WAX HYDROISOMERIZATION PROCESS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is related to co-pending application Serial No. 08/017,949 (continuation of S.N. 07/548,702) entitled Production of High Viscosity Index Lubricants, which describes a two-step process for producing high Viscosity Index lubricants by hydrocracking and hydroisomerization of petroleum wax feeds using a low acidity zeolite beta hydroisomerization catalyst. Serial No. 08/017,955, also entitled Production of High Viscosity Index Lubricants, describes a wax hydroisomerization process using zeolite catalysts of controlled low acidity at high pressures. The instant application is a continuation-in-part of Serial No. 08/017,955. The instant application is also a continuation-in-part of Serial No. 08/017,949. Serial No. 08/017,955 is incorporated by reference in the instant application. Corresponding European Patent No. 464,547A1, (a patent which specifies the use of low acidity zeolite beta for wax isomerization) is also incorporated by reference.

FIELD OF THE INVENTION

This invention relates to the production of high Viscosity Index lubricants by employing a process in which two dewaxing catalysts operate synergistically. The feed may be hydrocracked prior to the catalytic dewaxing process. The effluent of the dewaxing process may also be hydrotreated.

BACKGROUND OF THE INVENTION

Mineral oil based lubricants are conventionally produced by a separative sequence carried out in the petroleum refinery which comprises fractionation of a paraffinic crude oil under atmospheric pressure followed by fractionation under vacuum to produce distillate fractions (neutral oils) and a residual fraction which, after

deasphalting and severe solvent treatment may also be used as a lubricant basestock. This refined residual fraction is usually referred to as bright stock. Neutral oils, after solvent extraction to remove low viscosity index (V.I.) components, are conventionally subjected to dewaxing, either by solvent or catalytic dewaxing processes, to achieve the desired pour point. The dewaxed lube stock may be hydrofinished to improve stability and remove color bodies. Viscosity Index (V.I.) is a reflection of the amount of viscosity decrease a lubricant undergoes with an increase in temperature. The products of solvent dewaxing are dewaxed lube oil and slack wax. Slack wax typically contains 60% to 90% wax with the balance being entrained oil. In some instances it is desirable to purify the slack wax of entrained oil by subjecting the slack wax to a deoiling step in which the slack wax is diluted with dewaxing solvents and filtered at a temperature higher than that used in the filtering step used to produce the slack wax. The purified wax is termed deoiled wax, and contains greater than 95% wax. The byproduct of the second filtration typically contains 50% wax and is termed foots oil.

Catalytic dewaxing of lube stocks is accomplished by converting waxy molecules to light products by cracking, or by isomerizing waxy molecules to form species which remain in the dewaxed lube. Dewaxing catalysts preserve high yield primarily by having pore structures which inhibit cracking of cyclic and highly branched species, those generally associated with dewaxed lube, while permitting easier access to catalytically active sites to near-linear molecules, of which wax is generally composed. Catalysts which significantly reduce the accessibility of species on the basis of molecular size are termed shape selective. Increasing the shape selectivity of a dewaxing catalyst will frequently increase the yield of dewaxed oil.

The shape selectivity of a dewaxing catalyst is limited practically by its ability to convert waxy molecules which have a slightly branched structure. These

types of species are more commonly associated with heavier lube stocks, such as bright stocks. Highly shape selective dewaxing catalysts may be unable to convert heavy, branched wax species leading to a hazy lube appearance at ambient temperature and high cloud point relative to pour point.

Conventional lube refining techniques rely upon the proper selection and use of crude stocks, usually of a paraffinic character, which produce lube fractions with desired qualities in adequate amounts. The range of permissible crude sources may, however, be extended by the lube hydrocracking process which is capable of utilizing crude stocks of marginal or poor quality, usually with a higher aromatic content than the best paraffinic crudes. The lube hydrocracking process, which is well established in the petroleum refining industry, generally comprises an initial hydrocracking step carried out under high pressure, at high temperature, and in the presence of a bifunctional catalyst which effects partial saturation and ring opening of the aromatic components which are present in the feed. The hydrocracked product is then subjected to dewaxing in order to reach the target pour point since the hydrocracked product usually contains species with relatively high pour points. Frequently the liquid product from the dewaxing step is subjected to a low temperature, high pressure hydrotreating step to reduce the aromatic content of the lube to the desired level.

Current trends in the design of automotive engines are associated with higher operating temperatures as the efficiency of the engines increases. These higher operating temperatures require successively higher quality lubricants. One of the requirements is for higher viscosity indices (V.I.) in order to reduce the effects of the higher operating temperatures on the viscosity of the engine lubricants. High V.I. values have conventionally been attained by the use of V.I. improvers e.g. polyacrylates and polystyrenes. V.I. improvers tend to undergo degradation due to high temperatures and high shear rates encountered in the engine. The more stressing

conditions encountered in high efficiency engines result in even faster degradation of oils which employ significant amounts of V.I. improvers. Thus, there is a continuing need for automotive lubricants which are based on fluids of high Viscosity Index and which are resistant to the high temperature, high shear rate conditions encountered in modern engines.

Synthetic lubricants produced by the polymerization of olefins in the presence of certain catalysts have been shown to possess excellent V.I. values, but they are relatively expensive to produce. There is therefore a need for the production of high V.I. lubricants from mineral oil stocks which may be produced by techniques comparable to those presently employed in petroleum refineries.

U.S. Patent No. 4,975,177 discloses a two-stage dewaxing process for producing lube stocks of high V.I. from waxy feedstocks. In the first stage of this process, the waxy feed is catalytically dewaxed by isomerization over zeolite beta. The product of the isomerization step still contains waxy species and requires further dewaxing to meet target pour point. The second-stage dewaxing employs either solvent dewaxing, in which case the rejected wax may be recycled to the isomerization stage to maximize yield, or catalytic dewaxing. Catalysts which may be used in the second stage are ZSM-5, ZSM-22, ZSM-23, and ZSM-35. To preserve yield and V.I., the second stage dewaxing catalyst should have selectivity similar to solvent dewaxing. U.S. Patent 4,919,788 also teaches a two-stage dewaxing process in which a waxy feed is partially dewaxed by isomerization over a siliceous Y or beta catalyst with the product subsequently dewaxed to desired pour point using either solvent dewaxing or catalytic dewaxing. Dewaxing catalysts with high shape selectivity, such as ZSM-22 and ZSM-23, are preferred catalysts. These examples, however, do not teach synergistic effects involving more than one dewaxing catalyst.

Serial No. 08/017,949 discloses a two stage hydrocracking and hydroisomerization process. The first

stage employs a bifunctional catalyst comprising a metal hydrogenation component on an amorphous acidic support. The second stage, the hydroisomerization step, is carried out over zeolite beta. Subsequent dewaxing is optional but recommended. Either solvent dewaxing or catalytic dewaxing maybe used subsequently in order to obtain target V.I. and pour point. There is no teaching of catalytic synergism in this invention.

In S.N. 08/017,955, petroleum wax feed is subjected to hydroisomerization over a noble metal-containing zeolite catalyst of low acidity. The paraffins present in the feed are selectively converted to iso-paraffins of high V.I. but lower pour point so that a final lube product of good viscometric properties is produced with a minimal degree of subsequent dewaxing. The process, which operates under high pressure, is well suited for upgrading waxy feeds such as slack wax with aromatic contents greater than 15 wt.% to high Viscosity Index lubricating oils with high single pass yields and limited requirement for product dewaxing.

Related cases primarily emphasize solvent dewaxing with Catalytic dewaxing as a possible alternative or secondary step. The advantage of solvent dewaxing the product of the isomerization stage in that wax is rejected and can be recycled to the isomerization catalyst to improve the yield of high V.I. lube. However, operational costs for solvent dewaxing are higher than for catalytic dewaxing. Additionally, the pour point of the solvent dewaxed lube stock is restricted by solvent refrigeration capability to approximately -21 to -18°C. Catalytic dewaxing enables production of high V.I. lubes having pour points significantly lower than those possible for solvent dewaxing. An unexpected development of the total catalytic dewaxing process is that it can produce lubricants with equivalent or higher V.I. at equivalent or lower pour points than lubricants produced by solvent dewaxing.

SUMMARY OF THE INVENTION

The instant application involves the processing of a waxy hydrocarbon feedstock using an integrated catalyst system for the production of high Viscosity Index (V.I.) low aromatic content lubricant stocks with low pour point. The feedstock is initially contacted under high pressure (hydrogen partial pressure of at least 5617 kPa_{abs} with low acidity large pore zeolite catalyst into which a metal, preferably a noble metal such as Pt, has been incorporated. A substantial fraction of the waxy material in the feed is selectively isomerized over this catalyst. The reaction product is subsequently contacted with a constrained intermediate pore crystalline material, also containing a noble metal, which provides further isomerization and dewaxing. The final product is a lubricant which has a high Viscosity Index and a low pour point. A subsequent hydrotreating step may be included to reduce lube oil aromatic content to the desired target point.

