5, more preferably ≤ 0.2, still more preferably ≤ 0.1 micron along the direction of the pores (the "c-axis") in many cases and XRD line broadening for XRD lines corresponding to the pore direction is observed for these preferred crystallites. For the smaller size crystallites, particularly those having a crystallite size of ≤ 0.2 micron, acidity becomes much less important since the branched molecules can more readily escape before being cracked. This is even more true when the crystallite size is ≤ 0.1 micron. For crystallites larger than 1 to 2 microns, scanning electron microscope (SEM) or transmission electron microscope (TEM) is needed to estimate the crystallite length because the XRD lines are not measurably broadened. In order to use SEM or TEM accurately, the molecular sieve catalyst must be composed of distinct individual crystallites, not agglomerates of smaller particles in order to accurately determine the size. Hence, SEM and TEM measured values of crystallite length are somewhat less reliable than XRD values.

The method used to determine crystallite size using XRD is described in Klug and Alexander "X-ray Diffraction Procedures", Wiley, 1954 which is incorporated herein by reference. Thus,

$$D=(K \bullet \lambda)/(\beta \bullet \cos\theta),$$

where:

D = crystallite size, Å.
K = constant ≈ 1
λ = wavelength, Å.
β = corrected half width in radians.
θ = diffraction angle.

For crystallites $\geq$ about 0.1 micron in length, (along the pore direction) decreasing the number of acid sites (by exchange of H^+ by with an alkali or alkaline earth cation for example) can increase the isomerization selectivity to a certain extent. The isomerization selectivity of smaller crystallites is less dependent on the acidity since the branched products can more readily escape before being cracked. Titration during the isomerization process (by adding a base such as NH_3) to decrease acidity during a run can also increase isomerization selectivity to a small extent.

The most preferred catalysts of the invention are of the 10-membered ring variety (10 oxygen atoms in the ring defining the pore opening) with the molecular sieves having pore opening sizes of ≤ 7.1 Å, preferably ≤ 6.5Å. Such catalysts include ZSM-21, ZSM-22, ZSM-23, ZSM-35, ZSM-38, ZSM-48, ZSM-57, SSZ-32, ferrierite, SAPO-11 and MAPO-11. Other useful molecular sieves include SAPO-31, SAPO-41, MAPO-31 and SSZ-25, the precise structures of which are not known but whose adsorption characteristics and catalytic properties are such that they satisfy the pore size requirements of the catalysts useful in the process of the present invention. Also useful as catalysts are 12-membered ring zeolitic molecular sieves such as L zeolite and ZSM-12, having deformed (non-circular) pores which satisfy the requirement that they have no cross-dimension greater than 7.1 Å.

The present isodewaxing catalyst is described, for example, in U.S. Patent No. 5,282,958, the entire disclosure of which is incorporated herein by reference for all purposes. The present invention makes use of catalysts with selected acidity, selected pore diameter and selected crystallite size (corresponding to selected pore length). The selection is such as to insure that there is sufficient acidity to catalyze isomerization and such that the product can escape the pore system quickly enough so that cracking is minimized. The pore diameter requirements have been set forth above. The required relationship between acidity and crystallite size of the molecular sieves in order to provide an optimum high viscosity index oil with high yield is defined by carrying out standard isomerization selectivity tests for isomerizing n-hexadecane. The test conditions include a pressure of 1200 psig, hydrogen flow of 160 ml/min (at 1 atmosphere pressure and 25°C), a feed rate of 1 ml/hr and the use of 0.5 g of catalyst loaded in the center of a 3 feet long by 3/16 inch inner diameter stainless steel reactor tube (the catalyst is located centrally of the tube and extends about 1 to 2 inches in length) with alundum loaded upstream of the catalyst for preheating the feed. A catalyst, if it is to qualify as a catalyst of the invention, when tested in this manner, must convert at least 50% of the hexadecane at a temperature of 370°C or below and will preferably convert 96% or more of the hexadecane at a temperature below 355°C. Also, when the catalyst is run under conditions which lead to 96% conversion of hexadecane the isomerization selectivity obtained by raising the temperature, by which is meant the selectivity for producing isomerized hexadecane as opposed to cracked products must be 40 or greater, more preferably 50 or greater. The isomerization selectivity, based on 96% nC_{16} conversion, is a ratio defined as:

$$\frac{\text{wt\% branched } C_{16} \text{ in product}}{\text{wt\% branched } C_{16} \text{ in product} + \text{wt\% } C_{13}^{-} \text{ in product}} X\,100$$

This assures that the number of acid sites is sufficient to provide needed isomerization activity but is low enough so that cracking is minimized. Too few sites leads to insufficient catalyst activity. With too many sites with larger crystallites, cracking predominates over isomerization.

Increasing the crystallite size of a given catalyst (having a fixed SiO_2 /Al_2O_3 ratio) increases the number of acid, e.g., aluminum, sites in each pore. Above a certain crystallite size range, cracking, rather than isomerization, dominates.

The molecular sieve crystallites can suitably be bound with a matrix or porous matrix. The terms "matrix" and "porous matrix" include inorganic compositions with which the crystallites can be combined, dispersed, or otherwise intimately admixed. Preferably, the matrix is not catalytically active in a hydrocarbon cracking sense, i.e., is substantially free of acid sites. The matrix porosity can either be inherent or it can be caused by a mechanical or chemical means. Satisfactory matrices include diatomaceous earth and inorganic oxides. Preferred inorganic oxides include alumina, silica, naturally occurring and conventionally processed clays, for example bentonite, kaolin, sepiolite, attapulgite and halloysite.

Compositing the crystallites with an inorganic oxide matrix can be achieved by any suitable known method wherein the crystallites are intimately admixed with the oxide while the latter is in a hydrous state (for example, as a hydrous salt, hydrogel, wet gelatinous precipitate, or in a dried state, or combinations thereof). A convenient method is to prepare a hydrous mono or plural oxide gel or cogel using an aqueous solution of a salt or mixture of salts (for example aluminum and sodium silicate). Ammonium hydroxide carbonate (or a similar base) is added to the solution in an amount sufficient to precipitate the oxides in hydrous form. Then, the precipitate is washed to remove most of any water soluble salts and it is thoroughly admixed with the crystallites. Water or a lubricating agent can be added in an amount sufficient to facilitate shaping of the mix (as by extrusion).

The preferred isodewaxing catalyst comprises a medium pore size molecular sieve selected from SSZ-32, ZSM-23, SAPO-11, SAPO-31, SAPO-41 or mixtures thereof. More specifically, a layer of amorphous hydrotreating catalyst such as a noble metal silica alumina is placed on top of an isodewaxing catalyst such as SSZ-32 as described in U.S. 5,053,373 and the catalyst of U.S. 5,393,408, the specifications of which are completely incorporated herein by reference for all purposes.

