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(54) **HYDROISOMERIZATION PROCESSES
USING PRE-SULFIDED CATALYSTS**

(52) **U.S. Cl.** **208/27; 208/950**

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(57) **ABSTRACT**

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The present application relates to methods for producing a lubricant base oil from a waxy hydrocarbon feed using a pre-sulfided shape selective, intermediate pore size, noble metal-containing molecular sieve catalyst. According to the present invention, a shape selective, intermediate pore size, noble metal-containing molecular sieve catalyst is pre-sulfided to provide a sulfided catalyst, wherein the molar ratio of sulfur to noble metal in the sulfided catalyst is greater than one, and a waxy hydrocarbon feed is hydroisomerized by contacting the waxy hydrocarbon feed with the sulfided catalyst at hydroisomerization conditions, to produce a lubricant base oil.

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Publication Classification

(51) **Int. Cl.⁷ C10G 73/38**

Fig. 1
Hydroisomerization Yield of a Fischer-Tropsch Wax
Using a SAPO-11 Catalyst

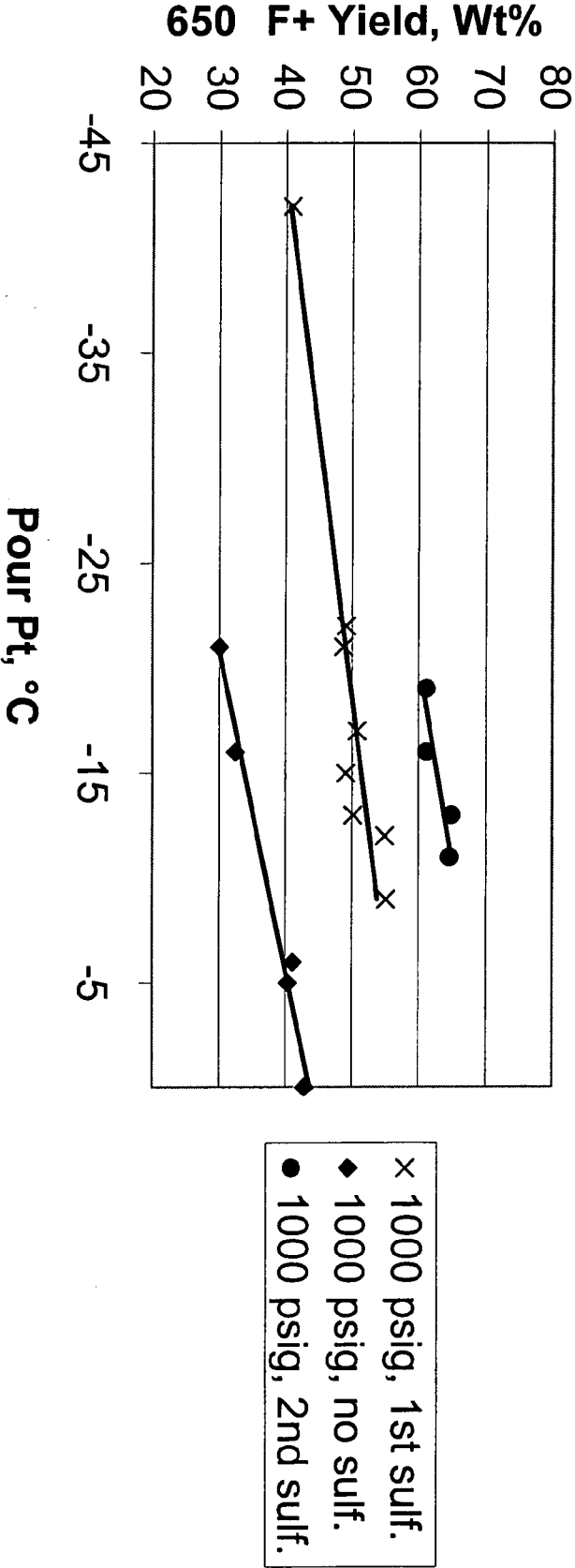


Fig. 2
Viscosity Index of a Hydroisomerized Fischer-Tropsch Wax
Using a SAPO-11 Catalyst

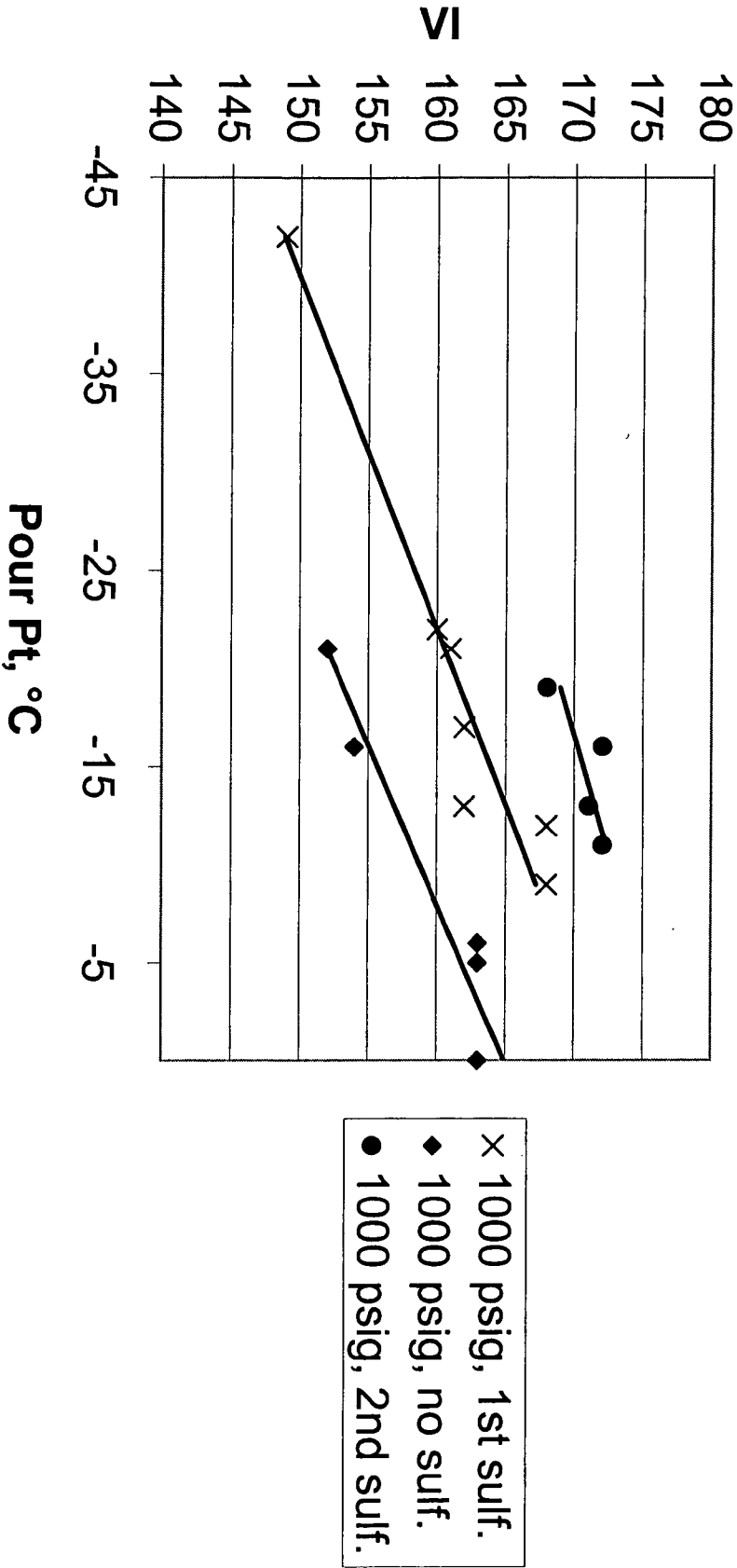


Fig. 3
Hydroisomerization Yield of a Fischer-Tropsch Wax
Using a SAPO-11 Catalyst

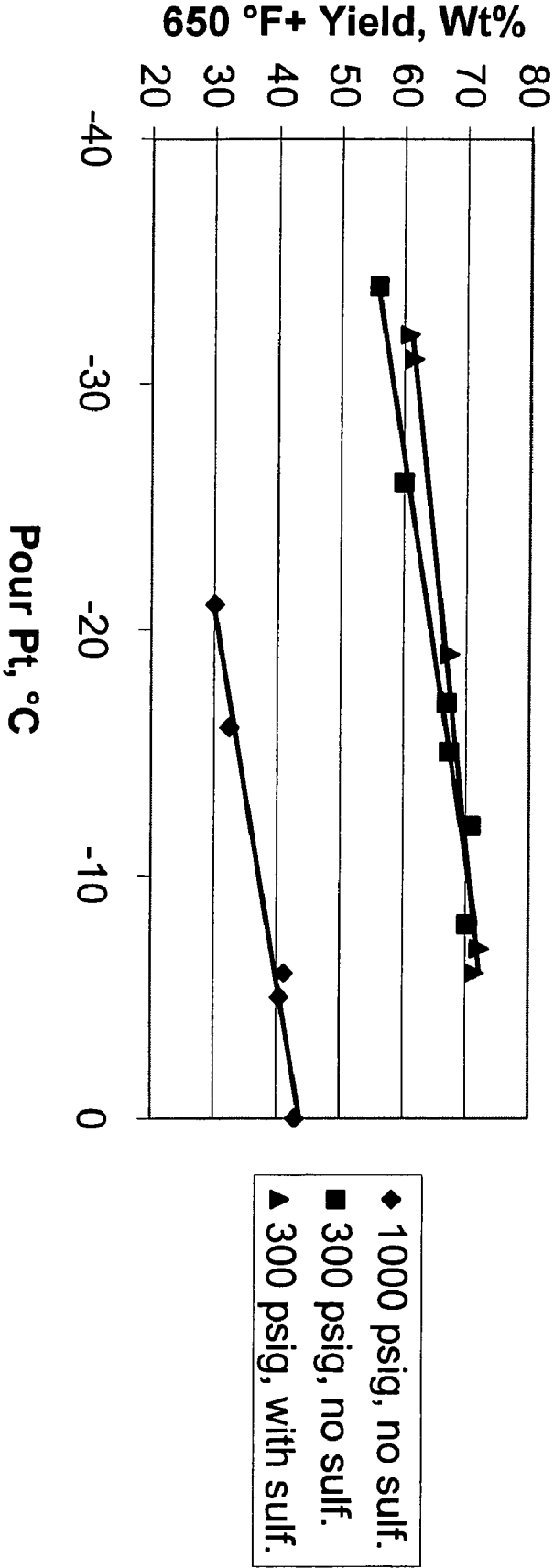


Fig. 4
Viscosity Index of a Hydroisomerized Fischer-Tropsch Wax Using a SAPO-11 Catalyst