The catalysts used in the instant invention behave synergistically. The yield and Viscosity Index (V.I.) of the product of the integrated catalyst system exceed the yield and V.I. of the product from either of the two catalysts operating alone. This synergism requires the reactor containing the large pore zeolite to be operated so as to convert 40 to 90% of the wax species in the feed. The conversion of the residual wax is accomplished in the second dewaxing step. Both V.I. and yield are inversely related to pour point below a pour point of approximately 27°C. The synergy of the process is illustrated by the reduction in yield and V.I. with decreasing pour point being significantly less than for either dewaxing catalyst operating alone. The improvement of yield and V.I. is not predictable by the study of each catalyst individually. Additionally, product appearance and cloud point are improved by the two-stage dewaxing system over those from the selective dewaxing catalyst operating alone.

The process of the instant invention can be used to upgrade feeds having low wax content, such as those

obtained by solvent extracting or hydrocracking vacuum distillates. However, the synergy is most evident with feedstocks which have a wax content of over 50%.

The synergy of the integrated low-acidity large pore zeolite catalyst and the intermediate pore catalyst permits the production of high quality base stocks by an all-catalytic route. Such base stocks generally have a Viscosity Index greater than 120, more preferably greater than 130, and contain less than 10% aromatics, more preferably less than 1% aromatics.

DESCRIPTION OF THE DRAWINGS

Figures 1, 2, 3 and 4 are plots which illustrate the synergistic relationship of the catalysts of this invention. Viscosity Indexes and yields obtained by using the catalysts together and individually are plotted against pour point. The figures are discussed in more detail in the Examples, infra.

DETAILED DESCRIPTION

In the present process, feeds with a relatively high wax content, such as slack wax, are converted to high V.I. lubricants in an integrated process employing two catalysts with synergistic properties. A hydroisomerization process using a noble metal containing low acidity zeolite hydroisomerization catalyst is employed first. The intermediate product of this process is then contacted with a noble metal containing intermediate pore crystalline material to accomplish further dewaxing. Product V.I. will vary with pour point, wax content of the feed, and whether the feed was subjected to a pretreatment step. For heavy neutral slack waxes which have been hydrorefined to remove nitrogen and sulfur containing species, product VI is typically at least 140 at -18°C pour point and usually in the range 143 to 147. The production of base stocks with V.I. greater than that obtained from the synergistic catalyst system is not possible with either catalyst operating alone to effect complete dewaxing.

Feed

The present processes are capable of operating with a wide range of feeds of mineral oil origin to produce a range of lubricant products with good performance characteristics. Such characteristics include low pour point, low cloud point, and high Viscosity Index. The quality of the product and the yield in which it is obtained is dependent upon the quality of the feed and its amenability to processing by the catalysts of the instant invention. Products of the highest V.I. are obtained by using preferred wax feeds such as slack wax, foots oil, deoiled wax or vacuum distillates derived from waxy crudes. Waxes produced by Fischer-Tropsch processing of synthesis gas may also be used as feedstocks. Products with lower V.I. values may also be obtained from other feeds which contain a lower initial quantity of waxy components.

The feeds which may be used should have an initial boiling point which is no lower than the initial boiling point of the desired lubricant. A typical initial boiling point of the feed exceeds 345°C. Feeds of this type which may be used include vacuum gas oils as well as other high boiling fractions such as distillates from the vacuum distillation of atmospheric resids, raffinates from the solvent extraction of such distillate fractions, hydrocracked vacuum distillates and waxes from the solvent dewaxing of raffinates and hydrocrackates.

The feed may require preparation in order to be treated satisfactorily in the hydroisomerization step. The preparation steps which are generally necessary are those which remove low V.I. components such as aromatics and polycyclic naphthenes. Removal of these materials will result in a feed for the hydroisomerization step which contains higher quantities of waxy paraffins which are then converted to high V.I., low pour point iso-paraffins. Catalytic synergy is most dramatically illustrated for feedstocks having a wax content of over 50%, although feeds with lower wax contents may be used effectively.

Suitable pre-treatment steps for preparing feeds for the hydroisomerization are those which remove the aromatics and other low V.I. components from the initial feed. Hydrotreatment is an effective pretreatment step, particularly at high hydrogen pressures which are effective for aromatics saturation e.g. 5617 kPa_{abs} or higher. Mild hydrocracking may also be employed as pretreatment and is preferred in the instant invention, if pretreatment is required. Example 3, infra, discusses the hydrocracking conditions employed in the instant invention in order to prepare a feed for the dewaxing process. Pressures over 6996 kPa_{abs} are preferred for hydrocracking treatment. Hydrocracking removes nitrogen containing and sulfur-containing species and reduces aromatics content as Table 6 below illustrates. Hydrocracking, in this example, has also slightly altered the boiling range of the feed, causing it to boil in a lower range. Commercially available catalysts such as fluoride nickel-tungsten on alumina ($NiWF/Al_2O_3$) may be employed for the hydrocracking pretreatment.

The preferred gas oil and vacuum distillate feeds are those which have a high wax content, as determined by ASTM D-3235, preferably over 50 weight percent. Feeds of this type include certain South-East Asian and mainland China oils. Minas Gas Oil, from Indonesia, is such a feed. These feeds usually have a high paraffin content, as determined by a conventional analysis for paraffins, naphthenes, and aromatics. The properties of typical feeds of this type are set out in S.N. 07/017,955.

As stated previously, the wax content of the preferred feeds is high, generally at least 50 wt% (as determined by ASTM Test D-3235) prior to pretreatment. The wax content before pretreatment is more usually at least 60 to 80 weight percent with the balance being occluded oil comprising iso-paraffins, aromatics and naphthenics. These waxy, highly paraffinic wax stocks usually have low viscosities because of their relatively low content of aromatics and naphthenes although the high content of waxy

paraffins gives them melting points and pour points which render them unacceptable as lubricants without further processing. Wax feeds are discussed further in S.N. 07/017,955.

The most preferred type of wax feeds are the slack waxes, (see Table 2, infra). These are the waxy products obtained directly from a solvent dewaxing process, e.g. an MEK or propane dewaxing process. The slack wax, which is a solid to semi-solid product, comprising primarily highly waxy paraffins (mostly n- and mono-methyl paraffins) together with occluded oil, may be used as such or it may be subjected to an initial deoiling step of a conventional character in order to remove the occluded oil. Removal of the oil results in a harder, more highly paraffinic wax which may then be used as the feed. The byproduct of the deoiling step is termed foots oil and may also be used as feed to the process. The Foots Oil contains most of the aromatics present in the original slack wax and with these aromatics, most of the heteroatoms. Slack wax and foots oil typically require pretreatment prior to catalytic dewaxing. The oil content of deoiled waxes may be quite low and for this purpose, measurement of the oil content by the technique of ASTM D721 may be required for reproducibility, since the D-3235 test referred to above tends to be less reliable at oil contents below 15 weight percent. At oil contents below 10 percent, however, the advantage of the present catalysts may not be as marked as with oil contents of from 10 to 50 weight percent and for this reason, wax feeds conforming to this requirement will normally be employed.

The compositions of some typical waxes are given in Table 1 below.

Table 1
Wax Composition - Arab Light Crude

	A	B	C	D
Paraffins, wt. pct.	94.2	81.8	70.5	51.4
Mono-naphthenes, wt. pct.	2.6	11.0	6.3	16.5
Poly-naphthenes, wt. pct.	2.2	3.2	7.9	9.9
Aromatics, wt. pct.	1.0	4.0	15.3	22.2

A typical slack wax feed has the composition shown in Table 2 below. This slack wax is obtained from the solvent (MEK) dewaxing of 65 cSt at 40°C neutral oil obtained from an Arab Light crude.

Table 2
Slack Wax Properties

API	39
Hydrogen, wt. pct.	15.14
Sulfur, wt. pct.	0.18
Nitrogen, ppmw	11
Melting point, °C	57
KV at 100°C, cSt	5.168
PNA, wt pct:	
Paraffins	70.3
Naphthenes	13.6
Aromatics	16.3

Simulated Distillation:

%	°C
5	375
10	413
30	440
50	460
70	482
90	500
95	507

Another slack wax suitable for use in the present process has the properties set out in Table 6 infra as part of Example 3. This wax is prepared by the solvent dewaxing of a heavy neutral furfural raffinate. As discussed previously, hydrocracking may be employed to prepare the slack wax for hydroisomerization.

Hydrocracking Process (Optional)

If hydrocracking is employed as a pretreatment step an amorphous bifunctional catalyst is preferably used to promote the saturation and ring opening of the low quality aromatic components in the feed to produce hydrocracked products which are relatively more paraffinic. Hydrocracking is carried out under high pressure to favor aromatics saturation but the boiling range conversion is maintained at a relatively low level in order to minimize cracking of the saturated components of the feed and of the products obtained from the saturation and ring opening of the aromatic materials. Consistent with these process objectives, the hydrogen pressure in the hydrocracking

stage is at least 5617 kPa_{abs} and usually is in the range of 6696 to 20786 kPa_{abs}. Normally, hydrogen partial pressures of at least 10444 kPa_{abs} are best in order to obtain a high level of aromatic saturation. Hydrogen circulation rates of at least 180 $n.l.l^{-1}$, preferably in the range of 900 to 1800 $n.l.l^{-1}$ are suitable.