Alternatively, the layered system can be used in a solvent extraction, hydrocracking, hydrotreating/isodewaxing process wherein a top layer of a dewaxing catalyst is a noble metal hydrotreating catalyst such as $Pd/SiO_2/Al_2O_3$ followed by SSZ-32. An important benefit of this invention is that there is essentially no yield loss across the hydrotreating layer of the dewaxing catalyst system. However, the additional VI upgrade in aromatic saturation which occurs in this upper hydrotreating layer results in dramatically higher yields of high VI lube stock and/or higher isodewaxing catalyst activity and longer isodewaxing catalyst life. Indeed, a surprising result of this invention is that the solvent extraction severity may be reduced leading to higher yield while maintaining increased final VI product. This is opposite to conventional wisdom which requires the extraction severity to increase and thus reduce yield in order to increase VI. Although the layered system will function with a catalytic dewaxer such as ZSM-5 as the dewaxing catalyst with an initial layer of the noble metal silica alumina catalyst, the use of SSZ-32 is particularly preferred. The catalysts for ZSM-5 are taught in U.S. 3,702,886 and U.S. 3,700,585, the specifications of which are completely incorporated herein by reference for all purposes.

This catalyst layering system can be used in a multiplicity of processes for hydrocracking/hydrotreating/isodewaxing and combinations thereof to extend the useful range of a primary catalyst such as SSZ 32, ZSM 5, and the like.

Dewaxing reaction conditions may be the same as, or different from, hydrotreating reaction conditions in the dewaxing reaction zone. At any rate, the conditions under which the isomerization/dewaxing process of the present invention is carried out generally include a temperature which falls within a range from about 200°C to about 475°C and a pressure from about 15 to about 4000 psig. More preferably the pressure is from about 100 to about 3000 psig. The liquid hourly space velocity during contacting is generally from about 0.1 to about 20 hr^{-1}, more preferably from about 0.2 to about 10 hr^{-1}. The contacting is preferably carried out in the presence of hydrogen. The hydrogen to hydrocarbon ratio preferably falls within a range from about 1.0 to about 50 moles H_2 per mole hydrocarbon, more preferably from about 10 to about 30 moles H_2 per mole hydrocarbon.

The product of the dewaxing process is a high quality oil suitable for a lubricating oil base stock. The preferred oil product is a low pour point oil, having a pour point of less than about 10°C, more preferably less than about 0°C. The most preferred oil product is a Group II or a Group III oil, according to API Publication 1509: Engine Oil Licensing and Certification System, "Appendix E-API Base Oil Interchangeability Guidelines for Passenger Car Motor Oil and Diesel Engine Oils". A Group II base stock contains greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulfur and has a viscosity index greater than or equal to 80 and less than 120. A Group III base stock contains greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulfur and has a viscosity index greater than or equal to 120. Test methods for evaluating group category properties including: saturates - ASTM D-2007; viscosity index - ASTM D2270; sulfur - one of ASTM D-2622, ASTM D-4294, ASTM D-4927, ASTM D-3120. The viscosity of the finished lube oil, when measured at 100°C, is generally greater than 2 cSt.

In the process of the present invention, a waxy hydrocrackate is contacted with hydrogen over the hydrotreating catalyst layer in the dewaxing reaction zone. The effluent, or at least a portion thereof, is contacted with hydrogen over an isodewaxing catalyst layer also contained in the dewaxing reaction zone. Thus:

(a) The entire effluent from the hydrotreating catalyst layer includes a normally liquid hydrotreated lube oil and a hydrogen-containing normally gaseous stream. In practicing one embodiment of the present process, the entire effluent from the hydrotreating catalyst layer is charged to a dewaxing catalyst layer. Dewaxing the entire effluent implies either having the hydrotreating and dewaxing catalyst layers in a single reactor, or sequential layers in separate reactors with no treating of the fluids between.

(b) In another embodiment, the hydrotreated lube oil is charged to a catalytic dewaxer. Dewaxing all of the hydrotreated oil implies either (a) above or separating the gas, probably to purify it, before sending the liquid, purified gas and additional fresh (i.e. make-up) H_2 to the dewaxing catalyst layer.

(c) In yet another embodiment, at least a portion of the hydrotreated lube oil is charged to a dewaxing catalyst layer. Dewaxing a portion of the hydrotreated oil implies either (b) above or using the hydrotreater as a second stage hydrocracker, with sufficient conversion in the 2nd stage that the liquid product is fractionated to remove cracked products and the gases purified to remove excess hydrogen sulfide, ammonia, and possibly light hydrocarbon gases. The fraction of the hydrotreated product boiling in the desired lube range is then combined with purified hydrogen and cat dewaxed.

Charging the entire effluent from the hydrotreating catalyst layer to the dewaxing catalyst layer is preferred in the present process.

Referring now to a preferred embodiment illustrated in Figure 1, the layered dewaxing catalyst system for producing a lubricating oil base stock is included in an integrated system. The integrated system includes separate reaction trains for simultaneously processing at least two distillate fractions. In general, these fractions are differentiated by normal boiling point. In the integrated system, a petroleum feedstock **5** is separated by normal boiling point into a multiplicity of fractions, two of which are shown in Figure 1. Of the multiplicity of distillate fractions, at least one light (i.e. relatively lower boiling) distillate fraction **102** and one heavy (i.e. relatively higher boiling) distillate fraction **202** are simultaneously reacted in a series of reaction steps in separate reaction trains to produce at least one light lubricating oil base stock **174** and at least one heavy lubricating oil base stock **274**. While only a single distillation column **10** is indicated, a sequence of distillation processes, including one or more flash distillation(s), atmospheric pressure distillation and distillation under a partial vacuum may be employed in making the desired separations. Typical mid-boiling points for the light distillate stream are in the range of 600°F to 900°F, in which the mid-boiling point is the temperature at which 50% by volume of the stream boils at standard pressure. Typical mid-boiling points for the heavy distillate stream are in the range of 700°F to 1000°F. The sulfur content of the light and the heavy distillate streams may be as high at 5% by weight or greater, and the nitrogen content may be as high as 2% by weight or greater.