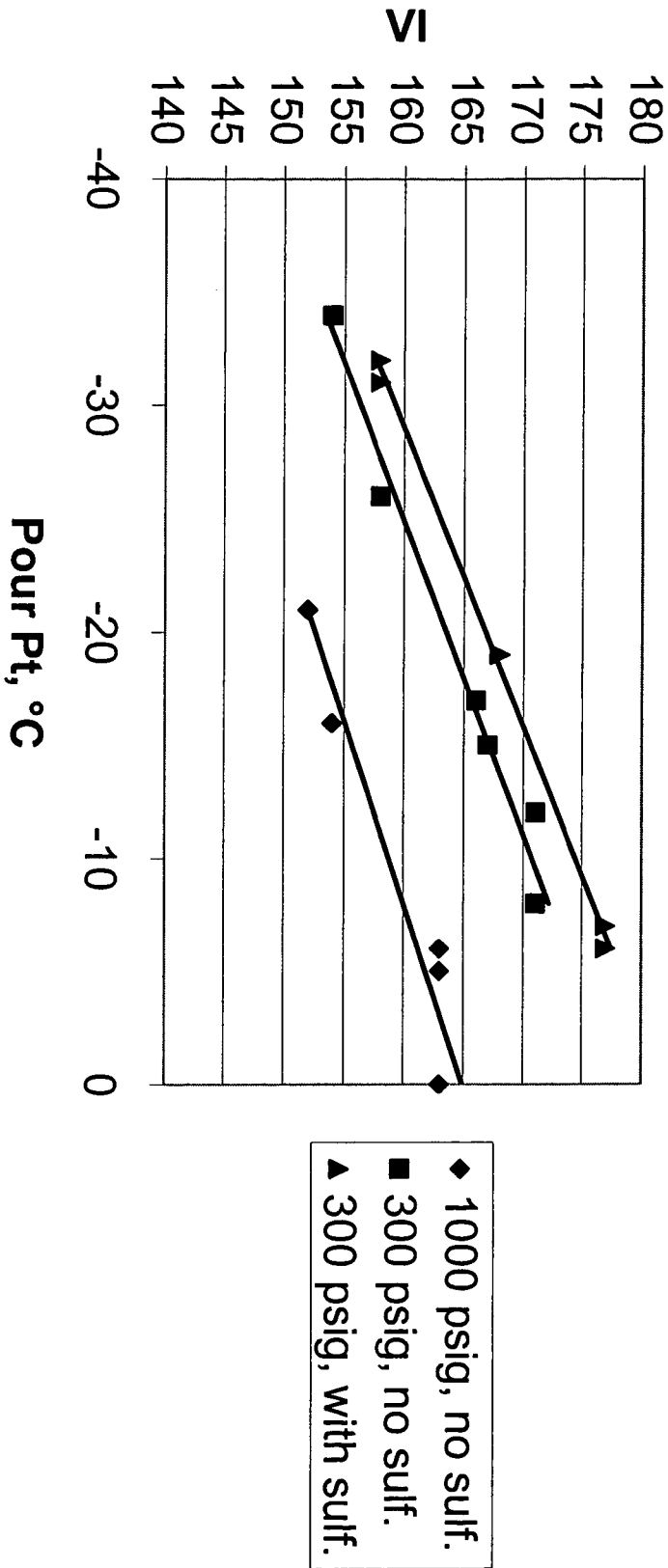


Fig. 5
Hydroisomerization Yield of a Fischer-Tropsch
Wax Using a SSZ-32 Catalyst

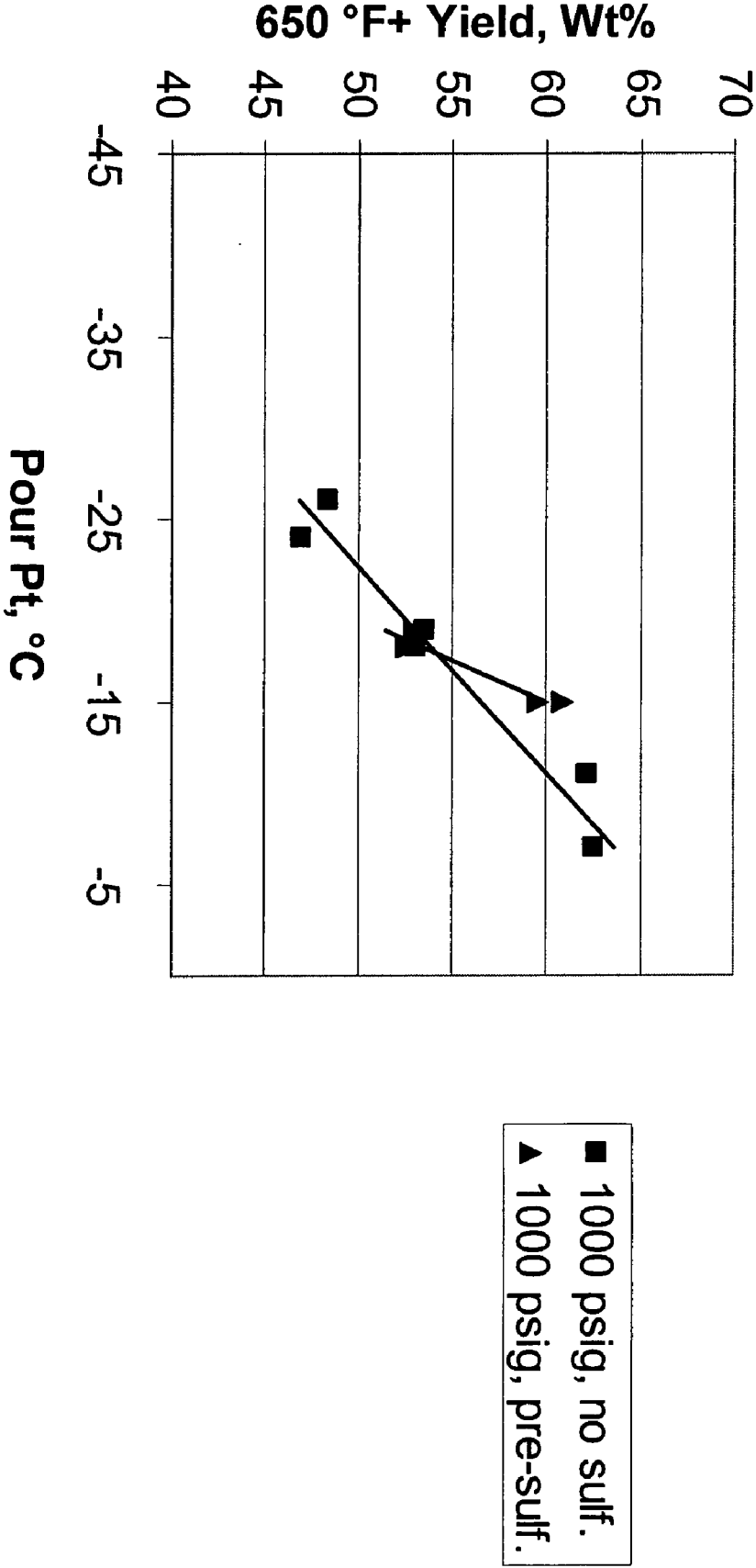


Fig. 6
Viscosity Index of a Hydroisomerized Fischer-Tropsch Wax Using a SSZ-32 Catalyst

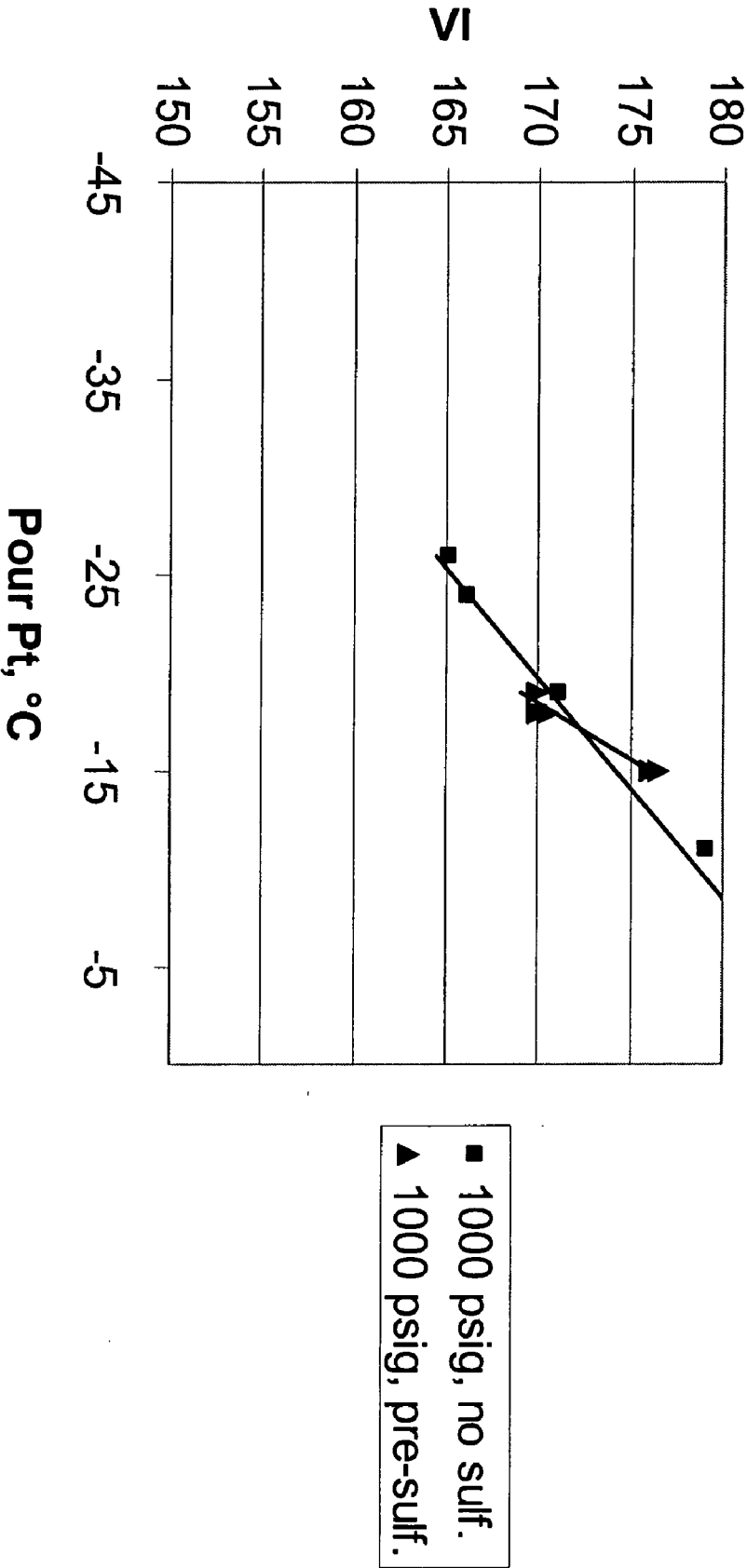


Fig. 7
i/n C4 Ratio vs. Time, (Sulfide at 150 Hrs) over
SAP0-11 Catalyst at 1000 psig