In the hydrocracking process, the conversion of the feed to products boiling below the lube boiling range, typically to 345°C- products is limited to no more than 50 weight percent of the feed and will usually be not more than 30 weight percent of the feed in order to maintain the desired high single pass yields which are characteristic of the process. The actual conversion is dependent on the quality of the feed with slack wax feeds requiring a lower conversion than petrolatum where it is necessary to remove more low quality polycyclic components. For slack wax feeds derived from the dewaxing of neutral stocks, the conversion to 345°C- products will, for all practical purposes not be greater than 10 to 20 weight percent, with 5-15 weight percent being typical for most slack waxes. Higher conversions may be encountered with petrolatum feeds because they typically contain more low quality components. With petrolatum feeds, the hydrocracking conversion will typically be in the range of 15 to 25 weight percent to produce high VI products. The conversion may be maintained at the desired value by control of the temperature in the hydrocracking stage which will normally be in the range 315° to 430°C and more usually in the range of 345° to 400°C). Space velocity variations may also be used to control severity although this will be less common in practice in view of mechanical constraints on the system. Generally, the space velocity will be in the range of 0.25 to 2 LHSV, $hr.^{-1}$ and usually in the range of 0.5 to 1.5 LHSV.

A characteristic feature of the hydrocracking operation is the use of a bifunctional catalyst. In general terms, these catalysts include a metal component for promoting the desired aromatics saturation reactions and usually a

combination of base metals is used, with one metal from the iron group (Group VIII) in combination with a metal of Group VIB. Thus, the base metal such as nickel or cobalt is used in combination with molybdenum or tungsten. The preferred combination is nickel/tungsten since it has been found to be highly effective for promoting the desired aromatics hydrocracking reaction. Noble metals such as platinum or palladium may be used since they have good hydrogenation activity in the absence of sulfur but they will normally not be preferred. The amounts of the metals present on the catalyst are conventional for lube hydrocracking catalysts of this type and generally will range from 1 to 10 weight percent of the Group VIII metal and 10 to 30 weight percent of the Group VI metal, based on the total weight of the catalyst. If a noble metal component such as platinum or palladium is used instead of a base metal such as nickel or cobalt, relatively lower amounts are in order in view of the higher hydrogenation activities of these noble metals, typically from 0.5 to 5 weight percent being sufficient. The metals may be incorporated by any suitable method including impregnation onto the porous support after it is formed into particles of the desired size or by addition to a gel of the support materials prior to calcination. Addition to the gel is a preferred technique when relatively high amounts of the metal components are to be added e.g. above 10 weight percent of the Group VIII metal and above 20 weight percent of the Group VI metal. These techniques are conventional in character and are employed for the production of lube hydrocracking catalysts.

The metal component of the catalyst is generally supported on a porous, amorphous metal oxide support and alumina is preferred for this purpose although silica-alumina may also be employed. Other metal oxide components may also be present in the support although their presence is less desirable. Consistent with the requirements of a lube hydrocracking catalyst, the support should have a pore size and distribution which is adequate to permit the

relatively bulky components of the high boiling feeds to enter the interior pore structure of the catalyst where the desired hydrocracking reactions occur. To this extent, the catalyst will normally have a minimum pore size of 50 Å i.e with no less than 5 percent of the pores having a pore size less than 50 Å pore size, with the majority of the pores having a pore size in the range of 50-400 Å (no more than 5 percent having a pore size above 400 Å), preferably with no more than 30 percent having pore sizes in the range of 200-400 Å. Preferred catalysts for the first stage have at least 60 percent of the pores in the 50-200 Å range. The pore size distribution and other properties of some typical lube hydrocracking (LHDC) catalysts suitable for use in the hydrocracking are shown in Table 3 below:

Table 3
LHDC Catalyst Properties

Form	1.5mm cyl.	1.5 mm. tri.	1.5 mm.cyl.
Pore Volume, cc/gm	0.331	0.453	0.426
Surface Area, m^2/gm	131	170	116
Nickel, wt. pct.	4.8	4.6	5.6
Tungsten, wt. pct.	22.3	23.8	17.25
Fluorine, wt. pct.	-	-	3.35
SiO_2/Al_2O_3 binder	-	-	62.3
Real Density, gm/cc	4.229	4.238	4.023
Particle Density, gm/cc	1.744	1.451	1.483
Packing Density, gm/cc	1.2	0.85	0.94

If necessary in order to obtain the desired conversion, the catalyst may be promoted with fluorine, either by incorporating fluorine into the catalyst during its preparation or by operating the hydrocracking in the presence of a fluorine compound which is added to the feed. Fluorine containing compounds may be incorporated into the catalyst by impregnation during its preparation with a suitable fluorine compound such as ammonium fluoride (NH_4F) or ammonium bifluoride ($NH_4F \cdot HF$) of which the latter is preferred. The amount of fluorine used in catalysts which contain this element is preferably from 1 to 10 weight percent, based on the total weight of the catalyst, usually from 2 to 6 weight percent. The fluorine may be

incorporated by adding the fluorine compound to a gel of the metal oxide support during the preparation of the catalyst or by impregnation after the particles of the catalyst have been formed by drying or calcining the gel. If the catalyst contains a relatively high amount of fluorine as well as high amounts of the metals, as noted above, it is preferred to incorporate the metals and the fluorine compound into the metal oxide gel prior to drying and calcining the gel to form the finished catalyst particles.

The catalyst activity may also be maintained at the desired level by in situ fluoriding in which a fluorine compound is added to the stream which passes over the catalyst in this stage of the operation. The fluorine compound may be added continuously or intermittently to the feed or, alternatively, an initial activation step may be carried out in which the fluorine compound is passed over the catalyst in the absence of the feed e.g. in a stream of hydrogen in order to increase the fluorine content of the catalyst prior to initiation of the actual hydrocracking. In situ fluoriding of the catalyst in this way is preferably carried out to induce a fluorine content of 1 to 10 percent fluorine prior to operation, after which the fluorine can be reduced to maintenance levels sufficient to maintain the desired activity. Suitable compounds for in situ fluoriding are orthofluorotoluene and difluoroethane.

The metals present on the catalyst are preferably used in their sulfide form and to this purpose pre-sulfiding of the catalyst should be carried out prior to initiation of the hydrocracking. Sulfiding is an established technique and it is typically carried out by contacting the catalyst with a sulfur-containing gas, usually in the presence of hydrogen. The mixture of hydrogen and hydrogen sulfide, carbon disulfide or a mercaptan such as butol mercaptan is conventional for this purpose. Presulfiding may also be carried out by contacting the catalyst with hydrogen and a sulfur-containing hydrocarbon oil such as a sour kerosene or gas oil.

Synergistic Catalyst Process

The paraffinic components present in the original wax feed possess good V.I. characteristics but have relatively high pour points as a result of their paraffinic nature. The objective of the synergistic catalyst process of the invention is, therefore, to effect a selective conversion of waxy species while minimizing conversion of more branched species characteristic of lube components. The conversion of wax occurs preferentially by isomerization to form more branched species which have lower pour points and cloud points. Some degree of cracking accompanies isomerization and cracking is required to produce very low pour point lube oils. The selectivity of the process is maximized by the use of a two-catalyst system in which the first catalyst selectively converts waxy species by isomerization and the second catalyst converts the residual wax by isomerization and cracking. The pore structure of the first catalyst is significantly less restricted than that of the second allowing for the conversion of bulky wax molecules and reducing cloud point and hazy appearance below that which would be achieved with the use of the second dewaxing catalyst alone.

Hydroisomerization Catalyst

The catalyst used in the hydroisomerization step is one which has a high selectivity for the isomerization of waxy, linear or near linear paraffins to less waxy, isoparaffinic products. Catalysts of this type are bifunctional in character, comprising a metal component on a large pore size, porous support of relatively low acidity. The acidity is maintained at a low level in order to reduce conversion to products boiling outside the lube boiling range during this stage of the operation. In general terms, the catalyst should have an alpha value below 30 prior to metals addition, with preferred values below 20. (See Example 1)

The alpha value is an approximate indication of the catalytic cracking activity of the catalyst compared to a

standard catalyst. The alpha test gives the relative rate constant (rate of normal hexane conversion per volume of catalyst per unit time) of the test catalyst relative to the standard catalyst which is taken as an alpha of 1 (Rate Constant = 0.016 sec $^{-1}$). The alpha test is described in U.S. Patent 3,354,078 and in J. Catalysis, 4, 527 (1965); 6, 278 (1966); and 61, 395 (1980), to which reference is made for a description of the test. The experimental conditions of the test used to determine the alpha values referred to in this specification include a constant temperature of 538°C and a variable flow rate as described in detail in J. Catalysis, 61, 395 (1980).