In the description which follows, reference will be made first to the reaction train for preparing light lubricating oil base stock **174.** The light distillate stream **102** is contacted with hydrogen in a hydrocracking reaction zone **110** at conditions sufficient to produce light waxy hydrocrackate **128** having a viscosity index which is increased relative to light distillate fraction **102.**

The hydrocracking catalyst also removes a substantial portion of the organonitrogen and organosulfur compounds from the hydrocarbonaceous feed. These reactions removing heteroatom compounds are important, as organonitrogen, and to a lesser extent organosulfur compounds, are detrimental to downstream processing of the lubricating oil base stock, such as dewaxing and hydrofinishing. Products of the heteroatom removal reactions, such as ammonia and hydrogen sulfide, are significantly less detrimental to these downstream processes. Furthermore, ammonia and hydrogen sulfide may be effectively removed in first separation zone **120** a produce a hydrocrackate stream **122** having nitrogen and sulfur contents of typically less than 25 ppm, usually less than 10 ppm, and levels as low as 1 ppm or less are often observed.

The first hydrocracking catalyst in hydrocracking reaction zone **110** comprises at least one hydrogenation component, and optionally a cracking component, on an oxide support. The hydrogenation component may be at least one noble metal and/or at least one non-noble metal. Suitable noble metals include platinum, palladium and other members of the platinum group such as iridium and ruthenium. Suitable non-noble metals include those of Groups VA, VIA, and VIIIA of the Periodic Table. Preferred non-noble metals are chromium, molybdenum, tungsten, cobalt and nickel and combinations of these metals such as nickel-tungsten. Non-noble metal components can be pre-sulfided prior to use by exposure to a sulfur-containing gas such as hydrogen sulfide at elevated temperature to convert the oxide form of the metal to the corresponding sulfide form. The hydrogenation component can be incorporated into the catalyst by any suitable method such as by commingling during a mixing step, by impregnation or by exchange. The metal can be incorporated in the form of a cationic, anionic or neutral complex; $Pt(NH_3)_4^{2+}$ and cationic complexes of this type will be found convenient for exchanging metals onto the zeolite. Anionic complexes such as heptamolybdate or metatungstate ions are also useful for impregnating metals into the catalysts. One or more active sources of the hydrogenation component may also be blended with a zeolite and an active source of a silica-aluminum matrix material during preparation of the catalyst. Active sources of the hydrogenation component include, for example, any material having a form which is not detrimental to the catalyst and which will produce the desired hydrogenating component during preparation, including any drying, calcining and reducing steps of the catalyst. Typical salts which may be used as sources of the hydrogenation component include the nitrates, acetates, sulfates, chlorides.

The amount of hydrogenation component can range from about 0.01 to about 45 percent by weight and is normally from about 0.1 to about 35 percent by weight. The precise amount will, of course, vary with the nature of the component, less of the highly active noble metals, particularly platinum, being required than of the less active base metals. In this application, the term "noble metal" includes one or more of ruthenium, rhodium, palladium, osmium, iridium or platinum. The term "base metal" includes one or more of Groups VB, VIB and VIII metals, including, for example, vanadium, chromium, molybdenum, tungsten, iron, cobalt, and nickel. Usually a combination of base metals are used, such as the Group VIII metals nickel or cobalt in combination with the Group VIB metals tungsten or molybdenum, and the base metal is usually sulfided or presulfided in the catalyst when or before the catalyst is put on stream. A preferred catalyst for the present process contains in the range from about 1 to about 15% by weight, and preferably from about 2 to about 10% by weight of at least one Group VIII base metal, calculated as the metal monoxide, and in the range from about 5 to about 30% by weight, and preferably from about 10 to about 25% by weight of at least one Group VIB metal, calculated as the metal trioxide.

The cracking component of the first hydrocracking catalyst may include amorphous cracking components, such as silica alumina, and/or a mixture of large pore aluminosilicate zeolites, such as, for example, zeolites such as X, Y, ultrastable Y, dealuminated Y, and faujasite. While within the broadest embodiment a wide variety of zeolites are suitable for the hydrocracking process, the preferred zeolite has low to moderate overall acidity, typically with a SiO_2/Al_2O_3 molar ratio in the range of about 5 to about 100, more preferably in the range of about 10 to about 60. Though it is believed that lube yield is not significantly affected by the use of a low SiO_2/Al_2O_3 ratio zeolite, low valued, low boiling products tend to be produced during hydrocracking at high conversions with a low SiO_2/Al_2O_3 ratio zeolite. Using a zeolite having a higher SiO_2/Al_2O_3 ratio tends to product a non-lube fraction having a higher boiling point. In order to optimize the generally conflicting objectives of low catalyst fouling rate and high VI selectivity of the catalyst, the catalyst generally contains less than about 20%, preferably less than about 10%, and more preferably less than about 8%, and still more preferably in the range of about 2 to about 6% zeolite on a volatiles-free basis.

The zeolite can be composited with porous inorganic oxide matrix materials and mixtures of matrix materials such as silica, alumina, silica-alumina, titania, magnesia, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania, titania-zirconia, as well as ternary compositions such as silica-alumina-thoria, silica-alumina-titania, silica-alumina-magnesia and silica-magnesia-zirconia. The matrix can be in the form of a cogel. A preferred support material to facilitate catalyst preparation and improve catalyst physical properties is an alumina support. Even more preferred is a zeolite composited with a silica alumina matrix material, with at least 1% additional alumina binder.

The preferred hydrocracking catalyst has a pore structure which enhances the performance of the catalyst for hydrocracking to produce a lubricating oil base stock, including a pore volume in the range of between about 0.25 and about 0.60 cm^3/g, a mean pore diameter between about 40 Å and about 100 Å, with at least about 5 percent of the pore volume being in pores having a diameter of greater than about 200 Å, and at least about 1 percent of the pore volume being in pores having a diameter of greater than 1000 Å. As used herein, "mean pore diameter", refers to the point on a plot of cumulative pore volume versus pore diameter that corresponds to 50% of the total pore volume of the catalyst as measured by mercury porosimetry or nitrogen physisorption porosimetry. One such hydrocracking catalyst which is useful in the present process is described in U.S. Patent No. 5,543,035, the entire disclosure of which is incorporated herein by reference for all purposes.

Typically, hydrocracking conditions include a temperature in the range of 400°F. to 950°F., a pressure in the range of 500 to 3500 psig, a liquid hourly space velocity in the range 0.1 to 20.0 hr^{-1}, and a total hydrogen supply in the range of 200 to 20,000 SCF of hydrogen per barrel of hydrocarbonaceous feed. Employing the foregoing hydrocracking conditions, conversion of feedstock to hydrocrackate product can be made to come within the range of from about 10 to about 80 weight percent. However, higher conversion rates generally result in lower selectivity and greater amount of light, rather than middle distillate or lube boiling range, products. Thus, a compromise must be drawn between conversion and selectivity, and conversions in the region of about 10 to about 70 percent are preferred. The balancing of reaction conditions to achieve the desired objectives is part of the ordinary skill of the art. As used herein, conversion is that fraction of feed boiling above a target temperature which is converted to products boiling below that temperature. Generally, the target temperature is taken as roughly the minimum of the boiling range of the feed.