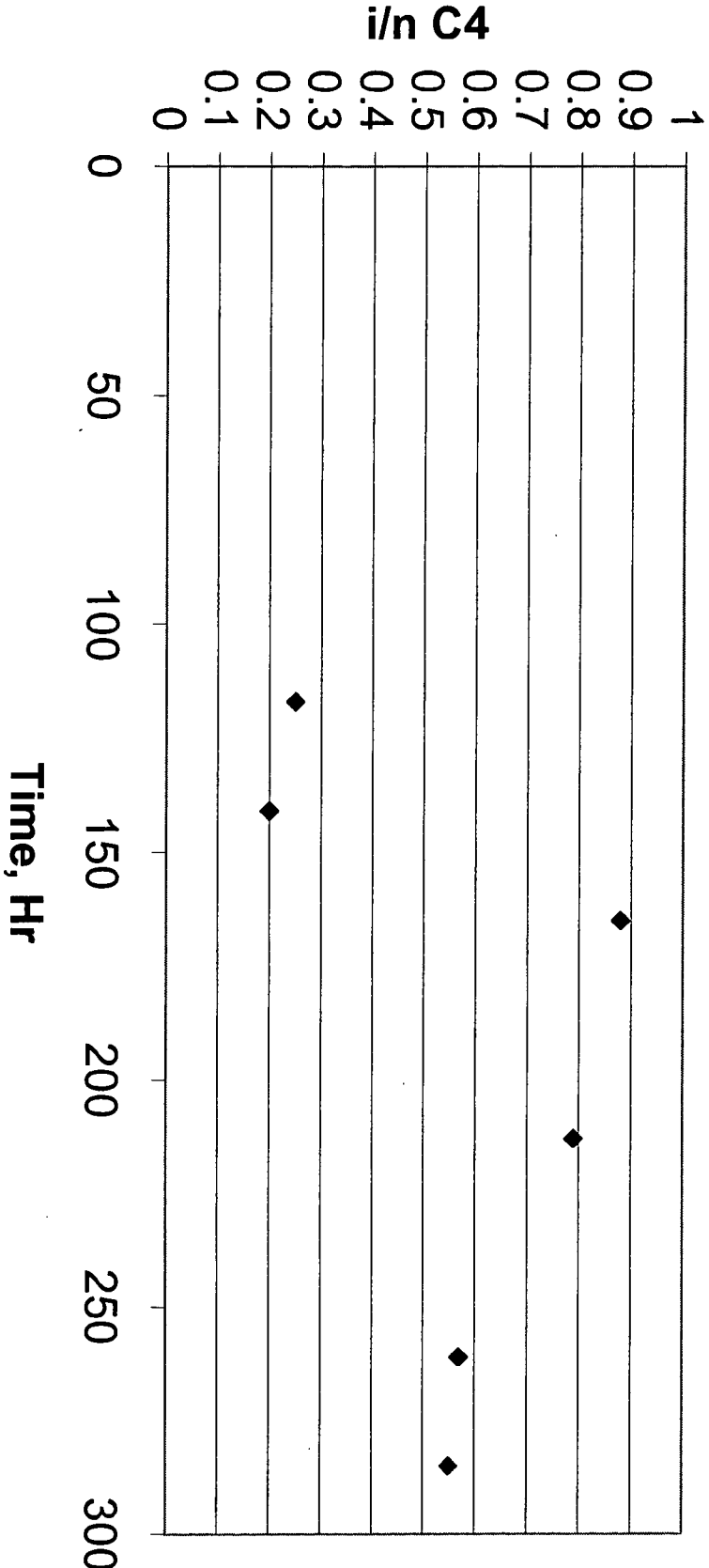


Fig. 8
Effect of Pre-Sulfiding SAPO-11 Catalyst on the
Amounts of Light Hydrocarbons Produced at 1000
psig and 650 °F