The hydroisomerization catalyst comprises a large pore zeolite metal. The large pore zeolite is supported by a porous binder. Large pore zeolites usually have at least one pore channel consisting of twelve-membered oxygen rings. Large pore zeolites usually have at least one pore channel with a major dimension greater than 7A. Zeolites beta, Y and mordenites are examples of large pore zeolites.

The preferred hydroisomerization catalyst employs zeolite beta since this zeolite has been shown to possess outstanding activity for paraffin isomerization in the presence of aromatics, as disclosed in U.S. 4,419,220. The low acidity forms of zeolite beta may be obtained by synthesis of a highly siliceous form of the zeolite e.g with a silica-alumina ratio above 500:1 or, more readily, by steaming zeolites of lower silica-alumina ratio to the requisite acidity level. They may also be obtained by extraction with acids such as dicarboxylic acid, as disclosed in U.S. Patent No. 5,200,168. U.S. Patent No. 5,164,169 discloses the preparation of highly siliceous zeolite beta employing a chelating agent such as tertiary alkenolamines in the synthesis mixture.

The most preferred zeolites are severely steamed and possess a framework silica-alumina ratio above 200:1. Preferably the silica-alumina ratio is above 400:1 and more preferably the silica-alumina ratio is greater than 600:1.

The steaming conditions should be adjusted in order to attain the desired alpha value in the final catalyst and typically utilize atmospheres of 100 percent steam, at temperatures of from 427° to 595°C. Normally, the steaming will be carried out at temperatures above 538°C, for 12 to 120 hours, typically 96 hours, in order to obtain the desired reduction in acidity.

Another method is by replacement of a portion of the framework aluminum of the zeolite with another trivalent element such as boron which results in a lower intrinsic level of acid activity in the zeolite. The preferred zeolites of this type are those which contain framework boron. Boron is usually added to the zeolite framework prior to the addition of other metals. In zeolites of this type, the framework consists principally of silicon tetrahedral coordinated and interconnected with oxygen bridges. The minor amount of an element (alumina in the case of alumino-silicate zeolite beta) is also coordinated and forms part of the framework. The zeolite also contains material in the pores of the structure although these do not form part of the framework constituting the characteristic structure of the zeolite. The term "framework" boron is used here to distinguish between material in the framework of the zeolite which is evidenced by contributing ion exchange capacity to the zeolite, from material which is present in the pores and which has no effect on the total ion exchange capacity of the zeolite. Zeolite beta possesses a constraint index between 0.60 and 2.0 at temperatures between 316°C and 399°C although Constraint Indexes less than 1 are preferred.

Methods for preparing high silica content zeolites containing framework boron are known and are described, for example, in U.S. Patents Nos. 4,269,813. A method for preparing zeolite beta containing framework boron is disclosed in U.S. Patent No. 4,672,049. As noted there, the amount of boron contained in the zeolite may be varied by incorporating different amounts of borate ion in the zeolite forming solution e.g. by the use of varying amounts

of boric acid relative to the forces of silica and alumina. Reference is made to these disclosures for a description of the methods by which these zeolites may be made.

The low acidity zeolite beta catalyst should contain at least 0.1 weight percent framework boron, preferably at least 0.5 weight percent boron. Boron may be added to the framework prior to the addition of other metals. Normally, the maximum amount of boron will be 5 weight percent of the zeolite and in most cases not more than 2 weight percent of the zeolite. The framework will normally include some alumina. The silica:alumina ratio will usually be at least 30:1, in the conditions of the zeolite as synthesized. A preferred boron-substituted zeolite beta catalyst is made by steaming an initial boron-containing zeolite containing at least 1 weight percent boron (as B_2O_3) to result in an ultimate alpha value no greater than 20 and preferably no greater than 10.

Properties

Acidity may be reduced by the introduction of nitrogen compounds, e.g. NH_3 or organic nitrogen compounds, with the feed to the hydroisomerization catalyst. However, the total nitrogen content of the feed should not exceed 100 ppm and should be preferably less than 20 ppm. The catalyst may also contain metals which reduce the number of strong acid sites of the catalyst and improve the selectivity of isomerization reactions to cracking reactions. Metals which are preferred for this purpose are those belong to the class of Group IIA metals such as calcium and magnesium.

The zeolite will be composites with a matrix material to form the finished catalyst and for this purpose conventional very low-acidity matrix materials such as alumina, silica-alumina and silica are suitable although aluminas such as alpha boehmite (alpha alumina monohydrate) may also be used, provided that they do not confer any substantial degree of acidic activity on the matrixed catalyst. The zeolite is usually composites with the

matrix in amounts from 80:20 to 20:80 by weight, typically from 80:20 to 50:50 zeolite:matrix. Compositing may be done by conventional means including mulling the materials together followed by extrusion into the desired finished catalyst particles. A preferred method for extruding the zeolite with silica as a binder is disclosed in U.S. 4,582,815. If the catalyst is to be steamed in order to achieve the desired low acidity, it is performed after the catalyst has been formulated with the binder, as is conventional. The preferred binder for the steamed catalyst is alumina.

The hydroisomerization catalyst also includes a metal component in order to promote the desired hydroisomerization reactions which, proceeding through unsaturated transitional species, require mediation by a hydrogenation-dehydrogenation component. In order to maximize the isomerization activity of the catalyst, metals having a strong hydrogenation function are preferred and for this reason, platinum and the other noble metals such as rhenium, gold, and palladium are given a preference. The amount of the noble metal hydrogenation component is typically in the range 0.1 to 5 weight percent of the total catalyst, usually from 0.1 to 2 weight percent. The platinum may be incorporated into the catalyst by conventional techniques including ion exchange with complex platinum cations such as platinum tetraamine or by impregnation with solutions of soluble platinum compounds, for example, with platinum tetraammine salts such as platinum tetraamminechloride. The catalyst may be subjected to a final calcination under conventional conditions in order to convert the noble metal to its reduced form and to confer the required mechanical strength on the catalyst. Prior to use the catalyst may be subjected to presulfiding as described above for the hydrocracking pretreatment catalyst.

Hydroisomerization Conditions

The conditions for the hydroisomerization step (also called the isomerization step) are adjusted to achieve the objective of isomerizing the waxy, linear and near-linear paraffinic components in the waxy feed to less waxy but high V.I. isoparaffinic materials of relatively lower pour point. This end is achieved while minimizing conversion to non-lube boiling range products (usually 345°C- materials). Since the catalyst used for the hydroisomerization has a low acidity, conversion to lower boiling products is usually at a relatively low level and by appropriate selection of severity, the operation of the process may be optimized for isomerization over cracking. At conventional space velocities of 1, using a Pt/zeolite beta catalyst with an alpha value below 20, temperatures for the hydroisomerization will typically be in the range of 300° to 415°C with conversion to 345°C- typically being from 5 to 30 weight percent, more usually 10 to 25 weight percent, of the waxy feed. Approximately 40 to 90 percent of the wax in the feed is converted in the isomerization step. However, temperatures may be used outside this range, for example, as low as 260°C and up to 425°C although the higher temperatures will usually not be preferred since they will be associated with a lower isomerization selectivity and the production of less stable lube products as a result of the hydrogenation reactions being thermodynamically less favored at progressively higher operating temperatures. Space velocities will typically be in the range of 0.5 to 2 LHSV ($hr.^{-1}$). The pour point of the effluent from the hydroisomerization step is in the range from -1 to 43°C, preferably in the range from 5 to 39°C.

The hydroisomerization is operated at hydrogen partial pressures (reactor inlet) of at least 5516 KPa_{abs}, usually 5167 to 20786 kP_{abs} and in most cases 5517 to 17339 kPa_{abs}. Hydrogen circulation rates are usually in the range of 90 to 900 $n.l.l.^{-1}$. Since some saturation of aromatic components present in the original feed takes place in the

presence of the noble metal hydrogenation component on the catalyst, hydrogen is consumed in the hydroisomerization even though the desired isomerization reactions are in hydrogen balance; for this reason, hydrogen circulation rates may need to be adjusted in accordance with the aromatic content of the feed and also with the temperature used in the hydroisomerization since higher temperatures will be associated with a higher level of cracking and, consequently, with a higher level of olefin production, some of which will be in the lube boiling range so that product stability will need to be assured by saturation. Hydrogen circulation rates of at least 180 n.l.l.$^{-1}$ will normally provide sufficient hydrogen to compensate for the expected hydrogen consumption as well as to ensure a low rate of catalyst aging.

An interbed quench is desirable to maintain temperature in the process. Cold hydrogen is generally used as the quench, but a liquid quench, usually recycled product, may also be used.