The hydrocracking reactor **111** containing the hydrocracking reaction zone **110** can also be operated as a layered catalyst system having at least two catalyst layers, with the lube hydrocracking catalyst of the present process converting a hydrocarbonaceous feed stream which was previously treated in a first hydroconversion catalyst layer. In a layered catalyst system, the first hydroconversion layer performs some cracking and removes nitrogen and sulfur from the feedstock before contact with the lube hydrocracking catalyst. Preferably, the organonitrogen content of the product leaving the top layer of catalyst is less than 500 ppm, more preferably less than 250 ppm, and still more preferably less than 100 ppm. The top layer of catalyst will generally comprise a hydroconversion catalyst comprising Group VI and/or Group VIII hydrogenation components on a silica or silica-alumina support. Preferred hydrogenation components for the hydrotreating catalyst include nickel, molybdenum, tungsten and cobalt or a combination thereof. An active zeolite, such as a Y-type zeolite, and preferably an active

Y-type zeolite having a SiO_2/Al_2O_3 of less than about 10, may be included with the hydroconversion catalyst in order to increase activity and catalyst stability. The relative amounts of catalyst used in the various catalyst layers is specific to each reactor system and feedstream used, depending on, for example, the severity of the operating conditions, the boiling range of the feed, the quantity of heteroatoms such as nitrogen and sulfur in the feed, and the desired lubricating oil base stock properties. Typically, in a catalyst system comprising a hydroconversion catalyst layer and a lube hydrocracking catalyst layer, the volumetric ratio of hydroconversion catalyst to hydrocracking catalyst is in the range between about 1/99 and about 99/1, preferably between about 10/90 and about 50/50.

Hydroconversion reaction conditions in the hydroconversion catalyst layer may be the same as or different from conditions in the hydrocracking layer. Generally, hydroconversion conditions include a temperature in the range of 400°F. to 950°F., a pressure in the range of 500 to 3500 psig, a liquid hourly space velocity in the range 0.1 to 20.0, and a total hydrogen supply in the range of 200 to 20,000 SCF of hydrogen per barrel of hydrocarbonaceous feed.

In the embodiment illustrated in Figure 1, the effluent from hydrocracking reaction zone **110** includes a normally gaseous stream comprising hydrogen, hydrogen sulfide, ammonia and low boiling hydrocarbonaceous reaction products. The liquid and gaseous products are separated in first separation zone **120** to produce a purified hydrogen rich gaseous stream **122** and a light waxy hydrocrackate stream **124**. Not shown are the details of the separation and purification process, which are known in the art. Such detail includes means for removing hydrogen sulfides, ammonia and other contaminants from the gaseous stream to produce a hydrogen rich stream **122** suitable for recycle or for other refinery use.

The light waxy hydrocrackate **124** produced by the present hydrocracking process will have a high viscosity index, a low nitrogen content and a low sulfur content. Prior to additional processing, it may be distilled in distillation column **130** into two or more fractions of varying boiling points, with each fraction being characterized by a particular viscosity, a particular viscosity index and a particular nitrogen and a particular sulfur content.

For the purposes of this description, an arbitrary number of three waxy oil fractions **132**, **134** and **136** are shown. Not shown are non-lube streams which are used elsewhere in the refinery, such as for fuels. Generally, at least one of the fractions will have a viscosity index greater than about 70 and preferably greater than about 80. However, the viscosity index can be as high as 95 or even 110, depending on the feedstock being treated. While methods are available for determining the viscosity index of a waxy stock, the viscosity index values given here are on a solvent dewaxed basis, i.e., they are based on lubricating oil base stocks which have been solvent dewaxed, using methods well known in the art, to a -10°C. pour point. In the specific embodiment of Figure 1, each waxy oil fraction is processed individually in turn in blocked operation in catalytic dewaxing reactor **141,** containing catalytic dewaxing reaction zone **140.**

Catalytic dewaxing reaction zone **140** contains the layered catalyst system of this invention. A first catalyst layer, comprising a noble metal hydrotreating catalyst, removes sulfur and nitrogen from the feed, opens aromatic and aliphatic ring structures, and increases the viscosity index of the feed. A second catalyst layer, comprising an isodewaxing catalyst of this invention, reduces the pour point of the feed by hydroisomerization reactions. Together the layered catalyst system layer and an isodewaxing catalyst layer produce high yields of low pour point, high quality dewaxed base oils.

The pour point of the dewaxed oil product **152** from the dewaxing reaction zone **140** desirably has a pour point of less than about 5°C., preferably less than about 0°C. and more preferably less than about -5°C.

The process of the invention also be employed in combination with conventional dewaxing processes to achieve a lube oil having particular desired properties. for example, the process of the invention can be used to reduce the pour point of a lube oil to a desired degree. Further reduction of the pour point can then be achieved using a conventional dewaxing process. Under such circumstances, immediately following the isomerization process of the invention, the lube oil may have a pour point greater than about 15°F. Further, the pour point of the lube oil produced by the process of the invention can be reduced by adding pour point depressant compositions thereto.