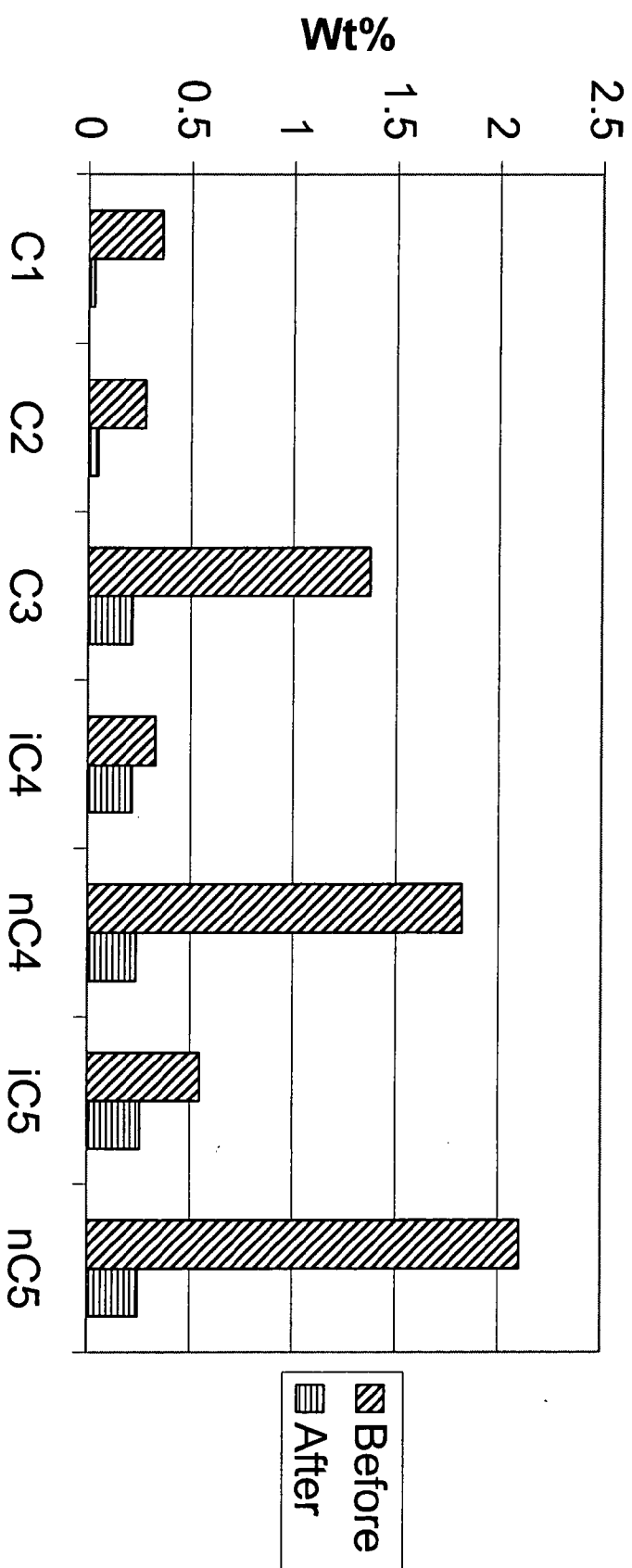


Fig. 9A
Yield for Isomerization Dewaxing of FT Wax Over
SAPO-11 Catalyst

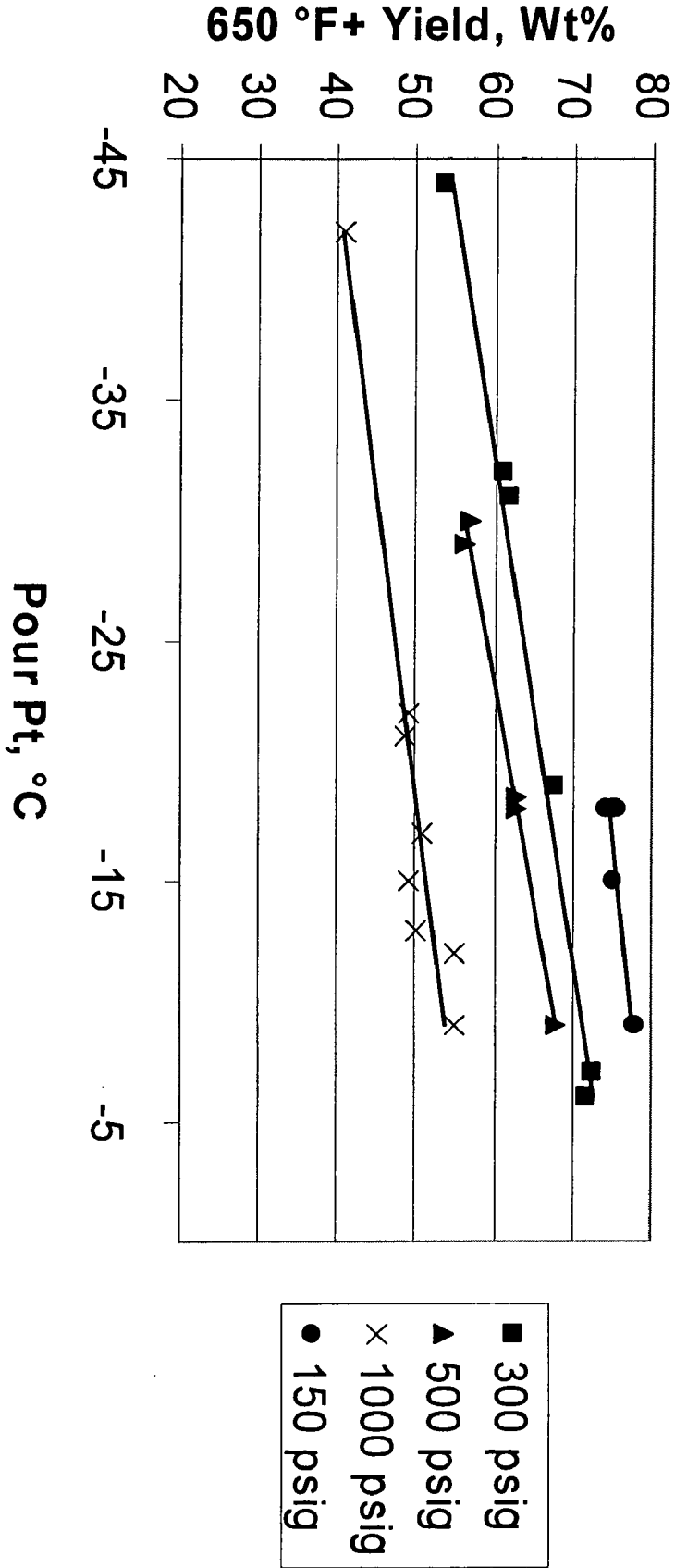


Fig. 9B
VI for Isomerization Dewaxing of FT Wax Over
SAPO-11 Catalyst

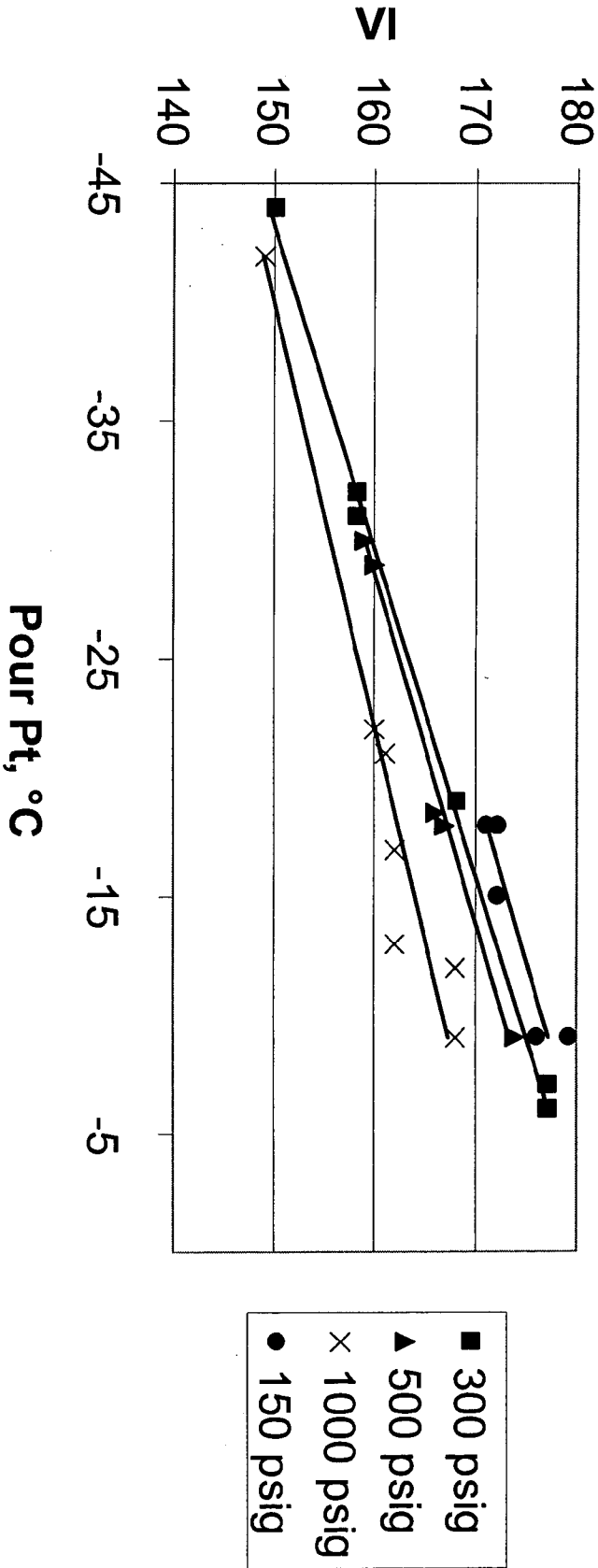
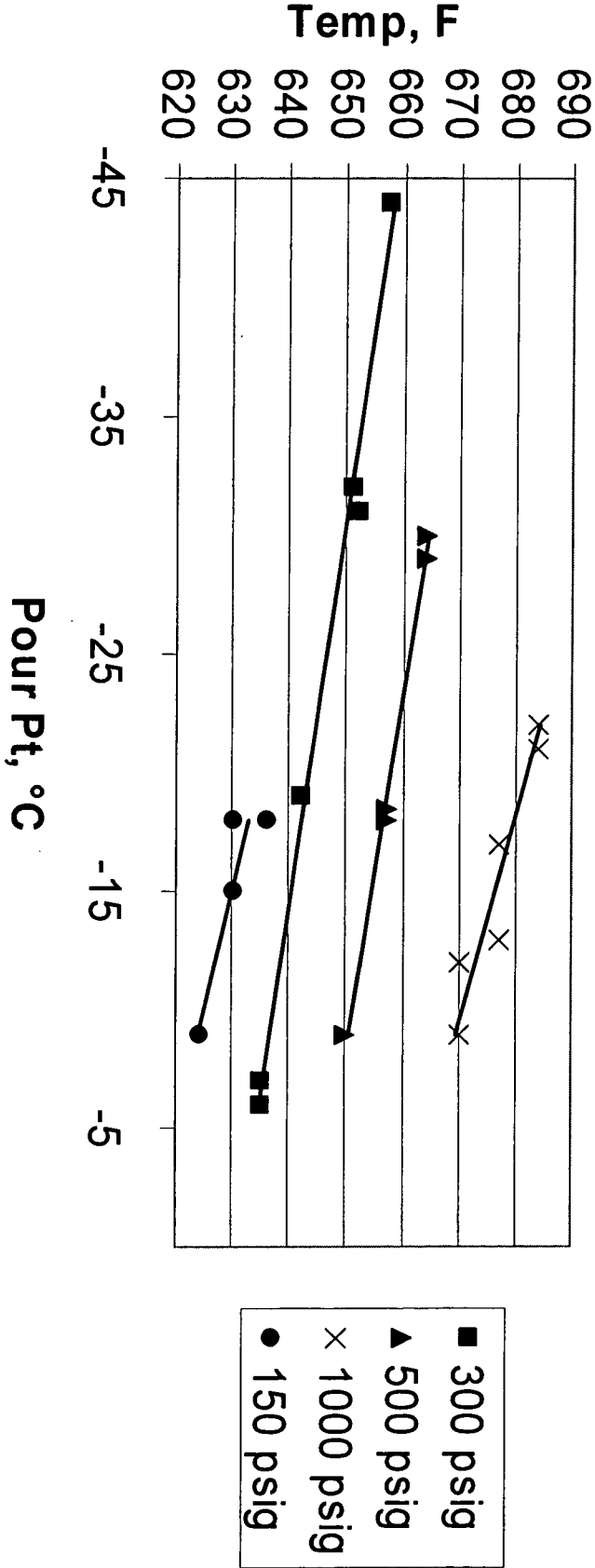


Fig. 9C
Temperature for Isomerization Dewaxing of FT
Max over SAPO-11 Catalyst



HYDROISOMERIZATION PROCESSES USING PRE-SULFIDED CATALYSTS

REFERENCE TO RELATED APPLICATIONS

[0001] The present application is related to and hereby incorporates by reference in its entirety U.S. patent application Ser. No. _____ (Docket No. 005950-827), entitled "Hydroisomerization Processes Using Re-Sulfided Catalysts," which is filed herewith.

FIELD OF THE INVENTION

[0002] The present invention relates in general to the production of Fischer-Tropsch derived lubricant base oils. More specifically, the present invention is directed toward using pre-sulfided, shape selective, intermediate pore size, noble metal-containing molecular sieve catalysts to produce lubricant base oils, having high viscosity indexes and low pour points, in high yield.

BACKGROUND OF THE INVENTION

[0003] Refining operations that produce large quantities of high-quality lubricant base oils are desirable. The demand placed on refineries for producing the high-quality lubricant base oils in the operation of modern machinery and automobiles is increasing. Many refining processes tend to produce large quantities of lighter grade products at the expense of producing lubricant base oil products.

[0004] It is well known in the art to produce lubricant base oils using hydroisomerization processes. For example, U.S. Pat. Nos. 5,135,638 and 5,082,986 disclose highly shape selective catalysts for hydroisomerizing waxy feeds. U.S. Pat. No. 5,135,638 discloses that low pressure hydroisomerization dewaxing and low liquid hourly space velocity provide enhanced isomerization selectivity, which results in more isomerization and less cracking of the feed, thus producing an increased yield. Accordingly, U.S. Pat. No. 5,135,638 discloses that the yield of lubricant base oil products obtained may be enhanced by lowering the pressure at which a hydroisomerization process is carried out.

[0005] It is also well known in the art to use base metal catalysts and noble metal catalysts in hydroisomerization processes. These catalysts may be used on molecular sieve supports. By way of example, U.S. Pat. No. 5,885,438 discloses a process for producing a high viscosity index lubricant from a waxy hydrocarbon feed comprising catalytically dewaxing waxy paraffins present in the feed by isomerization in the presence of hydrogen and in the presence of a low acidity large pore zeolite isomerization catalyst. The catalysts of U.S. Pat. No. 5,885,438 comprise a noble metal hydroisomerization catalyst, such as Pt. U.S. Pat. No. 5,885,438 further discloses that platinum or palladium catalysts have good hydrogenation activity, but only in the absence of sulfur.

[0006] There remains a need for effective and efficient methods for producing high yields of high quality lubricant base oil from a waxy hydrocarbon feed.

SUMMARY OF THE INVENTION

[0007] Embodiments of the present invention are directed toward methods for producing high yields of lubricant base oil from a waxy hydrocarbon feed. In one embodiment, the

method comprises pre-sulfiding a shape selective, intermediate pore size, noble metal-containing molecular sieve catalyst to provide a sulfided catalyst. The molar ratio of sulfur to noble metal in the sulfided catalyst is greater than one. The waxy hydrocarbon feed is hydroisomerized by contacting the waxy hydrocarbon feed with the sulfided catalyst at hydroisomerization conditions, to produce a lubricant base oil.

[0008] In another embodiment, a process for producing a lubricant base oil comprises contacting a shape selective, intermediate pore size, noble-metal containing molecular sieve catalyst with a sulfur-containing species to provide a pre-sulfided catalyst. The molar ratio of sulfur to noble metal in the pre-sulfided catalyst is greater than one. A Fischer-Tropsch waxy hydrocarbon feed is provided. The Fischer-Tropsch waxy hydrocarbon feed is contacted with the pre-sulfided catalyst to hydroisomerize the feed, and a lubricant base oil is isolated.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] FIGS. 1-2 illustrate the effect on yield and viscosity index of using a sulfided SAPO-11 catalyst to hydroisomerize a Fischer-Tropsch waxy feed at 1,000 psig.

[0010] FIGS. 3-4 illustrate the effect on yield and viscosity index of using a sulfided SAPO-11 catalyst to hydroisomerize a Fischer-Tropsch waxy feed at different pressures.

[0011] FIGS. 5-6 illustrate the effect on yield and viscosity index of using a sulfided zeolite catalyst to hydroisomerize a Fischer-Tropsch waxy feed at 1,000 psig.

[0012] FIG. 7 illustrates the effect on the iso-to-normal C₄ ratio of using an on-stream sulfided SAPO catalyst.

[0013] FIG. 8 illustrates the effect on the amounts of light hydrocarbons produced using a pre-sulfided SAPO catalyst.

[0014] FIGS. 9A-C illustrate the effect on yield, viscosity index, and temperature of using a pre-sulfided SAPO catalyst to hydroisomerize a Fischer-Tropsch waxy feed at different pressures.

DETAILED DESCRIPTION OF THE INVENTION

[0015] According to the method of the present invention, it has been surprisingly discovered that pre-sulfiding a shape selective, intermediate pore size, noble metal-containing molecular sieve catalyst improves selectivity of hydroisomerization over hydrocracking, thus increasing the yield of a lubricant base oil produced. Accordingly, contacting a waxy hydrocarbon feed with a pre-sulfided shape selective, intermediate pore size, noble metal-containing molecular sieve catalyst produces a high yield of a high quality lubricant base oil.

[0016] Catalyst Sulfiding

[0017] It has been discovered that hydroisomerization selectivity (the preference for isomerization reactions over cracking reactions) for shape selective, intermediate pore size, noble metal-containing molecular sieve catalysts is improved when the catalyst is sulfided. According to the present invention, preferably the catalyst is sulfided prior to conducting the hydroisomerization reaction. A noble metal is any metal that is resistant to corrosion or oxidation. A

noble-metal containing catalyst is any catalyst containing a noble metal. Noble metals catalysts include platinum, palladium and mixtures thereof.

[0018] According to the present invention, the shape selective, intermediate pore size, noble metal-containing molecular sieve catalyst for conducting the hydroisomerization process is sulfided. The catalyst may be sulfided at various stages in the hydroisomerization process. The catalyst may be sulfided prior to conducting the hydroisomerization reaction. According to the present invention, the process for sulfiding is termed catalyst "pre-sulfiding" if performed prior to introducing the waxy feed into the reactor for conducting the hydroisomerization process. The process for sulfiding is termed "on-stream sulfiding" if performed after the hydroisomerization reaction has been initiated. The on-stream sulfiding process may be conducted concurrently with the hydroisomerization process by using a feed for the hydroisomerization process that comprises the required sulfur for sulfiding. In the alternative, the on-stream sulfiding process may be conducted by pausing the hydroisomerization reaction process, sulfiding the catalyst, and then resuming the hydroisomerization reaction process. If the hydroisomerization process is paused, the sulfiding of the catalyst may be conducted by the same techniques employed for pre-sulfiding of the catalyst. The process for sulfiding is termed "re-sulfiding" if the catalyst that was initially pre-sulfided or sulfided in a previous on-stream sulfiding step is then again subjected to a sulfiding process. The re-sulfiding may be conducted concurrently with the hydroisomerization process or by pausing the hydroisomerization process, as described above for on-stream sulfiding. According to the present invention, preferably the catalyst is pre-sulfided.

[0019] According to the present invention, the sulfiding of the shape selective, intermediate pore size, noble metal-containing molecular sieve catalyst may be carried out by techniques known to those of skill in the art for sulfiding catalysts. By way of example, the catalyst may be sulfided by contacting the catalyst with a sulfur-containing species, usually in the presence of hydrogen. Mixtures of hydrogen and hydrogen sulfide, carbon disulfide or a mercaptan such as butyl mercaptan are conventionally used for sulfiding. Sulfiding may be carried out by contacting the catalyst with hydrogen and a sulfur-containing hydrocarbon oil (called a non-spiked feedstock) such as a sour kerosene or gas oil, or it may be accomplished by adding active sulfur to the waxy hydrocarbon feed (referred to as a sulfur spiked feedstock).

[0020] In particular, pre-sulfiding may be accomplished by techniques well-known to those of skill in the art. Procedures have been developed by those skilled in the art to pre-sulfide fresh catalyst charges for fixed bed reactor systems in-situ at the start of each run. These procedures normally involve a gas heat up step and catalyst drying step in the reactor vessel, followed by catalyst wetting/soaking with startup oil, and then subsequently sulfiding in a step that employs either non-spiked feedstock (a feedstock containing naturally occurring sulfur compounds) or a sulfur spiked feedstock (a feedstock to which active sulfur compounds are added). Alternatively, the sulfiding step may employ H_2/H_2S to sulfide the catalyst in the vapor phase. Exemplary sulfiding techniques known in the art have been discussed by Harman Hallie at a catalyst symposium in Amsterdam, May 1982, and published in the Dec. 20, 1982, issue of Oil and Gas Journal. Another description appears in

a paper entitled "Properties and Application of Commercial Presulfiding Agents," by William J. Tuzynski, presented at the 1989 NPRA Meeting.