Shape-selective Catalytic Dewaxing Phase

The effluent from the isomerization phase still contains quantities of the more waxy straight chain, n-paraffins, together with the higher melting non-normal paraffins. Because these contribute to unfavorable pour points, and because the effluent will have a pour point which is above the target pour point for the product, it is necessary to remove these waxy components. To do this without removing the desirable isoparaffinic components which contribute to high V.I. in the product, a shape-selective dewaxing catalyst is employed. This catalyst removes the n-paraffins together with the waxy, slightly branched chain paraffins, while leaving the more branched chain iso-paraffins in the process stream. Shape-selective catalytic dewaxing processes employ catalysts which are more highly selective for removal of n-paraffins and slightly branched chain paraffins than is the isomerization catalyst, zeolite beta. This phase of the synergistic

process is therefore carried out as described in U.S. Patent No. 4,919,788, to which reference is made for a description of this phase. The catalytic dewaxing step in the present process is carried out with a constrained, shape selective dewaxing catalyst based on a constrained intermediate pore crystallines material, such as an alumino-phosphate. A constrained intermediate crystalline material has at least one channel of 10-membered oxygen rings with any intersecting channel having 8-membered rings. ZSM-23 is the preferred zeolite for this purpose although other highly shape-selective zeolites such as ZSM-22 or the synthetic ferrierite ZSM-35 may also be used, especially with lighter stocks. Silicoaluminophosphates such as SAPO-11 and SAPO-41 maybe used as selective dewaxing catalysts.

The preferred catalysts for use as the dewaxing catalysts are the relatively constrained intermediate pore size zeolites. Such preferred zeolites have a Constraint Index in the range of 1-12, as determined by the method described in U.S. Patent No. 4,016,218. These preferred zeolites are also characterized by specific sorption properties related to their relatively constrained diffusion characteristics. These sorption characteristics are those which are set out in U.S. Patent No. 4,810,357 for the zeolites such as zeolite ZSM-22, ZSM-23, ZSM-35 and ferrierite. These zeolites have pore openings which result in a specific combination of sorption properties, namely, (1) a ratio of sorption of n-hexane to o-xylene, on a volume percent basis, of greater than 3, wherein sorption is determined at a P/P_o of 0.1 and at a temperature of 50°C for n-hexane and 80°C for o-xylene and (2) by the ability of selectively cracking 3-methylpentane (3MP) in preference to the doubly branched 2,3-dimethylbutane (DMB) at 538°C and 1 atmosphere pressure from a 1/1/1 weight ratio mixture of n-hexane/3-methyl-pentane/2,3-dimethylbutane, with the ratio of rate constants k_{3MP}/k_{DMB} determined at a temperature of 538°C being in excess of 2.

The expression, "P/P_o", is accorded its usual significance as described in the literature, for example, in "The Dynamical Character of Adsorption" by J.H. deBoer, 2nd Edition, Oxford University Press (1968) and is the relative pressure defined as the ratio of the partial pressure of sorbate to the vapor pressure of sorbate at the temperature of sorption. The ratio of the rate constants, k_{3MP}/k_{DMB}, is determined from 1st order kinetics, in the usual manner, by the following equation:

$$k = (1/T_c)\ \ln\ (1/1-\epsilon)$$

where k is the rate constant for each component, T_c is the contact time and ϵ is the fractional conversion of each component.

Zeolites conforming to these sorption requirements include the naturally occurring zeolite ferrierite as well as the synthetic zeolites ZSM-22, ZSM-23 and ZSM-35. These zeolites are at least partly in the acid or hydrogen form when they are used in the present process.

The preparation and properties of zeolite ZSM-22 are described in U.S. Patent No. 4,810,357 (Chester) to which reference is made for such a description.

The synthetic zeolite ZSM-23 is described in U.S. Patent Nos. 4,076,842 and 4,104,151 to which reference is made for a description of this zeolite, its preparation and properties.

The intermediate pore-size synthetic crystalline material designated ZSM-35 ("zeolite ZSM-35" or simply "ZSM-35"), is described in U.S. patent No. 4,016,245, to which reference is made for a description of this zeolite and its preparation. The synthesis of SAPO-11 is described in U.S. Patent Nos. 4,943,424 and 4,440,871. The synthesis of SAPO-41 is described in U.S. Patent No. 4,440,871.

Ferrierite is a naturally-occurring mineral, described in the literature, see, e.g., D.W. Breck, ZEOLITE MOLECULAR SIEVES, John Wiley and Sons (1974), pages 125-127, 146, 219 and 625, to which reference is made for a description of this zeolite.

The dewaxing catalysts used in the shape-selective catalytic dewaxing include a metal hydrogenation-dehydrogenation component. Although it may not be strictly necessary to promote the selective cracking reactions, the presence of this component has been found to be desirable to promote certain isomerization reactions which contribute to the synergy of the two catalyst dewaxing system. The presence of the metal component leads to product improvement, especially VI, and stability as well as helping to retard catalyst aging. The shape-selective, catalytic dewaxing is normally carried out in the presence of hydrogen under pressure. The metal will be preferably platinum or palladium. The amount of the metal component will typically be 0.1 to 10 percent by weight. Matrix materials and binders may be employed as necessary. Table 5 illustrates the properties of a ZSM-23 catalyst containing Pt.

Shape selective dewaxing using the highly constrained, highly shape-selective catalysts may be carried out in the same general manner as other catalytic dewaxing processes, such as those described above for the initial isomerization phase. Conditions will therefore be of elevated temperature and pressure with hydrogen, typically at temperatures from 250° to 500°C, more usually 300° to 450°C and in most cases not higher than 370°C. Pressures extend up to 20786 kPa_{abs}, and more usually up to 17339 kPa_{abs}. Space velocities extend from 0.1 to 10 hr^{-1} (LHSV), more usually 0.2 to 5 hr^{-1}. Hydrogen circulation rates range from 500 to 1000 $n.l.l.^{-1}$, and more usually 200 to 400 $n.l.l.^{-1}$. Reference is made to U.S. Patent 4,919,788 for a more extended discussion of the shape-selective catalytic dewaxing step. As indicated previously, hydrogen may be used as an interbed quench in order to provide maximum temperature control in the reactor. Example 6 and Figure 4, infra illustrate the effectiveness of employing ZSM-23 in combination with zeolite beta in an integrated catalyst system. Pt/ZSM-23, although primarily a shape selective catalyst, adds incremental isomerization capability.

The degree of conversion to lower boiling species in the dewaxing stage will vary according to the extent of dewaxing desired at this point, i.e. on the difference between the target pour point and the pour point of the effluent from the isomerization stage. It will also depend upon the selectivity of the shape-selective catalyst which is used. At lower product pour points, and with relatively less selective dewaxing catalysts, higher conversions and correspondingly higher hydrogen consumptions will be encountered. In general terms conversion to products boiling outside the lube range, e.g. 315°C-, more typically 345°C-, will be at least 5 weight percent, and in most cases at least 10 weight percent, with conversions of up to 30 weight percent being necessary only to achieve the lowest pour points with catalysts of the required selectivity. Boiling range conversion on a 345°C basis will usually be in the range of 10-25 weight percent.

After the pour point of the oil has been reduced to the desired value by selective dewaxing, the dewaxed oil may be subjected to treatments such as hydrotreating, in order to remove color bodies and produce a lube product of the desired characteristics. Fractionation may be employed to remove light ends and to meet volatility specifications.

It is apparent that the highly advantageous results achieved with the present process in terms of lube yield, V.I., and other product properties can be ascribed to the synergistic functioning of the two catalytic phases. In the first phase the large pore zeolite acts more preferentially than conventional dewaxing catalysts on the high molecular weight waxy species in the feed, i.e. the back end of the feed, isomerizing them with minimal cracking. These high molecular weight waxy species, if not removed nearly completely in the dewaxing process, contribute to high cloud point and a hazy appearance at near-ambient temperatures. Because access to the pore structure of the large pore zeolite is less restricted than the pore structures of conventional dewaxing catalysts, a large pore zeolite is not able to dewax the feed to low

pour point (less than -12°C) without incurring significant yield and V.I. losses due to cracking of branched species. However, zeolite beta is effective for selectively converting bulky wax molecules when operated to convert 40% to 90%, more preferably 50% to 80%, of the wax in the feed to the two-stage dewaxing process. The pour point of the product exiting the isomerization step, on an approximate 345°C+ basis, will depend on the nature of the feedstock but is typically between 5°C and 32°C. The intermediate pore size catalysts are, by contrast, more effective at removing the waxes in the front end (low boiling components) of the feed. As Example 6 and Figure 4 infra illustrate, intermediate pore size molecular sieves such as Pt/ZSM-23 possesses incremental isomerization capabilities in addition to shape-selective dewaxing capabilities. Thus, by applying these properties of the intermediate pore size molecular sieves in combination with the properties of a large pore zeolites as described above, it has become possible to evolve a synergistic catalytic dewaxing process which makes the most effective use of the two types of zeolites. A large pore zeolite is used in an initial stage to convert waxy paraffins to less waxy iso-paraffins by isomerization, acting preferentially on the waxy components in the back end of the feed. The partly dewaxed feed is then processed over an intermediate pore size zeolite to convert the residual waxy components so that the final product has a low pour point and low cloud point.