The effluent from the catalytic dewaxing reaction zone **142** in Figure 1 comprises a dewaxed light oil fraction **152** and a hydrogen rich gaseous stream **154**. The dewaxed light oil fraction is combined with a hydrogen-rich gaseous stream **156** and contacted with a hydrogenation catalyst in hydrogenation reaction zone **160** contained within hydrogenation reactor **151**. In a preferred embodiment, the entire effluent **142** from the dewaxing reaction zone, without separation and without added hydrogen or a hydrogen-rich gaseous stream, is contacted in hydrogenation reaction zone **160** at conditions sufficient to produce a light lubricating oil base stock **174**. The effluent **162** from the hydrogenation reaction zone **160** is separated in separation zone **170**, with hydrogen containing gaseous stream **172** recovered for use elsewhere in the refinery or for disposal and the lubricating oil base stock **174** recovered for use as a lubricating oil base stock. The hydrogenation catalyst has activity for improving the storage stability of a dewaxed oil in the preparation of a lubricating oil base stock. Reactions such as removing aromatics, nitrogen- and sulfur-containing molecules and color bodies to very low concentrations, while minimizing cracking reactions leading to yield loss, are particularly desirable. The preferred catalyst for the hydrogenation step contains a hydrogenation component on an oxide matrix material. The hydrogenation component may be at least one noble metal and/or at least one non-noble metal. Suitable noble metals include platinum, palladium and other members of the platinum group such as iridium and ruthenium. Suitable non-noble metals include those of Groups VA, VIA, and VIIIA of the Periodic Table. Preferred non-noble metals are chromium, molybdenum, tungsten, cobalt and nickel and combinations of these metals such as nickel-tungsten. Non-noble metal components can be pre-sulfided prior to use by exposure to a sulfur-containing gas such as hydrogen sulfide at elevated temperature to convert the oxide form of the metal to the corresponding sulfide form. The hydrogenation component can be incorporated into the catalyst by any suitable method such as by commingling during a mixing step, by impregnation or by exchange. The amount of hydrogenation component can range from about 0.01 to about 45 percent by weight and is normally from about 0.1 to about 35 percent by weight. The precise amount will, of course, vary with the nature of the component, less of the highly active noble metals, particularly platinum, being required than of the less active base metals. Preferred hydrogenation catalysts include between 0.1 weight percent and 1 weight percent platinum and/or palladium on alumina or silica-alumina, including a platinum-palladium alloy having a molar ratio of platinum to palladium in the alloy of between about 2.5:1 and 1:2.5, preferably between 2:1 and 1:1 and most preferably equal to about 1:1.5.

The most preferred hydrogenation catalyst has a total pore volume greater than about 0.45 cm^3/g, preferably greater than about 0.55 cm^3/g, with at least about 1%, and preferably at least about 3%, of the total pore volume being in macropores of diameter of greater than about 1000 angstroms, with the minimum amount of macropore volume preferably being greater than 0.07 cm^3/g. As used herein, the term "macroporous" refers to a catalyst having a relatively large amount of pore volume, i.e., at least 1%, in pores of diameter greater than about 1000 Angstroms, with a minimum macropore volume preferably being greater than 0.07 cm^3/g.

In Figure 1, a reaction train for treating a heavy feed, with reference numbers in the 200 series, matches the reaction train described above for treating a light feed, with reference numbers in the 100 series. To avoid duplication, a detailed description of the reaction train for producing a heavy lubricating oil base stock **274** will not be included here. While the catalysts used in the corresponding reaction zones (e.g. first hydrocracking reaction zone **110** and second hydrocracking reaction zone **210**, etc.) are not necessarily identical, they fall within the catalyst specification as described here.

The process illustrated in Figure 1 provides for a single source of feedstock to the integrated process through distillation in fractionator **10**. In practice, fraction **102** to the first hydrocracking reaction zone and fraction **202** to the second hydrocracking reaction zone may originate from different sources. Thus, as a non-limiting example, one of **102** and **202** may originate as a vacuum gas oil stream, and the other may originate as a waxy feed, such as slack wax or a waxy petroleum feedstock, for producing a Group III lubricating oil base stock.

EXAMPLE

An isodewaxing catalyst comprising 65% SSZ-32 in an alumina binder, and containing 0.325 wt% platinum, using a procedure which was similar to that of given in U.S. Patent No. 5,376,260. This catalyst was designated Catalyst A.

A hydrotreating catalyst was prepared using a procedure similar to that of U.S. Patent No. 5,393,408. The hydrotreating catalyst contained 0.5 weight percent platinum on a silica-alumina base containing 66% Al_2O_3. This catalyst was designated Catalyst B.

Catalyst A (10 cc) was contacted with a waxy hydrocracked feed having physical properties as follows:

Nitrogen	3.1 nanograms/microlitre
Sulfur	0.005 wt%
Wax content	16 wt%
Pour Point	45°C.
Viscosity @ 100°C.	11.77 cSt
Density	0.89 g/cm^3

at 2300 psig total pressure, a hydrogen flow rate of 237 ml/min, and a feed rate of 16 ml/hr. The reaction temperature was adjusted to produce product at differing pour points, and the yield and VI of dewaxed product were determined. Figures 2 and 3 show the range of data from the test. Figures 2 and 3 also provide baseline data for a solvent dewaxed sample. Figure 4 shows how the pour point of the dewaxed product varied with reaction temperature.

The experiment was repeated with a layered catalyst of Catalyst B (0.25 cc) over Catalyst A (0.75 cc) at the same reaction conditions. The data is also plotted in Figures 2-4. According to the data, the layered catalyst system produced a higher viscosity index product at constant pour point (Figure 3) while maintaining essentially equal product yield (Figure 2) at constant catalytic activity (Figure 4). The VI improvement was increased at very low pour points, in that the VI did not decrease, while the VI of the product from Catalyst A decreased as pour point decreased.

The reference to any prior art in this specification is not, and should not be taken as, an acknowledgment or any form of suggestion that that prior art forms part of the common general knowledge in Australia.

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be understood that the invention includes all such variations and modifications which fall within its spirit and scope. The invention also includes all the steps, features, compositions and compounds referred to or indicated in this specification, individually or collectively, and any and all combinations of any two or more of said steps or features.

WHAT IS CLAIMED IS:

1. A refinery operation for producing a dewaxed oil and having at least one dewaxing reaction zone containing an isodewaxing catalyst, for reducing the pour point of a waxy oil, the process comprising:

   a. including in the at least one dewaxing reaction zone a second catalyst layer on top of the isodewaxing catalyst in said reactor, the catalyst in said second catalyst layer selected from the group consisting of noble metal amorphous catalysts, noble metal hydrocracking catalysts or combinations thereof;

   b. contacting said waxy oil with hydrogen over said second catalyst layer;

   c. contacting the entire effluent from the second catalyst layer over the isodewaxing catalyst; and

   d. recovering a dewaxed oil having a pour point which is reduced relative to that of the waxy oil.

2. The process according to Claim 1 wherein the isodewaxing catalyst comprises an intermediate pore size molecular sieve having a crystallite size of no more than about 0.5 microns, having pores with a minimum pore diameter of at least 4.8 Å and with a maximum pore diameter of no more than 7.1 Å, the catalyst:

   a. having sufficient acidity so that 0.5 g thereof when positioned in a ¼ inch internal diameter tube reactor converts at least 50% of hexadecane at a temperature of 370°C., a pressure of 1200 psig, a hydrogen flow of 160 ml/min and a feed rate of 1 ml/hr, and

   b. exhibiting 40 or greater isomerization selectivity which is defined as

$$\frac{\text{wt\% branched } C_{16} \text{ in product}}{\text{wt\% branched } C_{16} \text{ in product} + \text{wt\% } C_{13}^{-} \text{ in product}} \times 100$$

when used under conditions leading to 96% conversion of hexadecane.