[0021] According to embodiments of the present invention, sulfiding the catalyst comprises the addition of at least one mole of sulfur per mole of noble metal contained in the catalyst, preferably, platinum and/or palladium. The noble metal is dispersed within the shape selective, intermediate pore size, noble metal-containing molecular sieve catalyst. It is to be understood by those skilled in the art that the number of moles of metal in the catalyst is calculated by computing the grams of catalyst times the weight percent of the metal, divided by the molecular weight of the metal. In a preferred embodiment, the molar ratio of sulfur to noble metal is at least 3:1. In an example of this embodiment, sufficient sulfur is added in a pre-sulfiding treatment step to result in a molar ratio of sulfur to noble metal of at least 2:1. During the course of the hydroisomerization process, additional sulfur is added to the catalyst to result in a molar ratio of sulfur to noble metal of at least 3:1. In another embodiment, the ratio is 5:1.

[0022] Generally, pre-sulfiding techniques that make use of non-spiked feedstocks involve decomposition of sulfur compounds into H_2S , where the sulfur compounds are naturally present in a selected startup hydrocarbon feed. The reactor temperatures in these techniques generally range from about 300 to 350° C. (572 to 662° F.). In contrast, pre-sulfiding techniques that make use of spiked feedstocks can be carried out by injecting active, sulfur-containing organic compounds into a selected startup hydrocarbon feed such that the injected compounds decompose into H_2S at temperatures lower than those that would be required to decompose naturally occurring sulfur compounds (if present). Preferred spiking agents are dimethylsulfide and dimethyldisulfide as these compounds allow sulfiding procedures to be accomplished at temperatures ranging from about 250 to 275° C.

[0023] Pre-sulfiding and startup procedures are tailored to maintain the quality of the initial waxy hydrocarbon feed and reactor temperature conditions such that the sulfiding and hydrogenation reactions do not create deleterious temperature conditions in the interior of catalyst pellets. Such deleterious temperature conditions may result in carbon deposition or metal sintering, both of which reduce catalyst activity and thus are undesirable. The severity of the hydrogenation reactions that occur during the initial catalyst conditioning and sulfiding period is limited by the quality of the initial waxy hydrocarbon feed (e.g., the sulfur content) and reactor temperatures, which persist until the sulfiding reactions diminish or essentially stop. Present day state of the art techniques allow in-situ presulfiding to be initiated at temperatures below about 200° C. (392° F.) and are completed before temperatures are elevated above about 300° C. (572° F.).

[0024] Techniques are known for pretreating catalysts by impregnation with a sulfur compound (e.g., a polysulfide, as described in U.S. Pat. No. 5,786,293) before the catalysts are charged to the reactor. This is termed ex-situ presulfiding. When using ex-situ presulfiding, the catalyst may still need to undergo drying, wetting, and conversion to a metal sulfide state in-situ within the reactor during startup procedures. An economical method for ex-situ presulfiding of fresh batches

of catalyst, which are to be added to an on-stream reactor operating at elevated temperatures and hydrogen pressures, is disclosed in U.S. Patent Application 2002/0043483, the contents of which is hereby incorporated by reference in its entirety.

[0025] Waxy Hydrocarbon Feeds

[0026] Feeds useful in the hydroisomerization processes according to the present invention are waxy hydrocarbons including gas oil, lubricating oil stock, synthetic oil, Fischer-Tropsch derived wax, oligomerized Fischer-Tropsch derived olefins, foots oil, slack wax, de-oiled wax, normal alpha olefin wax, microcrystalline wax, and mixtures thereof. The preferred feeds are Fischer-Tropsch derived wax, slack wax, de-oiled wax, normal alpha olefin wax, and oligomerized Fischer-Tropsch derived olefins. Fischer-Tropsch derived waxes are especially preferred feedstocks.

[0027] In some embodiments of the present invention it is desirable to use waxy hydrocarbon feeds containing less than 10 ppm sulfur. Accordingly, waxy hydrocarbon feeds that contain high levels of sulfur (greater than 10 ppm) are preferably hydrotreated prior to the hydroisomerization reaction to remove sulfur. Therefore, waxy hydrocarbon feeds having low amounts of sulfur, preferably less than 10 ppm sulfur, are preferred. These low sulfur feeds include Fischer-Tropsch derived wax, oligomerized Fischer-Tropsch derived olefins, normal alpha olefin wax, and slack wax derived from hydroprocessed feeds.

[0028] The waxy hydrocarbon feed contains at least 10 wt % wax, and often contains greater than 50 wt % wax, and often greater than 80 wt % wax.

[0029] Fischer-Tropsch Synthesis

[0030] Preferably, the waxy hydrocarbon feed of the present invention is derived from a Fischer-Tropsch waxy feed.

[0031] In Fischer-Tropsch chemistry, syngas is converted to liquid hydrocarbons by contact with a Fischer-Tropsch catalyst under reactive conditions. Typically, methane and optionally heavier hydrocarbons (ethane and heavier) can be sent through a conventional syngas generator to provide synthesis gas. Generally, synthesis gas contains hydrogen and carbon monoxide, and may include minor amounts of carbon dioxide and/or water. The presence of sulfur, nitrogen, halogen, selenium, phosphorus and arsenic contaminants in the syngas is undesirable. For this reason and depending on the quality of the syngas, it is preferred to remove sulfur and other contaminants from the feed before performing the Fischer-Tropsch chemistry. Means for removing these contaminants are well known to those of skill in the art. For example, ZnO guardbeds are preferred for removing sulfur impurities. Means for removing other contaminants are well known to those of skill in the art. It also may be desirable to purify the syngas prior to the Fischer-Tropsch reactor to remove carbon dioxide produced during the syngas reaction and any additional sulfur compounds not already removed. This can be accomplished, for example, by contacting the syngas with a mildly alkaline solution (e.g., aqueous potassium carbonate) in a packed column.

[0032] In the Fischer-Tropsch process, contacting a synthesis gas comprising a mixture of H_2 and CO with a

Fischer-Tropsch catalyst under suitable temperature and pressure reactive conditions forms liquid and gaseous hydrocarbons. The Fischer-Tropsch reaction is typically conducted at temperatures of about 300-700° F. (149-371° C.), preferably about 400-550° F. (204-228° C.); pressures of about 10-600 psia, (0.7-41 bars), preferably about 30-300 psia, (2-21 bars); and catalyst space velocities of about 100-10,000 cc/g/hr, preferably about 300-3,000 cc/g/hr. Examples of conditions for performing Fischer-Tropsch type reactions are well known to those of skill in the art.

[0033] The products of the Fischer-Tropsch synthesis process may range from C_1 to C_{200+} with a majority in the C_5 to C_{100+} range. The reaction can be conducted in a variety of reactor types, such as fixed bed reactors containing one or more catalyst beds, slurry reactors, fluidized bed reactors, or a combination of different type reactors. Such reaction processes and reactors are well known and documented in the literature.

[0034] The slurry Fischer-Tropsch process, which is preferred in the practice of the invention, utilizes superior heat (and mass) transfer characteristics for the strongly exothermic synthesis reaction and is able to produce relatively high molecular weight, paraffinic hydrocarbons when using a cobalt catalyst. In the slurry process, a syngas comprising a mixture of hydrogen and carbon monoxide is bubbled up as a third phase through a slurry which comprises a particulate Fischer-Tropsch type hydrocarbon synthesis catalyst dispersed and suspended in a slurry liquid comprising hydrocarbon products of the synthesis reaction which are liquid under the reaction conditions. The mole ratio of the hydrogen to the carbon monoxide may broadly range from about 0.5 to about 4, but is more typically within the range of from about 0.7 to about 2.75 and preferably from about 0.7 to about 2.5. A particularly preferred Fischer-Tropsch process is taught in EP0609079, also completely incorporated herein by reference for all purposes.

[0035] In general, Fischer-Tropsch catalysts contain a Group VIII transition metal on a metal oxide support. The catalysts may also contain a noble metal promoter(s) and/or crystalline molecular sieves. Suitable Fischer-Tropsch catalysts comprise one or more of Fe, Ni, Co, Ru and Re, with cobalt being preferred. A preferred Fischer-Tropsch catalyst comprises effective amounts of cobalt and one or more of Re, Ru, Pt, Fe, Ni, Th, Zr, Hf, U, Mg and La on a suitable inorganic support material, preferably one which comprises one or more refractory metal oxides. In general, the amount of cobalt present in the catalyst is between about 1 and about 50 weight percent of the total catalyst composition. The catalysts can also contain basic oxide promoters such as ThO_2 , La_2O_3 , MgO, and TiO_2 , promoters such as ZrO_2 , noble metals (Pt, Pd, Ru, Rh, Os, Ir), coinage metals (Cu, Ag, Au), and other transition metals such as Fe, Mn, Ni, and Re. Suitable support materials include alumina, silica, magnesia and titania or mixtures thereof. Preferred supports for cobalt containing catalysts comprise titania. Useful catalysts and their preparation are known and illustrated in U.S. Pat. No. 4,568,663, which is intended to be illustrative but non-limiting relative to catalyst selection.

[0036] Certain catalysts are known to provide chain growth probabilities that are relatively low to moderate, and the reaction products include a relatively high proportion of low molecular (C_{2-8}) weight olefins and a relatively low

proportion of high molecular weight (C_{30+}) waxes. Certain other catalysts are known to provide relatively high chain growth probabilities, and the reaction products include a relatively low proportion of low molecular (C_{2-8}) weight olefins and a relatively high proportion of high molecular weight (C_{30+}) waxes. Such catalysts are well known to those of skill in the art and can be readily obtained and/or prepared.

[0037] The product from a Fischer-Tropsch process contains predominantly paraffins. The products from Fischer-Tropsch reactions generally include a light reaction product and a waxy reaction product. The light reaction product (i.e., the condensate fraction) includes hydrocarbons boiling below about 700° F. (e.g., tail gases through middle distillate fuels), largely in the C_5 - C_{20} range, with decreasing amounts up to about C_{30} . The waxy reaction product includes hydrocarbons boiling above about 600° F. (e.g., vacuum gas oil through heavy paraffins), largely in the C_{20+} range, with decreasing amounts down to C_{10} .

[0038] Both the light reaction product and the waxy product are substantially paraffinic. The waxy product generally comprises greater than 70 weight percent normal paraffins, and often greater than 80 weight percent normal paraffins. The light reaction product comprises paraffinic products with a significant proportion of alcohols and olefins. In some cases, the light reaction product may comprise as much as 50 weight percent, and even higher, alcohols and olefins. It is the waxy reaction product (i.e., the wax fraction) that may be used as a feedstock for the processes of the present invention.

[0039] According to the present invention, lubricant base oils may be prepared by hydroisomerizing waxy Fischer-Tropsch reaction products. Other processes that may be used in preparing lubricant base oils from waxy Fischer-Tropsch reaction products include hydrotreating, oligomerization, solvent dewaxing, atmospheric and vacuum distillation, hydrocracking, hydrofinishing, and other forms of hydroprocessing.

[0040] Hydroisomerization

[0041] According to the present invention, the waxy hydrocarbon feeds are subjected to a hydroisomerization process using sulfided shape selective, intermediate pore size, noble metal-containing molecular sieve catalysts. Hydroisomerization is intended to improve the cold flow properties of a lubricant base oil by selective addition of branching into the molecular structure. Hydroisomerization ideally will achieve high conversion of a waxy hydrocarbon feed to non-waxy iso-paraffins while minimizing conversion by cracking.