Products

The products from the process are high V.I., low pour point, and low cloud point materials which are obtained in excellent yield. Besides having excellent viscometric properties they are also highly stable, both oxidatively and thermally. They are also stable when exposed to ultraviolet light. V.I. values in the range of 130 to 150 are typically obtained with the preferred wax feeds to the process. Values of at least 140 at-18°C pour point, are readily achievable, with product yields at -18°C pour point

of at least 50 weight percent, usually at least 60 weight percent, based on the original wax feed. The isomerization of the paraffins to iso-paraffins with high VI values at low pour points permits the production of lube products with a unique combination of low pour point and VI. Typically the current products have a VI in the range of 130-150 at -18°C pour and a VI of 120-145 at --40°C pour point.

Examples

The following examples are given in order to illustrate various aspects of the present process and are not to be considered limiting. Examples 1 and 2, directly following, illustrate the preparation of a low acidity Pt/zeolite beta catalyst and Pt/ZSM-23 catalyst, respectively.

Example 1

Zeolite beta with a bulk SiO_2/Al_2O_3 ratio of 40 was bound in a 65% zeolite formulation using Hisil 233 precipitated silica and LUDOX HS-40 sodium-stabilized colloidal silica. The mixture was extruded using a 3% NaOH solution to form 1/16" quadrulobe extrudates. The catalyst was calcined in a nitrogen atmosphere at 482°C for 3 hours and then in air at 538°C for an additional 6 hours. Following calcination, the extrudates were treated with 2M oxalic acid for 6 hours at 71°C. After acid extraction, the catalyst was calcined in air at 538°C Platinum was added to the catalyst by ion exchange using $Pt(NH_3)_4Cl_2$. Following platinum addition, the catalyst was dried and calcined in air at 349°C for 3 hours. Properties of the catalyst are given in Table 4.

Table 4

Properties of Low-Acidity Zeolite Beta

Platinum, wt%	0.6
Sodium, ppm	245
Al_2O_3, wt%	0.4
Surface Area, m^2/g	316
Pore volume, cc/g	0.978
Alpha (before Pt addition)	8

Example 2

A ZSM-23 zeolite with a bulk SiO_2/Al_2O_3 ratio of 120 was extruded with Versal alumina into 1/16" cylindrical extrudates. Following extrusion, the material was calcined in a nitrogen atmosphere at 538°C for 3 hours, then cooled to ambient temperature. It was then ammonium exchanged to reduce the sodium level, air calcined at 538°C for 6 hours, then steamed at 482°C for 4 hours. After steaming, the catalyst was cooled down to ambient temperature and then platinum was added to the catalyst by ion exchange with $Pt(NH_3)_4Cl_2$. Following Pt addition, the catalyst was dried and calcined in air at 349°C for 3 hours. Properties of the catalyst are given by Table 5.

Table 5

Properties of Pt/ZSM-23

Platinum, wt%	0.2
Sodium, ppm	92
Surface Area, m^2/g	242
Pore Volume, cc/g	1.119
Alpha (before Pt addition)	31

Example 3

A slack wax obtained by solvent dewaxing a heavy neutral furfural raffinate (HNSW) was pretreated by hydrocracking at low boiling range conversion (9%

conversion to 345°C or below) using a commercially available fluorided-NiW/Al_2O_3 catalyst. Hydrocracking slack waxes serves to lower the nitrogen content of the wax and to upgrade the occluded oil in the wax to higher V.I. components. Conditions for the hydrocracking were: 1 LHSV, 393°C, 8375 kPa_{abs}, 712 $n.l.l.^{-1}$ circulation. Properties of the slack wax and mildly hydrocracked slack wax are given by Table 6.

Table 6

Properties of Heavy Neutral Slack Wax and Mildly Hydrocracked Slack Wax

	Slack Wax	Hydrocracked Slack Wax
API Gravity	36.0	37.2
Nitrogen, ppm	20	<5
Sulfur, ppm	1000	<5
KV at 100°C, cSt	7.1	-
Wax Content, % (on 345°C+ basis)	66	55
Composition, %		
Paraffins	55	-
Mononaphthenes	13	-
Polynaphthenes	20	-
Aromatics	12	-
Sim Dist, °C		
IBP	382	186
5% Off	429	314
10%	442	391
50%	491	477
90%	544	535
FBP	586	575

Example 4

Approximately 70 cc of the Pt/zeolite beta catalyst of Example 1 and the Pt/ZSM-23 catalyst of Example 2 were loaded into two separate reactors. Zeolite beta was loaded into the first reactor and ZSM-23 was loaded in to the second reactor. The mildly hydrocracked slack wax of Example 3 was fed to the first reactor containing zeolite beta with hydrogen in concurrent downward flow. The total effluent from the first reactor was bypassed around the second reactor. Conditions for the experiment were:

LHSV, hr^{-1}:	1.0
H_2, $n.l.l.^{-1}$:	712 $n.l.l.^{-1}$
Pressure:	13891 kPa_{abs}

The total liquid product from the reaction process was analyzed by simulated distillation and then distilled to a nominal 345°C+ cutpoint. The distilled bottoms were analyzed for viscosity, pour point. Figure 1 illustrates how VI varies with pour point for Pt/zeolite beta, if used

alone. Figures 3 shows how V.I. yield varies, respectively, with decreasing pour point of the distilled bottoms. Lube yield is based on the HNSW (heavy neutral slack wax) feed to the mild hydrocracking pretreatment step.

Several of the liquid products produced from these experiments were solvent dewaxed to -18°C pour. The relationship between solvent dewaxed lube yield and wax conversion is shown by Figure 4. Wax conversion is defined by:

$$\text{Wax Conversion} = \frac{\text{Wax Content of Feed} - \text{Wax Content of Reaction Product}}{\text{Wax Content of Feed}}$$

Low acidity Pt/zeolite beta is an effective isomerization catalyst converting wax to lube with mineral cracking to light products up to a wax conversion of 55-60%. When wax conversion increases above 80%, isomerized paraffins, which have ready access to the Pt/zeolite beta pore structure crack more rapidly than they can be formed by isomerizing the remaining wax. The result is that yield decreases rapidly with further increases in conversion.

Example 5

The mildly hydrocracked slack wax of Example 3 was bypassed around the first reactor and fed to the second reactor containing Pt/ZSM-23. Process conditions were identical to those of Example 4. The total liquid product was treated as in Example 4. Variation of V.I. and yield with bottoms pour point are shown by Figures 1 and 3 respectively.

Figure 1 shows that for isomerization/dewaxing over either Pt/zeolite beta or Pt/ZSM-23, V.I. drops sharply with decreasing pour point. The slopes of the curves depicting the variation of V.I. with pour point are similar at a given pour point when the reaction occurs over

Pt/zeolite beta or Pt/ZSM-23 alone. Despite V.I. being approximately 5-6 numbers higher for Pt/ZSM-23 than for Pt/zeolite beta at a given pour point, it is not possible to produce a lubricant stock having a V.I. greater than 135 with the use of either Pt/zeolite beta or Pt/ZSM-23 alone to dewax the lube to a -12°C pour point. The production of 135+ V.I. base stocks with either of these catalysts operating alone requires operation of the catalyst to achieve wax conversion typically less than 85% with the residual wax being removed from the product by solvent dewaxing.

Example 6

The mildly hydrocracked slack wax of Example 3 was fed to the Pt/zeolite beta reactor and the effluent from the Pt/zeolite beta passed over the Pt/ZSM-23. Both reactors operated at the conditions of Example 4 (1 LHSV over each reactor). The zeolite beta was operated at 322°C to convert approximately 70% of the wax in the mildly hydrocracked waxy feed where wax conversion is defined by the equation in Example 4.

A sample of the product from the first reactor was distilled with the 345°C bottoms found to have a pour point of 30°C. The total effluent from the first reactor was cascaded to the Pt/ZSM-23 reactor and temperature varied in the second reactor to effect changes in product pour point. Variation of V.I. and yield with bottoms pour point are compared to the variations obtained by operating the catalysts individually by Figures 2 and 3 respectively.

Operating the Pt/zeolite beta to a distilled bottoms pour point of 30°C and removing the residual wax with Pt/ZSM-23 results in a lubricant having a VI which is less sensitive to pour point variation than a lubricant produced by either catalyst operating alone, as shown by Figure 2. The integrated, synergistic catalyst system allows production of 135+ V.I. lubricants at -12°C pour for which either catalyst operating alone does not.

The relatively shallow slope also implies that very low pour points can be achieved without incurring a substantial V.I. penalty.

The integrated catalyst system also offers significant yield benefit over either catalyst operating alone (Figure 3). The shallow slopes of the branch emanating from the Pt/zeolite beta curve where Pt/zeolite beta is operating at 322°C, implies that very low pour points can be achieved without substantial yield penalty by the synergistic catalyst system.