3. The process according to Claim 1 wherein the isodewaxing catalyst comprises a zeolite selected from the group consisting of ZSM-5, ZSM-12, ZSM-21, ZSM-22, ZSM-23, ZSM-35, ZSM-38, ZSM-57, offretite, ferrierite and SUZ-4.

4. The process according to Claim 1 wherein the isodewaxing catalyst comprises a zeolite selected from the group consisting of SSZ-31, SSZ-32, SSZ-36 and SSZ-41.

5. The process according to Claim 1 wherein the isodewaxing catalyst comprises a non-zeolitic molecular sieve selected from the group consisting of SAPO-11, SAPO-31, SAPO-41, MAPO-11 and MAPO-31.

6. The process according to Claim 1 wherein the second catalyst is a noble metal amorphous catalyst comprising between about 0.1 and about 1 weight percent of a noble metal hydrogenation and an amorphous matrix material.

7. The process according to Claim 6 wherein the noble metal hydrogenation component is selected from the group consisting of platinum, palladium or mixtures thereof, and wherein the amorphous matrix material comprises silica-alumina.

8. The process according to Claim 7 wherein the second catalyst comprises a platinum-palladium alloy and a SiO_2/Al_2O_3 oxide matrix, wherein the molar ratio of platinum to palladium in the alloy is between about 2.5:1 and about 1:2.5.

9. The process according to Claim 1 wherein the second catalyst is a noble metal hydrocracking catalyst comprising between about 0.1 and about 1 weight percent of a noble metal hydrogenation component and from about 0.1 to about 20 weight percent of a zeolite selected from the group consisting of faujasite, zeolite Y and ultrastable zeolite Y.

10. The process according to Claim 1 wherein the waxy oil has a boiling point in the range of about 260°C. to about 650°C.

11. The process according to Claim 1 wherein the waxy oil is a waxy hydrocrackate from a hydrocracker reaction zone.

12. The process according to Claim 1 wherein the waxy oil has a viscosity index of at least about 80 on a solvent dewaxed basis.

13. The process according to Claim 12 wherein the waxy oil has a viscosity index of at least about 95 on a solvent dewaxed basis.

14. The process according to Claim 12 wherein the waxy oil has a viscosity index of at least about 110 on a solvent dewaxed basis.

15. The process according to Claim 1 wherein the pour point of the dewaxed oil is less than about -5°C.

16. The process according to Claim 1 at reaction conditions which include a reaction temperature in the range of about 550°F to about 850°F (288-454°C), a reaction pressure in the range of about 15 psig to about 3500 psig (0.103-24.1 MPa) and a feed rate in the range of about 0.1 to about 20 hr^{-1}.

17. The process according to Claim 1 further comprising contacting the dewaxed oil with hydrogen at hydrogenation reaction conditions over a noble metal hydrogenation catalyst to produce a lubricating oil base stock.

18. The process according to Claim 17 wherein the lubricating oil base stock is a Group II oil.

19. The process according to Claim 17 wherein the lubricating oil base stock is a Group III oil.

20. The process according to Claim 1 wherein the waxy oil contains greater than 50% wax.

21. An integrated process for preparing a multiplicity of lubricating oil base stocks, which are differentiated from each other by viscosity, wherein the process according to Claim 1 is conducted simultaneously in at least two separate and parallel trains.

22. The process according to Claim 21 for producing at least one light lubricating oil base stock and at least one heavy lubricating oil base stock.

23. The process according to Claim 22 wherein the light lubricating oil base stock is a Group II oil and the heavy lubricating oil base stock is a Group II oil.

24. The process according to Claim 22 wherein the light lubricating oil base stock is a Group III oil.

25. The process according to Claim 22 wherein the heavy lubricating oil base stock is a Group III oil.

26. The process according to Claim 24 wherein the heavy lubricating oil base stock is a Group III oil.

27. A process substantially as hereinbefore described with reference to the drawings and/or the Examples.

28. A dewaxed oil produced by a process according to any one of claims 1 to 20 or 27.

29. A lubricating oil base stock prepared by a process according to any one of claims 21 to 26.

DATED this 19th day of July 2000

Chevron U.S.A. Inc.