[0042] According to the present invention, hydroisomerization is conducted using a shape selective, intermediate pore size, noble metal-containing molecular sieve catalyst. The phrase "intermediate pore size," as used herein means an effective pore aperture in the range of from about 4.0 to 7.1 Å when the porous inorganic oxide is in the calcined form. The shape selective intermediate pore size molecular sieves used in the practice of the present invention are generally 1-D 10-, 11- or 12-ring molecular sieves. The preferred molecular sieves of the invention are of the 1-D 10-ring variety, where 10-(or 11-or 12-) ring molecular sieves have 10 (or 11 or 12) tetrahedrally-coordinated atoms

(T-atoms) joined by oxygens. In the 1-D molecular sieve, the 10-ring (or larger) pores are parallel with each other, and do not interconnect. The classification of intrazeolite channels as 1-D, 2-D and 3-D is set forth by R. M. Barrer in *Zeolites, Science and Technology*, edited by F. R. Rodrigues, L. D. Rollman and C. Naccache, NATO ASI Series, 1984 which classification is incorporated in its entirety by reference (see particularly page 75).

[0043] The shape selective, intermediate pore size, noble metal-containing molecular sieve catalysts according to the present invention may be zeolitic molecular sieves, non-zeolitic molecular sieves, or mixtures thereof. Preferably, shape selective, intermediate pore size, noble metal-containing molecular sieve catalysts are non-zeolitic.

[0044] As used herein, non-zeolitic molecular sieve refers to a molecular sieve comprising a crystalline, three-dimensional microporous framework structure of tetrahedrally-bound AlO_2 and PO_2 oxide units, and optionally one or more metals in tetrahedral coordination with oxygen atoms. Preferably non-zeolitic molecular sieves are characterized by a three-dimensional microporous framework structure of AlO_2 , and PO_2 tetrahedral oxide units with a unit empirical formula on an anhydrous basis of:



[0045] wherein:

[0046] "M" represents at least one element, other than aluminum and phosphorous, which is capable of forming an oxide in tetrahedral coordination with AlO_2 and PO_2 oxide structural units in the crystalline molecular sieve; and

[0047] "x", "y", and "z" represent the mole fractions, respectively, of element "M", aluminum, and phosphorus, wherein "x" has a value equal to or greater than zero (0), and "y" and "z" each have a value of at least 0.01.

[0048] In a preferred embodiment, metallic element "M" is selected from the group consisting of arsenic, beryllium, boron, chromium, cobalt, gallium, germanium, iron, lithium, magnesium, manganese, silicon, titanium, vanadium, nickel, and zinc, more preferably selected from the group consisting of silicon, magnesium, manganese, zinc, and cobalt; and still more preferably silicon. As used herein, element "M" is considered to be a component of the non-zeolitic molecular sieve.

[0049] According to the present invention, preferred shape selective intermediate pore size molecular sieves used for hydroisomerization are non-zeolitic molecular sieves. Preferred shape selective intermediate pore size non-zeolitic molecular sieves are based upon aluminum phosphates (i.e., SAPO catalysts), such as SAPO-11, SAPO-31, and SAPO-41. SAPO-11 and SAPO-31 are more preferred, with SAPO-11 being even more preferred. SM-3 is a preferred shape selective intermediate pore size SAPO, which has a crystalline structure falling within that of the SAPO-11 molecular sieves. The preparation of SM-3 and its unique characteristics are described in U.S. Pat. Nos. 4,943,424 and 5,158,665.

[0050] In another embodiment of the present invention, zeolitic molecular sieve may be used. These include ZSM-

22, ZSM-23, ZSM-35, ZSM-48, ZSM-57, SSZ-32, offretite, and ferrierite, with SSZ-32 and ZSM-23 being preferred.

[0051] A preferred intermediate pore size molecular sieve is characterized by selected crystallographic free diameters of the channels, selected crystallite size (corresponding to selected channel length), and selected acidity. Desirable crystallographic free diameters of the channels of the molecular sieves are in the range of from about 4.0 to 7.1 Å, having a maximum crystallographic free diameter of not more than 7.1 and a minimum crystallographic free diameter of not less than 3.9 Å. Preferably the maximum crystallographic free diameter is not more than 7.1 and the minimum crystallographic free diameter is not less than 4.0 Å. Most preferably the maximum crystallographic free diameter is not more than 6.5 and the minimum crystallographic free diameter is not less than 4.0 Å. The crystallographic free diameters of the channels of molecular sieves are published in the "Atlas of Zeolite Framework Types", Fifth Revised Edition, 2001, by Ch. Baerlocher, W. M. Meier, and D. H. Olson, Elsevier, pp 10-15, which is incorporated herein by reference.

[0052] A particularly preferred intermediate pore size molecular sieve, which is useful in the present process is described, for example, in U.S. Pat. Nos. 5,135,638 and 5,282,958, the contents of which are hereby incorporated by reference in their entirety. In U.S. Pat. No. 5,282,958, such an intermediate pore size molecular sieve has a crystallite size of no more than about 0.5 microns and pores with a minimum diameter of at least about 4.8 Å and with a maximum diameter of about 7.1 Å. The catalyst has sufficient acidity so that 0.5 grams thereof when positioned in a tube reactor converts at least 50% of hexadecane at 370° C., a pressure of 1200 psig, a hydrogen flow of 160 ml/min, and a feed rate of 1 ml/hr. The catalyst also exhibits isomerization selectivity of 40 percent or greater (isomerization selectivity is determined as follows: $100 \times (\text{weight percent branched } C_{16} \text{ in product}) / (\text{weight percent branched } C_{16} \text{ in product} + \text{weight percent } C_{13-} \text{ in product})$ when used under conditions leading to 96% conversion of normal hexadecane (n-C₁₆) to other species.

[0053] Such a particularly preferred molecular sieve may further be characterized by pores or channels having a crystallographic free diameter in the range of from about 4.0 to 7.1 Å, and preferably in the range of 4.0 to 6.5 Å. The crystallographic free diameters of the channels of molecular sieves are published in the "Atlas of Zeolite Framework Types", Fifth Revised Edition, 2001, by Ch. Baerlocher, W. M. Meier, and D. H. Olson, Elsevier, pp 10-15, which is incorporated herein by reference.

[0054] If the crystallographic free diameters of the channels of a molecular sieve are unknown, the effective pore size of the molecular sieve can be measured using standard adsorption techniques and hydrocarbonaceous compounds of known minimum kinetic diameters. See Breck, Zeolite Molecular Sieves, 1974 (especially Chapter 8); Anderson et al., J. Catalysis 58, 114 (1979); and U.S. Pat. No. 4,440,871, the pertinent portions of which are incorporated herein by reference. In performing adsorption measurements to determine pore size, standard techniques are used. It is convenient to consider a particular molecule as excluded if does not reach at least 95% of its equilibrium adsorption value on the molecular sieve in less than about 10 minutes ($p/p_0 =$

0.5; 25° C). Intermediate pore size molecular sieves will typically admit molecules having kinetic diameters of 5.3 to 6.5 Å with little hindrance.

[0055] Hydroisomerization catalysts useful in the present invention comprise a catalytically active noble metal. The presence of a catalytically active noble metal leads to product improvement, especially viscosity index and stability. Typical catalytically active noble metals include platinum and palladium and mixtures thereof, with platinum preferred. If platinum and/or palladium is used, the total amount of active noble metal is typically in the range of 0.1 to 5 weight percent of the total catalyst, usually from 0.1 to 2 weight percent, and not to exceed 10 weight percent.

[0056] The refractory oxide support may be selected from those oxide supports, which are conventionally used for catalysts, including silica, alumina, silica-alumina, magnesia, titania and combinations thereof.

[0057] The conditions for hydroisomerization will be tailored to achieve a lubricant base oil with specific branching properties, as described above, and thus will depend on the characteristics of feed used. In general, conditions for hydroisomerization in the present invention are mild, such that the conversion of wax to materials boiling between about 650 and 1400° F. is maintained between 40 and 95 weight percent in producing the lubricant base oil.

[0058] Mild hydroisomerization conditions are achieved through operating at a lower temperature, generally between about 390 and 650° F. and a liquid hourly space velocity (LHSV) generally between about 0.5 and 20 hr⁻¹. The pressure is typically from about 15 to 2,500 psig, preferably from about 50 psig to 2,000 psig, more preferably from about 100 to 1,500 psig, even more preferably about 150 psig to 1,000 psig, and even more preferably about 250 to 600 psig. Using the sulfided, shape selective, intermediate pore size, noble metal containing molecular sieve catalysts, low pressure may provide enhanced isomerization selectivity, which results in more isomerization and less cracking of the feed, thus producing an increased yield. Exemplary processes are described in U.S. Pat. Nos. 5,135,638, 5,246,566, and 6,337,010, the contents of which are hereby incorporated by reference in their entirety.

[0059] In addition, using the sulfided, shape selective, intermediate pore size, noble metal containing molecular sieve catalysts according to the present invention, the hydroisomerization process may be conducted at higher pressures while maintaining acceptable yield and quality of the lubricant base oil product. In fact, the present invention provides a hydroisomerization process which may be conducted at relatively higher pressures and achieve an acceptable yield of a high quality lubricant base oil product. Conducting a hydroisomerization process using a sulfided, shape selective, intermediate pore size, noble metal containing molecular sieve catalyst provides an acceptable yield of a high quality lubricant base oil even at relatively high pressures. Although sulfiding the catalyst improves the yield of lubricant base oil produced when conducting the hydroisomerization reaction at both relatively high and relatively low pressures, the effect on yield of lubricant base oil product produced may be more pronounced when conducting the hydroisomerization at high pressure. Since there may be difficulties in operating the hydroisomerization process at relatively lower pressures, using the sulfided catalysts

according to the present invention surprisingly provides a process by which the hydroisomerization may be operated at a relatively higher pressure while achieving acceptable yield of a high quality lubricant base oil. Accordingly, in one embodiment it is preferable to conduct the hydroisomerization at relatively higher pressure (i.e., between about 500 and 1,000 psig).

[0060] Hydrogen is present in the reaction zone during the hydroisomerization process, typically in a hydrogen to feed ratio from about 0.5 to 30 MSCF/bbl (thousand standard cubic feet per barrel), preferably from about 1 to 10 MSCF/bbl. Hydrogen may be separated from the product and recycled to the reaction zone.

[0061] Solvent Dewaxing

[0062] According to the present invention, at least a portion of the lubricant base oil produced by the hydroisomerization process may be solvent dewaxed. Solvent dewaxing techniques are known in the art. Solvent dewaxing may be used to remove any residual waxy molecules by dissolving the waxy components into a solvent such as methyl ethyl ketone, methyl iso-butyl ketone, or toluene; precipitating the waxy components; and then removing the waxy components by filtration. Solvent dewaxing has been discussed in "Chemical Technology of Petroleum," 3rd Edition, by William Gruse and Donald Stevens (McGraw Hill, New York, 1960) pages 566-570. See also U.S. Pat. Nos. 4,477,333, 3,773,650, and 3,775,288.

[0063] According to the present invention, solvent dewaxing may be advantageously used to dewax at least a portion of the product from the hydroisomerization process to remove any residual unconverted waxy components following the isomerization step(s). The wax extracted from a solvent dewaxing process (referred to as "slack wax"), may be recycled to the hydroisomerization process of the present invention to obtain even higher lubricant base oil yields.

[0064] Hydrotreating and Hydrofinishing

[0065] Hydrotreating and hydrofinishing are optional processing steps that may also be included in the processes of the present invention. Hydrotreating may be conducted on the waxy hydrocarbon feed prior to the hydroisomerization process. Hydrotreating refers to a catalytic process, usually carried out in the presence of free hydrogen, the primary purpose of which is to remove various metal contaminants such as arsenic; heteroatoms such as sulfur and nitrogen, and aromatic compounds from the feedstock. Generally, it is desirable during a hydrotreating step to minimize the amount of cracking of hydrocarbon molecules (i.e., the breaking of larger molecules into smaller ones). During hydrotreating, unsaturated hydrocarbons are either fully or partially hydrogenated. The waxy hydrocarbon feed to the present process may be hydrotreated prior to hydroisomerization.