The synergy of the system reflects the difference in shape selectivities of the two catalysts, and their ability to isomerize waxes. The incremental isomerization capability of Pt/ZSM-23 is illustrated by Figure 4 which shows solvent dewaxed oil lube as a function of wax conversion for products generated by these experiments having a pour point above -12°C. Above 75% wax conversion, dewaxed oil yield decreases for Pt/zeolite beta operating alone. However, using Pt/ZSM-23 to dewax the Pt/zeolite beta effluent results in an increase in solvent dewaxed lube yield implying that Pt/ZSM-23 adds incremental isomerization ability. In addition to converting some waxy species to lube, Pt/ZSM-23 has sufficient shape selectivity to prevent most of the isoparaffins formed over Pt/zeolite beta from cracking and reducing lube yield.

Example 7

The mildly hydrocracked slack wax of Example 3 was fed to the Pt/zeolite beta reactor at the conditions of Example 4. The Pt/zeolite beta reactor was operated at 329°C to achieve approximately 88% wax conversion with wax conversion being defined in Example 4. A sample of the product from the first reactor was distilled and the 345°C bottoms found to have a pour point of 16°C. The total effluent from the first reactor was fed to the Pt/ZSM-23 reactor and temperature varied in the second reactor to effect changes in product pour point. Variation of V.I. and yield with bottoms pour point are shown by Figures 2

and 3 respectively. Lube yield is based on heavy neutral slack wax fed to the hydrocracking reactor.

Similar to Example 6, the slopes of the VI and lube yield curves with pour point are significantly shallower than for either catalyst operating alone. This suggests that the synergy of the dual catalyst system exists for a range of Pt/zeolite beta operating conditions. Figure 3 shows that yield at low pour point, e.g. less than -12°C, is highest for the two-catalyst system. Neither catalyst operating alone gives a yield exceeding 55% while the two examples of the two-catalyst system each gave yields at -12°C pour of at least 60%.

Table 7 shows a yield and V.I. comparison for Examples 4 through 7 for a lubricant of 10°F pour point.

Table 7

Comparison of Synergistic Catalyst System Selectivity with Stand-alone Catalysts(1)

Conditions: 1 LHSV Over Each Reactor, 1389 kPa_{abs}, 712 $n.l.l.^{-1}$

At -12°C Pour Point

	Pt/zeolite /beta	Pt/ZSM-23	Pt/zeolite// beta Pt/ZSM-23	Pt/zeolite/ beta Pt/ZSM-23
Example	4	5	6	7
Pt/β Temp,°C	341	-	322	329
Pt/ZSM-23 Temp,°C	-	350	329	332
345 °C+ Product				
V.I.	121	133	142	135
Yield, % HNSW	38	53	70	60

(1) Interpolated and extrapolated from Figures 1 and 2

Example 8

The mildly hydrocracked slack wax of Example 3 was processed over Pt/zeolite beta at the conditions of Example 4 to achieve approximately 82% wax conversion. The total reactor effluent was processed over Pt/ZSM-23 at a temperature of 346°C. The reaction product was distilled to a normal 345°C cutpoint. The distilled bottoms had the following properties:

Table 8

Properties of Distilled Bottoms

Viscosity, Kinematic at 100°C, cSt	5.20
V.I., Viscosity Index	132
Pour Point, °C	-37
Cloud Point, °C	-24
Simulated Distillation, C	
Initial Boiling Point	304
5% Off	334
10%	356
50%	447
90%	516
Final Boiling Point	564
Aromatics (by UV), %	<1

This example shows that the integrated Pt/zeolite beta/Pt/ZSM-23 catalyst system is capable of producing base stocks with viscosity indices exceeding 135 at very low pour points. The superior cloud point of -24°C reflects the benefit of processing the feed over zeolite beta prior to ZSM-23. Zeolite beta, because of its less constrained pore nature, has the ability to convert large waxy molecules which often lead to high pour/cloud differentials. Intermediate pore zeolites, such as ZSM-23, have more difficulty converting high molecular weight waxes frequently leading to low pour point base stocks with relatively high cloud points.

UV absorptivity measurements show the benefit of high pressure for producing high V.I., low aromatics base stocks.

Example 9

A heavy hydrocracked vacuum distillate having the properties below was dewaxed by Pt/ZSM-23 operating alone and by the Pt/zeolite beta // Pt/ZSM-23 catalytic dewaxing system.

API Gravity	30.3
Viscosity, KV at 100°C, cSt	9.90
Pour Point, °C	49
Sulfur, ppm	<20
Nitrogen, ppm	2
Wax Content, %	15
Sim Distillation, °C	
IBP	368
5% Off	385
10%	399
50%	485
90%	564

The data, tabulated below, show a slight synergy for the combination catalyst system for low wax content feeds in that yield is at least equivalent and sometimes slightly higher at constant pour point. The less restrictive nature of the Pt/zeolite beta catalyst enables some incremental conversion of high boiling waxes leading to lower cloud points for the combination catalyst system. This is an

especially critical benefit since highly shape selective dewaxing catalysts can give hazy products with high cloud points when dewaxing heavy feeds.

Catalyst	PT/ZSM-23			Pt/zeolite beta// Pt/ZSM-23			
Pour Point of 345°C+ Fraction After Pt/zeolite beta Dewaxing,°C				18			
345 C+ Fraction							
Pour Point, °C	-21	-26	-37	-15	-23	-29	-37
Cloud Point, °C	3	-2	-9	1	-8	-9	-14
Difference Cloud/Pour, C°	24	24	28	16	15	20	23
Yield, wt%	94	92	88	94	92	91	90
VI	107	104	103	-104	104	103	

Example 10

A 650 SUS heavy neutral slack wax was hydrocracked and stripped to remove ammonia and H_2S. A material having the following properties was produced.

API Gravity	37.4
Sulfur, ppm	2
Nitrogen, ppm	<2
Oil Content on 650 F+ Fraction, °C	>49
Sim Dist, °C	
IBP/5%	125/255
10%/20%	330/434
50%/80%	497/527
90%/FBP	538/566

This hydrocracked material was dewaxed to very low pour point over the Pt/ZSM-23 catalyst of Example 2. It was also dewaxed to very low pour point with the Pt/zeolite beta // Pt/ZSM-23 catalyst system where the Pt/zeolite beta temperature was maintained to convert 65% of the wax in the hydrocracked feed. Wax conversion is defined in Example 4.

The Pt/ZSM-23 catalyst used in the dual catalyst system was the same as that used in Example 2.

The Pt/zeolite beta was prepared by extruding beta zeolite with Versal 250 pseudoboehmite alumina to form 1/16" extrudate. The extrudate was dried and calcined in nitrogen for 3 hours at 482°C, then calcined in air at 1000 for 6 hours. Following calcination, the extrudate was steamed in 100% steam at 549°C for 96 hours. Platinum was incorporated on the extrudate by ion exchange with an aqueous solution of platinum tetraamine chloride to achieve a loading of 0.6 wt%. The catalyst was then calcined in air at 349°C for 3 hours.

The dewaxed products were distilled to a nominal 345°C+ cutpoint and the pour point and cloud points were measured to be:

Dewaxing Catalysts	Pt/ZSM-23	Pt/zeolite beta// Pt/ZSM-23
Wax Conversion Over Pt/B, %	-	65
Pour Point of 650°F+ Fraction After Pt/B Dewaxing, °C	-	29
Dewaxed Lube		
Pour Point, °C	-37	-43
Cloud Point, °C	-7	-34
Sim Dist., °C IBP/5%/10%	300/300/353	313/341/361

This example shows that the incremental conversion of high pour point waxes over Pt/zeolite beta leads to low product cloud point. Pt/ZSM-23, because of its less accessible structure is not as effective at converting waxy species throughout the feed boiling range thus leading to a relatively high cloud points.

WHAT IS CLAIMED IS:

1. A process for producing a high Viscosity Index (VI) lubricant having a VI of at least 120 from a waxy hydrocarbon feed having a wax content of at least 30 wt%, the process employing two catalysts operating synergistically, and comprising the following steps:

(a) catalytically dewaxing waxy paraffins present in the feed primarily by isomerization, in the presence of hydrogen and in the presence of a low acidity large pore zeolite isomerization catalyst, the catalyst having an alpha value of not more than 30 and containing a noble metal hydrogenation component;

(b) subjecting the effluent of the initial catalytic dewaxing step to a second catalytic dewaxing step in which the effluent is contacted with a constrained intermediate pore crystalline material, which contains a metal hydrogenation dehydrogenation component.

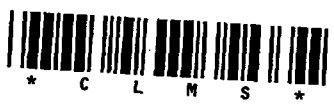
2. The process of claim 1 wherein the large pore zeolite of step (a) possesses at least one pore channel of 12-membered oxygen rings.

3. The process of claim 1, wherein the large pore zeolite of step (a) possesses a Constraint Index less than 1.

4. The process of claim 1, wherein the large pore zeolite of step (a) is zeolite beta.

5. A process of claim 1 in which the isomerization catalyst is a zeolite beta isomerization catalyst having an alpha value of not greater than 20.