by DAVIES COLLISON CAVE
Patent Attorneys for the Applicants

FIGURE 1

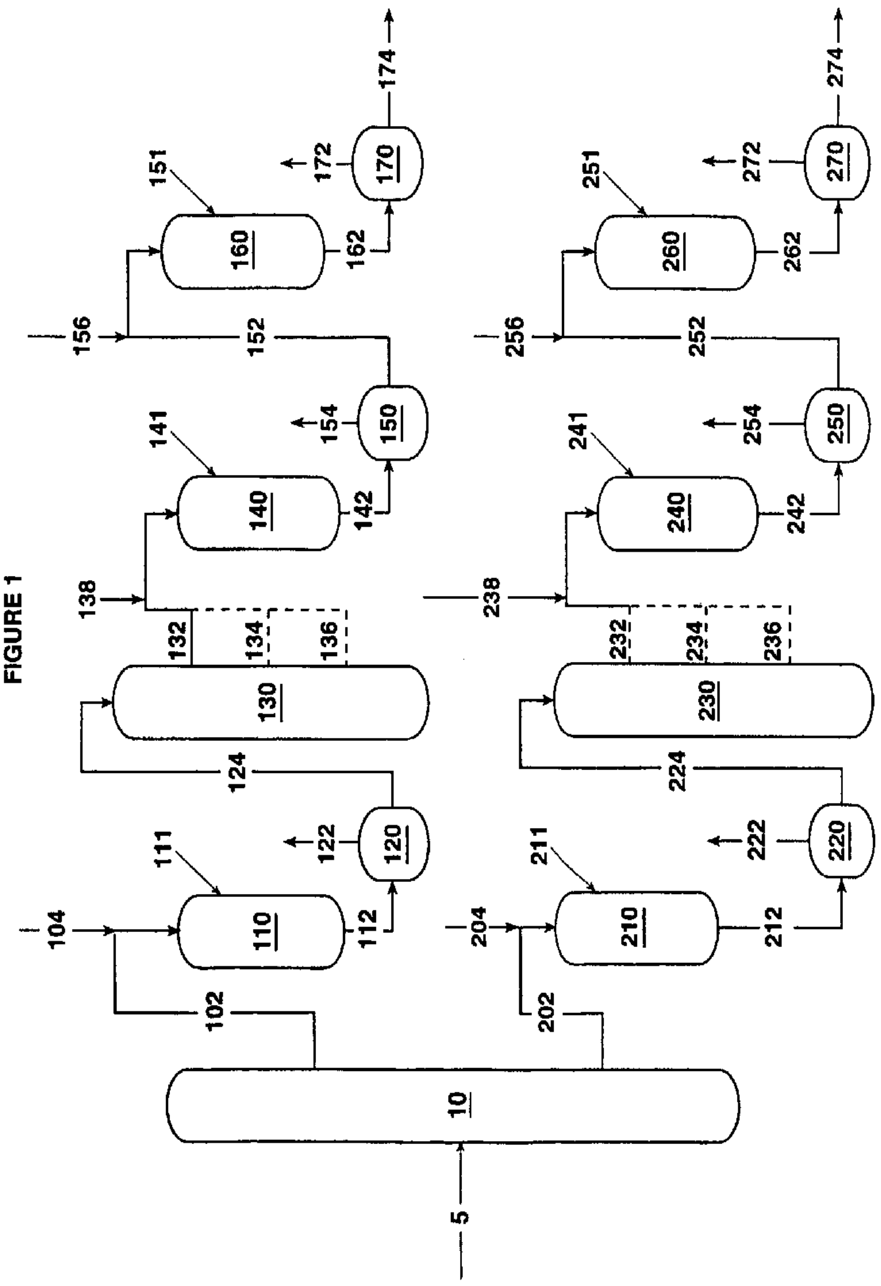
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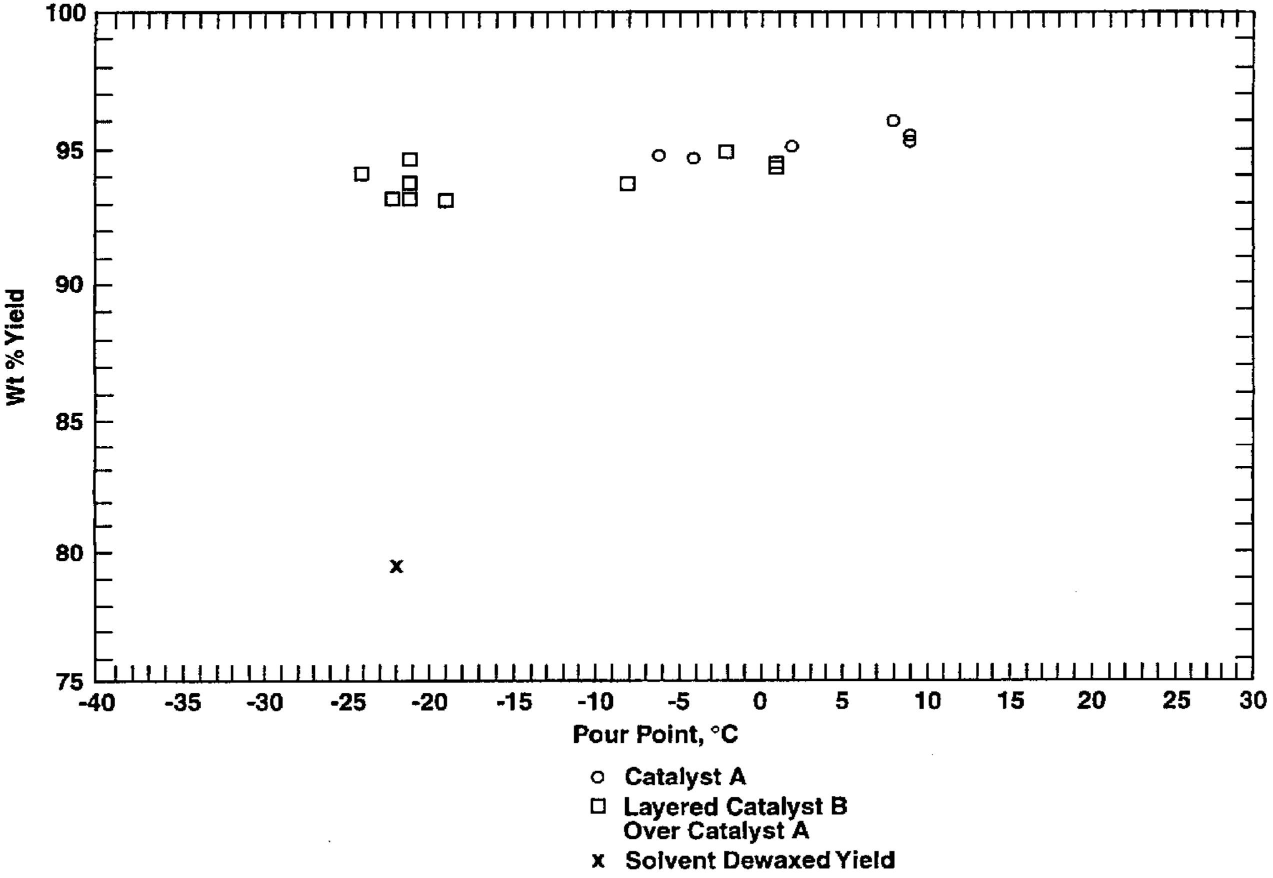
FIGURE 2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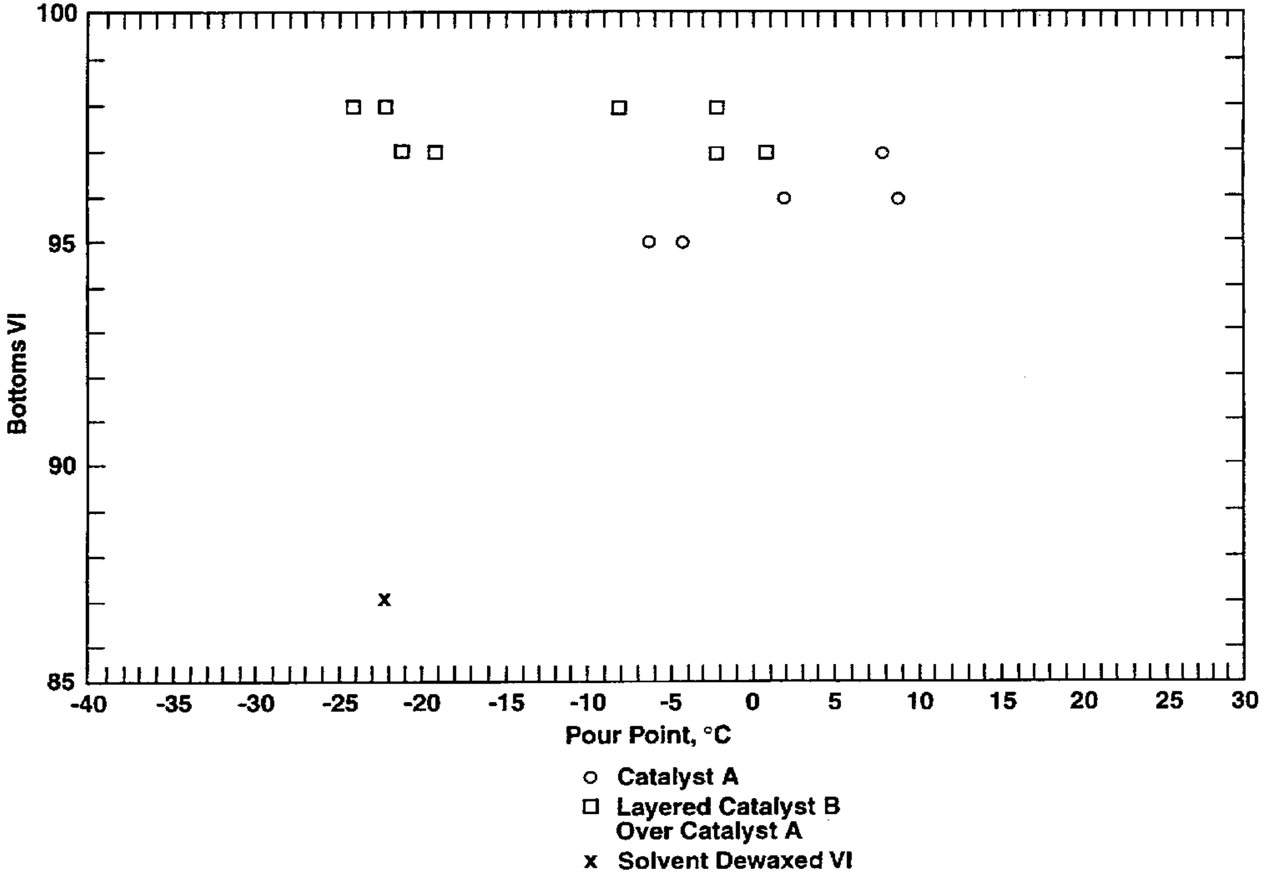
95
90
85
80
75
Wt % Yield
-40
-35
-30
-25
-20
-15
-10
-5
0
5
10
15
20
25
30
Pour Point, °C
○ Catalyst A
□ Layered Catalyst B Over Catalyst A
x Solvent Dewaxed Yield