[0066] Catalysts used in carrying out hydrotreating operations are well known in the art. See, for example, U.S. Pat. No. 4,347,121 and 4,810,357, the contents of which are hereby incorporated by reference in their entirety, for general descriptions of hydrotreating and of typical catalysts used in this process. Suitable catalysts include noble metals from Group VIIIA (according to the 1975 rules of the International Union of Pure and Applied Chemistry), such as platinum or palladium on an alumina or siliceous matrix, and

Group VIII and Group VIB, such as nickel-molybdenum or nickel-tin on an alumina or siliceous matrix. U.S. Pat. No. 3,852,207 describes a suitable noble metal catalyst and mild conditions for carrying out the reaction. Other suitable catalysts are described, for example, in U.S. Pat. Nos. 4,157,294 and 3,904,513. The non-noble hydrogenation metals, such as nickel-molybdenum, are usually present in the final catalyst composition as oxides, but may be employed in their reduced or sulfided forms.

[0067] Preferred non-noble metal catalyst compositions contain in excess of about 5 weight percent, preferably about 5 to 40 weight percent, molybdenum and/or tungsten, and at least about 0.5 weight percent, and generally about 1 to 15 weight percent, of nickel and/or cobalt determined as the corresponding oxides. Catalysts containing noble metals, such as platinum, contain in excess of 0.01 percent metal; in some embodiments, between about 0.1 and 1.0 weight percent metal. Combinations of noble metals may also be used, such as mixtures of platinum and palladium.

[0068] Typical hydrotreating conditions vary over a wide range. In general, the overall LHSV is about 0.25 to 2.0 hr⁻¹, preferably about 0.5 to 1.0 hr⁻¹. Hydrogen partial pressure in hydrotreating may be greater than about 200 psia, preferably ranging from about 500 to 2,000 psia. Hydrogen recirculation rates are typically greater than about 50 SCF/Bbl, and are preferably between 1,000 and 5,000 SCF/Bbl. Temperatures in a hydrotreating reactor may range from about 300 to 750° F. (150 to 400° C.), preferably ranging from about 450 to 600° F. (230 to 315° C.).

[0069] Hydrofinishing is a hydrotreating process that may be conducted as a final step on the lubricant base oil product in the lubricant base oil manufacturing process. This final step is intended to improve the UV stability and appearance of the product by removing trace amounts of aromatics, olefins, color bodies, and solvents. As used in this disclosure, the term UV stability refers to the stability of the lubricant base oil or the finished lubricant when exposed to UV light and oxygen. Instability is indicated when a visible precipitate forms, usually seen as floc or cloudiness, or a darker color developing upon exposure to ultraviolet light and air. A general description of hydrofinishing may be found in U.S. Pat. Nos. 3,852,207 and 4,673,487. Clay treating to remove these impurities is an alternative final process step.

[0070] Oligomerization

[0071] The waxy hydrocarbon feed used in the processes of the present invention may include oligomerized Fischer-Tropsch derived olefins. Depending on the conditions under which the Fischer-Tropsch synthesis is carried out, the Fischer-Tropsch condensate will contain varying amounts of olefins. Additionally, most Fischer-Tropsch condensates will contain some alcohols, which may be readily converted into olefins by dehydration. As already noted, the condensate may also be olefin enriched through a cracking operation, preferably by thermal cracking. In one embodiment of the present invention these olefins may be oligomerized to produce Fischer-Tropsch derived olefins. During oligomerization the lighter olefins are not only converted into heavier molecules, but the carbon backbone of the oligomers will display branching at the points of molecular addition. Due to the introduction of branching into the molecule, the pour point of the products is reduced.

[0072] Oligomerization of olefins has been reported in the literature, and a variety of commercial processes are available. See, for example, U.S. Pat. Nos. 4,417,088, 4,434,308, 4,827,064, 4,827,073, and 4,990,709. Although various types of reactor configurations may be employed, the fixed catalyst bed reactor is commercially in use. More recently, a method of performing the oligomerization in an ionic liquid media has been proposed. Since oligomerization catalysts are very active and the contact between the catalyst and the reactants is efficient, the separation of the catalyst from the oligomerization products is facilitated.

[0073] Oligomerization reactions proceed over a wide range of conditions. Typical temperatures for carrying out the reaction range from about 32 to 800° F. (0 to 425° C.). Other conditions include a space velocity from 0.1 to 3 hr⁻¹ and a pressure ranging from about 0 to 2,000 psig. Catalysts for the oligomerization reaction may comprise virtually any acidic material, such as for example zeolites, clays, resins, BF₃ complexes, HF, H₂SO₄, AlCl₃, ionic liquids (preferably ionic liquids containing a Bronsted or Lewis acidic component or a combination of Bronsted and Lewis acid components), transition metal-based catalysts (such as Cr/SiO₂), superacids, and the like. In addition, non-acidic oligomerization catalysts including certain organometallic or transition metal oligomerization catalysts may be used, such as, for example, zirconocenes.

[0074] Lubricant Base Oil Products and Properties

[0075] Lubricant base oils made by the processes of the present invention are of high quality, as characterized by viscosity index and pour point of the lubricant base oil. Accordingly, the lubricant base oils have high viscosities, low pour points, and exceptionally high VI's.

[0076] Lubricant base oils having high viscosity indexes are desirable. Viscosity Index (VI) is an empirical, unitless number indicating the effect of temperature change on the kinematic viscosity of the oil. Liquids change viscosity with temperature, becoming less viscous when heated; the higher the VI of an oil, the lower its tendency to change viscosity with temperature. High VI lubricants are needed wherever relatively constant viscosity is required at widely varying temperatures. For example, in an automobile, engine oil must flow freely enough to permit cold starting, but must be viscous enough after warm-up to provide full lubrication. VI may be determined as described in ASTM D 2270-93. The lubricant base oils of the present invention have a high viscosity index ranging from about 140 to 190.

[0077] Pour point is the temperature at which a sample of the lubricant base oil will begin to flow under carefully controlled conditions. Where pour point is given herein, unless stated otherwise, it has been determined by standard analytical method ASTM D 5950-02. The lubricant base oils according to the present invention have excellent pour points. The pour points of the lubricant base oils are between about -5 and -60° C. Preferably, the pour points of the lubricant base oils are less than -9° C., more preferably $\leq$ -15° C., and even more preferably less than -15° C.

[0078] Cloud point is a measurement complementary to the pour point, and is expressed as a temperature at which a sample of the lubricant base oil begins to develop a haze under carefully specified conditions. Cloud point may be determined by, for example, ASTM D 5773-95. The lubri-

cant base oils with optimized branching according to the present invention have cloud points of less than 0° C.

[0079] In addition, the lubricant base oils of the present invention typically have high oxidation stability, high UV stability, low volatility and excellent low temperature properties. The lubricant base oils of the present invention have a kinematic viscosity between about 2 and 40 cSt at 100° C. Preferably the lubricant base oils of the present invention have a kinematic viscosity greater than 2.6 cSt at 100° C., more preferably greater than 3 cSt at 100° C.

[0080] The American Petroleum Institute (API) has classified base oils according to their chemical composition. As defined by the API, Group III oils are very high viscosity index oils (>120) having a total sulfur content less than 300 ppm and a saturates content of greater than or equal to 90%. API Group III oils also are traditionally manufactured by severe hydrocracking and or wax isomerization. Lubricant base oils of the present invention are generally classified as API Group III base oils. When they are made from waxy feeds with a low total sulfur content, such as a Fischer-Tropsch feeds, the lubricant base oils will also have a total sulfur content less than 300 ppm.

[0081] Lubricant base oils according to the present invention made from Fischer-Tropsch waxy feeds generally have total sulfur contents of less than about 5 ppm. Total sulfur is determined using ultraviolet fluorescence by ASTM D 5453-00.

[0082] Blends

[0083] The lubricant base oils of the present invention may be used alone or may be blended with additional base oils selected from the group consisting of conventional Group I base oils, conventional Group II base oils, conventional Group III base oils, isomerized petroleum wax, poly-alphaolefins (PAO), poly internal olefins (PIO), diesters, polyol esters, phosphate esters, alkylated aromatics, and mixtures thereof.

[0084] Since the lubricant base oils of the present invention have excellent cold flow properties, high VI's, and high oxidation stability, they are ideal blending stocks for upgrading conventional lubricant base oils.

[0085] It is preferred that when the lubricant base oils of the present invention are blended with one or more additional lubricant base oils, the additional base oils be present in an amount of less than 95 wt % of the total resultant base oil composition.

[0086] Finished Lubricants

[0087] Lubricant base oils are the most important component of finished lubricants, generally comprising greater than 70% of the finished lubricants. Finished lubricants comprise a lubricant base oil and at least one additive. Finished lubricants may be used in automobiles, diesel engines, axles, transmissions, and industrial applications. Finished lubricants must meet the specifications for their intended application as defined by the concerned governing organization.

[0088] The lubricant base oils of the present invention are useful in commercial finished lubricants. As a result of their excellent VI's and low temperature properties, the lubricant base oils of the present invention are suitable for formulating

finished lubricants intended for many of these applications. In addition, the excellent oxidation stability of the lubricant base oils of the present invention makes them useful in finished lubricants for many high temperature applications.

[0089] The lubricant base oils of the present invention are suitable for blending into a wide variety of finished lubricants, including but not limited to automotive engine oils, natural gas engine oils, automatic transmission fluid, industrial gear oils, turbine oils, textile oils, heat transfer oils, hydraulic oils, paper machine oils, spindle oils, rock drill oils, pump oils, compressor oils, way oils, and metalworking fluids. The lubricant base oils of the present invention may also be used as workover fluids, packer fluids, coring fluids, completion fluids, and in other oil field and well-servicing applications.

[0090] Additives, which may be blended with the lubricant base oil of the present invention, to provide a finished lubricant composition include those which are intended to improve select properties of the finished lubricant. Typical additives include, for example, anti-wear additives, EP agents, detergents, dispersants, antioxidants, pour point depressants, VI improvers, viscosity modifiers, friction modifiers, demulsifiers, antifoaming agents, corrosion inhibitors, rust inhibitors, seal swell agents, emulsifiers, wetting agents, lubricity improvers, metal deactivators, gelling agents, tackiness agents, bactericides, fluid-loss additives, colorants, and the like.

[0091] Other hydrocarbons, such as those described in U.S. Pat. Nos. 5,096,883 and 5,189,012, may be blended with the lubricant base oil provided that the finished lubricant has the necessary pour point, kinematic viscosity, flash point, and toxicity properties. These other hydrocarbons include base oils particularly useful in drilling fluids. By way of example, U.S. Pat. No. 5,096,883 relates to a substantially non-toxic base oil that consists essentially of branched-chain paraffins or branched-chain paraffins substituted with an ester functionality, or mixtures thereof, the base-oil preferably having between about 18 and about 40 carbon atoms per molecule and, more preferably, between about 18 and about 32 carbon atoms per molecule. U.S. Pat. No. 5,189,012 relates to synthetic hydrocarbons selected from the group consisting of branched chain oligomers synthesized from one or more olefins containing a C₂ to C₁₄ chain length and wherein the oligomers have an average molecular weight of from 120 to 1000.

[0092] Typically, the total amount of additives in the finished lubricant will be approximately 1 to about 30 weight percent of the finished lubricant. However, since the lubricant base oils of the present invention have excellent properties including low pour point, high VI's, and excellent oxidative stability, a lower amount of additives may be required to meet the specifications for the finished lubricant than is typically required with base oils made by other processes. The use of additives in formulating finished lubricants is well documented in the literature and well known to those of skill in the art.