FIGURE 3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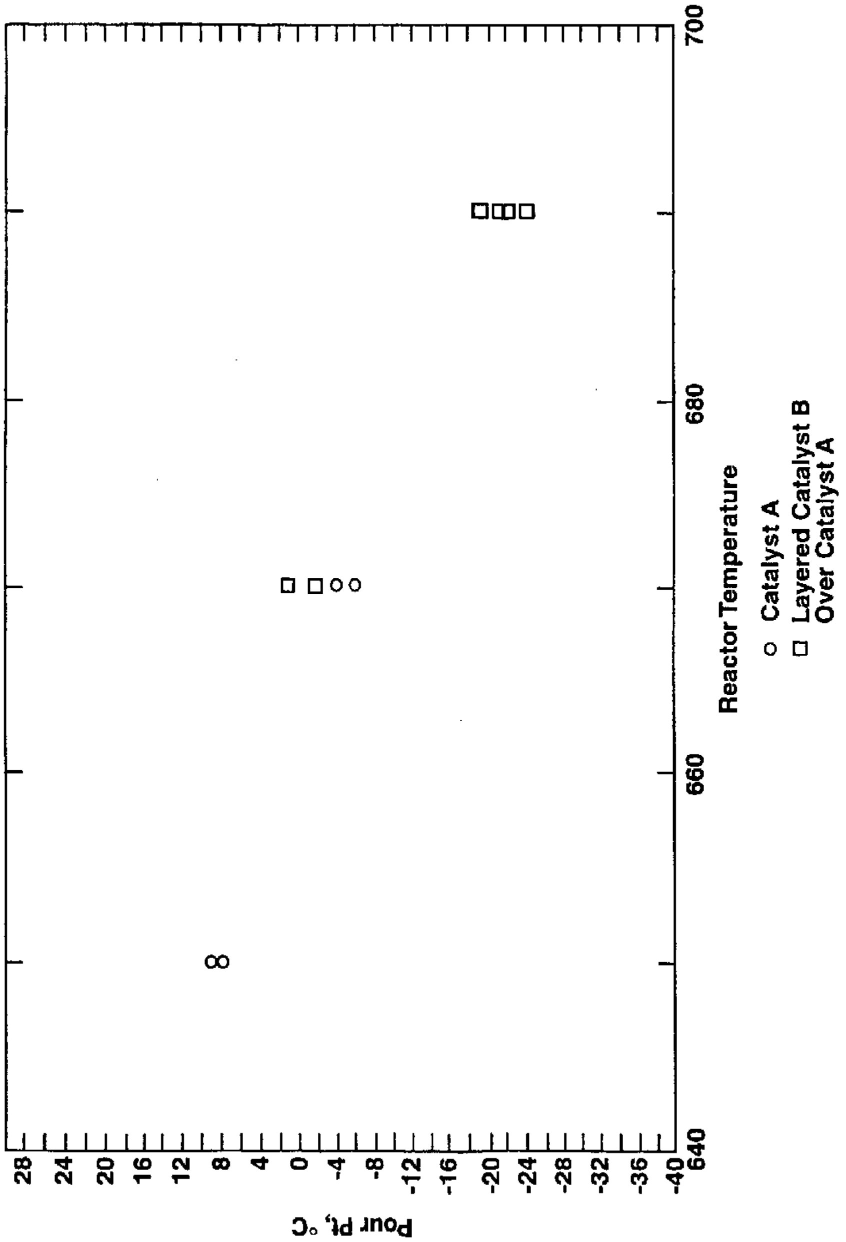
95
90
85
Bottoms VI
-40
-35
-30
-25
-20
-15
-10
-5
0
5
10
15
20
25
30
Pour Point, °C
○ Catalyst A
□ Layered Catalyst B Over Catalyst A
x Solvent Dewaxed VI

FIGURE 4


Pour Pt, °C
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24
20
16
12
8
4
0
-4
-8
-12
-16
-20
-24
-28
-32
-36
-40
640
660
680
700
Reactor Temperature
○ Catalyst A
□ Layered Catalyst B Over Catalyst A