EXAMPLES

[0093] The invention will be further explained by the following illustrative examples that are intended to be non-limiting.

[0094] Each of these examples were carried out in a continuous-flow, high-pressure pilot plant designed to hydroprocess waxy hydrocarbon feeds. The isomerization catalyst was laboratory prepared platinum on SAPO-11 and contained 15 weight percent Catapal alumina binder. The catalyst was crushed to 24-42 mesh prior to being loaded into the reactor. Process conditions included an LHSV of 1.0 hr⁻¹ over the isomerization catalyst, and a once-through H₂ rate of 5300 SCF/bbl. The entire effluent from the isomerization reactor was passed directly to a second reactor containing crushed Pt—Pd/SiO₂—Al₂O₃ hydrofinishing catalyst, run at 450° F. and LHSV of 2 hr⁻¹. The feed used for these examples was a hydrotreated, Fischer-Tropsch derived wax, and the properties of the feed (the hydrotreated Fischer-Tropsch wax) are as follows:

Gravity, API	40.3
Nitrogen, ppm	1.6
Sulfur, ppm	2
Sim. Dist., Wt %	Temperature (° F.)
St/5	512/591
10/30	637/708
50	764
70/90	827/911
95/EP	941/1047

[0095] In the following examples, the effectiveness of sulfiding the hydroisomerization catalyst was evaluated by measuring the 650° F.+yield (weight percent) and the viscosity index of the isomerized Fischer-Tropsch wax. It is known in the art that 650° F.+yield (weight percent) is the weight percent of the total product boiling above 650° F., and is defined or calculated at a particular pour point.

Example 1

Hydroisomerization Using a Sulfided SAPO Catalyst at 1,000 psig

[0096] This example illustrates the effect of sulfiding a SAPO-11 catalyst. In FIG. 1, the 650° F.+yield (weight percent) obtained when a Fischer-Tropsch derived wax was hydroisomerized is plotted as a function of pour point (° C.) for three situations: 1) when the SAPO 11 catalyst is not sulfided prior to the hydroisomerization reaction, 2) when the catalyst was pre-sulfided, and 3) when the catalyst was re-sulfided after being on-stream for 2040 hours. Each of the three experiments was conducted at a hydrogen partial pressure of 1,000 psig.

[0097] For comparative purposes, data points at a pour point of about -15° C. may be considered. The 650° F.+yield for the un-sulfided catalyst was about 32 weight percent, which increased to a yield of about 50 weight percent when the catalyst was pre-sulfided, representing an increase of about 18 weight percent. After re-sulfiding the catalyst, the yield increased an additional 15 weight percent, to about 65 weight percent.

[0098] The viscosity index was similarly enhanced with sulfiding, as shown in FIG. 2. At a pour point of -15° C., the viscosity index of the hydroisomerized wax increased from about 155 to 162 by pre-sulfiding the catalyst, and with

re-sulfiding after 2,040 hours on-stream, the viscosity index increased even further to about 172. This represents an absolute increase of about 7 by pre-sulfiding, and about 10 with re-sulfiding.

Example 2

Hydroisomerization Using a Sulfided SAPO Catalyst at Varying Pressures

[0099] The effects of sulfiding at two different pressures (and the effects of pressure without sulfiding), are shown in **FIGS. 3 and 4**. The 1,000 psig curves in **FIGS. 3 and 4** are the same as those in **FIGS. 1 and 2**; in other words, the 1,000 psig data has simply been re-plotted. Decreasing the hydrogen partial pressure from 1,000 to 300 psig during hydroisomerization results in a 650° F.+yield increase from about 35 to 68 weight percent, and an increase in viscosity index of about 155 to 168. Thus, this example shows that hydroisomerization yield and viscosity index are both enhanced as the hydroisomerization pressure is decreased.

[0100] Additionally, comparing **FIGS. 1 and 2** with **FIGS. 3 and 4** illustrate that sulfiding a SAPO-11 had a larger beneficial effect at higher pressures (e.g., 1,000 psig) than at lower pressures (e.g., 300 psig). Sulfiding the SAPO-11 catalyst had a modest effect on 650° F.+yield at 300 psig, and a modest effect on viscosity index (an increase of about 5), within the range of pour points plotted. Again, the pressures in this context refer to the hydrogen partial pressure within the hydroisomerization reactor, although the hydrogen partial pressure is substantially the same (or nearly the same) as the total pressure.

Example 3

Hydroisomerization Using a Sulfided Zeolite Catalyst

[0101] This example was conducted as described for Example 1, but using SSZ-32 as the catalyst. **FIG. 5** shows that the 650° F.+yield (weight percent) from Fischer-Tropsch wax hydroisomerized at 1,000 psig for both sulfided and un-sulfided SSZ-32 catalysts. The yield was about 55 (at a pour point of -15° C.). Likewise, the viscosity index was about 175.

Example 4

Hydroisomerization Using an On-Stream Sulfided SAPO Catalyst

[0102] The effect of on-stream sulfiding on the iso-to-normal C₄ ratio is shown in **FIG. 7**. In this example, a SAPO-11 catalyst was on-stream sulfided after 150 hours of a hydroisomerization process, and the iso-to-normal C₄ ratio plotted as a function of time. **FIG. 7** illustrates that on-stream sulfiding the catalyst resulted in the iso-to-normal C₄ ratio increasing from about 0.2 to over 0.8, representing a more than 4-fold increase. A higher iso-to-normal C₄ ratio indicates improved selectivity to isomerization, over cracking, reactions by the catalyst.

Example 5

Hydroisomerization Using a Pre-Sulfided SAPO Catalyst

[0103] The effect of pre-sulfiding a SAPO-11 catalyst on the amounts of light hydrocarbons produced by hydroi-

somerization is shown in **FIG. 8**. The total pressure in the reactor was 1,000 psig, and the temperature was 650° F. There is a substantial reduction in the amounts of normal-C₄ and normal-C₅, and much less of a decrease in the amounts of iso-C₄ and iso-C₅.

Example 6

Hydroisomerization Using a Pre-Sulfided SAPO Catalyst at Varying Temperature

[0104] **FIGS. 9A-C** illustrate some observed relationships between hydroisomerization temperatures and pressures. The graph in **FIG. 9C** is a plot of hydroisomerization temperature as a function of pour point for each of the four runs (at total pressures of 150, 300, 500, and 1,000 psig) shown in **FIGS. 9A and 9B**, the former figure reporting 650° F.+yield (weight percent) results, and the latter figure reporting viscosity index results. An advantage to producing lubricant base oils at low pressure, in addition to enhanced production yields and viscosity indexes with a sulfided SAPO catalyst according to the present embodiments, is that the hydroisomerization process may be accomplished at significantly lower operating temperatures than otherwise would have been the case.

[0105] Lowering the hydroisomerization reaction temperature provides a greater temperature range for the reaction to operate. Referring to **FIG. 9C**, for example, at a pour point of -15° C., the temperature required by the catalyst to properly hydroisomerize decreases by about 22° C. when the operating pressure is reduced from 1,000 to 500 psig. Under analogous conditions, the required temperature is decreased by about 37° C. when the operating pressure is reduced from 1,000 to 300 psig. Finally, the required temperature is decreased by about 47° C. when the operating pressure is reduced from 1,000 to 150 psig.

[0106] All of the publications, patents and patent applications cited in this application are herein incorporated by reference in their entirety to the same extent as if the disclosure of each individual publication, patent application or patent was specifically and individually indicated to be incorporated by reference in its entirety.

[0107] Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention. Other objects and advantages will become apparent to those skilled in the art from a review of the preceding description. Accordingly, the invention is to be construed as including all structure and methods that fall within the scope of the appended claims.

What is claimed is:

1. A method for producing a lubricant base oil from a waxy hydrocarbon feed, the method comprising:

- a) pre-sulfiding a shape selective, intermediate pore size, noble metal-containing molecular sieve catalyst to provide a sulfided catalyst, wherein the molar ratio of sulfur to noble metal in the sulfided catalyst is greater than one; and
- b) hydroisomerizing the waxy hydrocarbon feed by contacting the waxy hydrocarbon feed with the sulfided catalyst at hydroisomerization conditions, to produce a lubricant base oil.

2. The method of claim 1, wherein the molar ratio of sulfur to noble metal in the sulfided catalyst prior to the step of hydroisomerizing is at least 2:1, and wherein the molar ratio of sulfur to noble metal in the sulfided catalyst during the step of hydroisomerizing is at least 3:1.

3. The method of claim 1, wherein the molar ratio of sulfur to noble metal in the sulfided catalyst is at least 3:1.

4. The method of claim 1, wherein the molar ratio of sulfur to noble metal in the sulfided catalyst is at least 5:1.

5. The method of claim 1, wherein the waxy hydrocarbon feed is selected from the group consisting of gas oil, lubricating oil stock, synthetic oil, Fischer-Tropsch derived wax, oligomerized Fischer-Tropsch derived olefins, foos oil, slack wax, de-oiled wax, normal alpha olefin wax, microcrystalline wax, and mixtures thereof.

6. The method of claim 5, wherein the waxy hydrocarbon feed is a Fischer-Tropsch derived wax.

7. The method of claim 1, wherein the molecular sieve has channel diameters in the range of from about 4.0 to 7.1 Å.

8. The method of claim 1, wherein the molecular sieve is non-zeolitic.

9. The method of claim 8, wherein the catalyst is a SAPO catalyst.

10. The method of claim 9, wherein the SAPO catalyst is selected from the group consisting of SAPO-11, SAPO-31, and SAPO-41.

11. The method of claim 1, wherein the noble metal is selected from the group consisting of platinum, palladium, and mixtures thereof.

12. The method of claim 1, wherein the pre-sulfiding step comprises contacting the catalyst with a sulfur-containing species in the presence of hydrogen, the sulfur-containing species being selected from the group consisting of hydrogen sulfide, carbon disulfide, and a mercaptan.

13. The method of claim 12, wherein the waxy hydrocarbon feed contains less than about 10 ppm sulfur.

14. The method of claim 1, wherein the waxy hydrocarbon feed is a sulfur spiked feedstock.

15. The method of claim 1, wherein the hydroisomerization conditions include a total pressure of between about 150 and 1,000 psig.

16. The method of claim 15, wherein the hydroisomerization conditions include a total pressure of between about 150 and 500 psig.

17. The method of claim 16, wherein the hydroisomerization conditions include a total pressure of between about 150 and 300 psig.

18. The method of claim 15, wherein the hydroisomerization conditions include a total pressure of between about 500 and 1,000 psig.

19. The method of claim 1, wherein between about 40 and 95 weight percent of the lubricant base oil has a boiling point of between about 650 and 1400° F.

20. The method of claim 1, wherein the lubricant base oil has a viscosity index between about 140 and 190.

21. The method of claim 1, wherein the lubricant base oil has a pour point between about -5 and -60° C.

22. The method of claim 1, wherein the lubricant base oil has a viscosity at 100° C. of greater than 3 cSt.

23. The method of claim 1, further comprising solvent dewaxing at least a portion of the lubricant base oil, thereby removing a slack wax.

24. The method of claim 23, further comprising hydroisomerizing the slack wax with the waxy hydrocarbon feed.

25. A process for producing a lubricant base oil comprising:

a) contacting a shape selective, intermediate pore size, noble-metal containing molecular sieve with a sulfur-containing species to provide a pre-sulfided catalyst, wherein the molar ratio of sulfur to noble metal in the pre-sulfided catalyst is greater than one;

b) providing a Fischer-Tropsch waxy hydrocarbon feed;

c) contacting the Fischer-Tropsch waxy hydrocarbon feed with the pre-sulfided catalyst to hydroisomerize the feed; and

d) isolating a lubricant base oil.

26. The process of claim 25, wherein the lubricant base oil has a pour point between about -5 and -60° C. and a viscosity index at 100° C. of greater than 3 cSt.

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