6. The process of claim 5, wherein in which the isomerization catalyst is a low acidity zeolite beta which has been severely steamed, having a framework silica:alumina ratio of at least 200:1.



7. The process of claim 6, in which the isomerization catalyst comprises from 0.3 to 2 wt% Pt on a support comprising zeolite beta.

8. A process of claim 1, wherein the constrained intermediate pore crystalline material of step (b) possesses one channel of 10-membered oxygen rings, with any channel intersecting the channel of 10-membered oxygen rings being composed of 8 membered oxygen rings.

9. The process of claim 1 in which the catalyst of the second catalytic dewaxing step is selected from the group consisting of ZSM-22, ZSM-23, ZSM-35, SAPO-11 and SAPO-41.

10. The process of claim 1 in which the catalyst of the second catalytic dewaxing step is an intermediate pore crystalline material having specific characteristics defined by:

(1) a ratio of sorption of n-hexane to o-xylene, on a volume percent basis, of greater than 3, which sorption is determined at a P/Po of 0.1 and at a temperature of 50°C for n-hexane and 80°C for o-xylene and (2) by the ability of selectively cracking 3-methylpentane in preference to 2,3-dimethylbutane at 538°C and 1 atmosphere pressure from a 1/1/1 weight ratio mixture of n-hexane/3-methylpentane/2,3-dimethylbutane mixture with the ratio of rate constants k_{3MP}/k_{DMB} being in excess of 2.

11. The process of claim 1, in which the metal hydrogenation-dehydrogenation component of the catalyst of the second dewaxing step is either Pt or Pd.

12. A process of claim 1 in which the feed comprises a waxy hydrocarbon feed having a wax content of at least 50 wt% and an aromatic content of less than 25 wt%.

13. The process of claim 1 wherein the feedstock is selected from the group consisting of a slack wax, deoiled

wax, wax from Fischer-Tropsch processes, foots oils, petrolatum, vacuum gas oil, or a raffinate from solvent extraction of a vacuum distillate.

14. The process of claim 1, in which the isomerization step is carried out in the presence of hydrogen to convert from 40 to 90 wt% of the wax contained in the feed to the isomerization step.

15. The process of claim 14, in which the wax conversion during the isomerization step is from 50 to 80 wt% based on the feed to the isomerization step.

16. The process of claim 1, wherein the effluent from the isomerization step has a pour point which ranges from -1°C to 43°C.

17. The process of claim 1 in which the isomerization step is carried out at hydrogen partial pressure ranging from a temperature from 288° to 427°C.

18. A process of claim 1, wherein the preferred range of VI is from 130 to 150.

19. The process of claim 1, in which the dewaxed effluent of step (b) is hydrotreated by contacting it with a catalyst comprising a metal hydrogenation component on an amorphous, porous support material at a pressure in the range from 3549 kPa_{abs} to 20786 kPa_{abs}, a reaction temperature in the range from 260°C to 427°C, a space velocity which is in a range from 0.1 to 10 LHSV, and a once-through hydrogen circulation rate which extends from 178 $n.l.l.^{-1}$ to 1780 $n.l.l.^{-1}$, in order to improve the thermal and oxidative stability of the lubricant.

20. A process for producing a high Viscosity Index (VI) lubricant having a VI of at least 120 from a waxy hydrocarbon feed having a wax content of at least 30 wt%,

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the process employing two catalysts operating synergistically, and comprising the following steps:

(a) hydrocracking of the feed in order to reduce its nitrogen content as well as to remove naphthenic and aromatic components, thereby improving VI, the hydrocracking process comprising contacting the feed with a catalyst composed of a metal hydrogenation component on an acidic support;

(b) catalytically dewaxing waxy paraffins present in the feed primarily by isomerization, in the presence of hydrogen and in the presence of a low acidity large pore zeolite isomerization catalyst, the catalyst having an alpha value of not more than 30 and containing a noble metal hydrogenation component;

(c) subjecting the effluent of the initial catalytic dewaxing step to a second catalytic dewaxing step in which the effluent is contacted with a constrained intermediate pore crystalline material, which contains a metal hydrogenation dehydrogenation component.

21. The process of claim 20 wherein the large pore zeolite of step (a) possesses at least one pore channel of 12-membered oxygen rings.

22. The process of claim 20, wherein the large pore zeolite of step (a) possesses a Constraint Index less than 1.

23. The process of claim 20, wherein the large pore zeolite of step (a) is zeolite beta.

24. A process of claim 20 in which the isomerization catalyst is a zeolite beta isomerization catalyst having an alpha value of not greater than 20.

25. The process of claim 24, wherein in which the isomerization catalyst is a low acidity zeolite beta which has been severely steamed, having a framework silica:alumina ratio of at least 200:1.



26. The process of claim 20, in which the isomerization catalyst comprises from 0.3 to 2 wt% Pt on a support comprising zeolite beta.

27. A process of claim 20, wherein the constrained intermediate pore crystalline material of step (b) possesses one channel of 10-membered oxygen rings, with any channel intersecting the channel of 10-membered oxygen rings being composed of 8 membered oxygen rings.

28. The process of claim 20 in which the catalyst of the second catalytic dewaxing step is selected from the group consisting of ZSM-22, ZSM-23, ZSM-35, SAPO-11 and SAPO-41.

29. The process of claim 20 in which the catalyst of the second catalytic dewaxing step is an intermediate pore crystalline material having specific characteristics defined by:

(1) a ratio of sorption of n-hexane to o-xylene, on a volume percent basis, of greater than 3, which sorption is determined at a P/Po of 0.1 and at a temperature of 50°C for n-hexane and 80°C for o-xylene and (2) by the ability of selectively cracking 3-methylpentane in preference to 2,3-dime-thylbutane at 1000°F and 1 atmosphere pressure from a 1/1/1 weight ratio mixture of n-hexane/3-methylpentane/2,3-dimethylbutane mixture with the ratio of rate constants k_{3MP}/k_{DMB} being in excess of 2.

30. The process of claim 20, in which the metal hydrogenation-dehydrogenation component of the catalyst of the second dewaxing step is either Pt or Pd.

31. A process of claim 20 in which the feed comprises a waxy hydrocarbon feed having a wax content of at least 50 wt% and an aromatic content of less than 25 wt%.

32. The process of claim 20, in which the isomerization step is carried out in the presence of hydrogen to convert



from 40 to 90 wt% of the wax contained in the feed to the isomerization step.

33. The process of claim 20 wherein the feedstock is selected from the group consisting of a slack wax, deoiled wax, wax from Fischer-Tropsch processes, foots oils, petrolatum, vacuum gas oil, or a raffinate from solvent extraction of a vacuum distillate.

34. The process of claim 32, in which the wax conversion during the isomerization step is from 50 to 80 wt% based on the feed to the isomerization step.

35. The process of claim 20, wherein the effluent from the isomerization step has a pour point which ranges from -1 to 43°C.

36. The process of claim 20 in which the isomerization step is carried out at hydrogen partial pressure ranging from 5617 to 17,339 kPa_{abs} and at a temperature from 288°C to 427°C.

37. A process of claim 20, wherein the preferred range of VI is from 130 to 150.

* C L M S *

38. The process of claim 20, in which the dewaxed effluent of step (b) is hydrotreated by contacting it with a catalyst comprising a metal hydrogenation component on an, amorphous, porous support material at a pressure in the range from 3549 kPa_{abs} to 20786 kPa_{abs}, a reaction temperature in the range from 500°F to 427°C, a space velocity which is in a range from 0.1 to 10 LHSV, and a once-through hydrogen circulation rate which extends from 178 $n.l.l.^{-1}$ to 1780 $n.l.l.^{-1}$, in order to improve the thermal and oxidative stability of the lubricant.

ABSTRACT OF THE DISCLOSURE

Petroleum waxes are converted to high Viscosity Index lubricants by a synergistic process which employs two catalysts. Viscosity Index and yield are greater for product of the integrated catalyst process than they are for the product of either of the catalysts alone. The wax feed which may be pretreated by mild hydrocracking, is first subjected to isomerization in the presence of hydrogen over a low acidity zeolite isomerization catalyst which effects a preferential isomerization of the paraffin components in the feed to less waxy, high V.I. isoparaffins. The isomerization is operated at a pressure of at least 5617 kPa_{abs} hydrogen partial pressure (reactor inlet). The catalyst is preferably a noble metal containing zeolite beta catalyst which contains boron as a framework component of the zeolite in order to give a low alpha value, typically below 20. The isomerization is carried out at a temperature of 345°C with conversion in the range of 10 to 40 wt.% of the feed. The product of the isomerization process is then contacted with a shape-selective catalyst in order to further reduce the pour point. Preferably ZSM-22, ZSM-23 or ZSM-35 is used. The shape-selective catalyst preferably contains noble metals such as Pd or Pt.

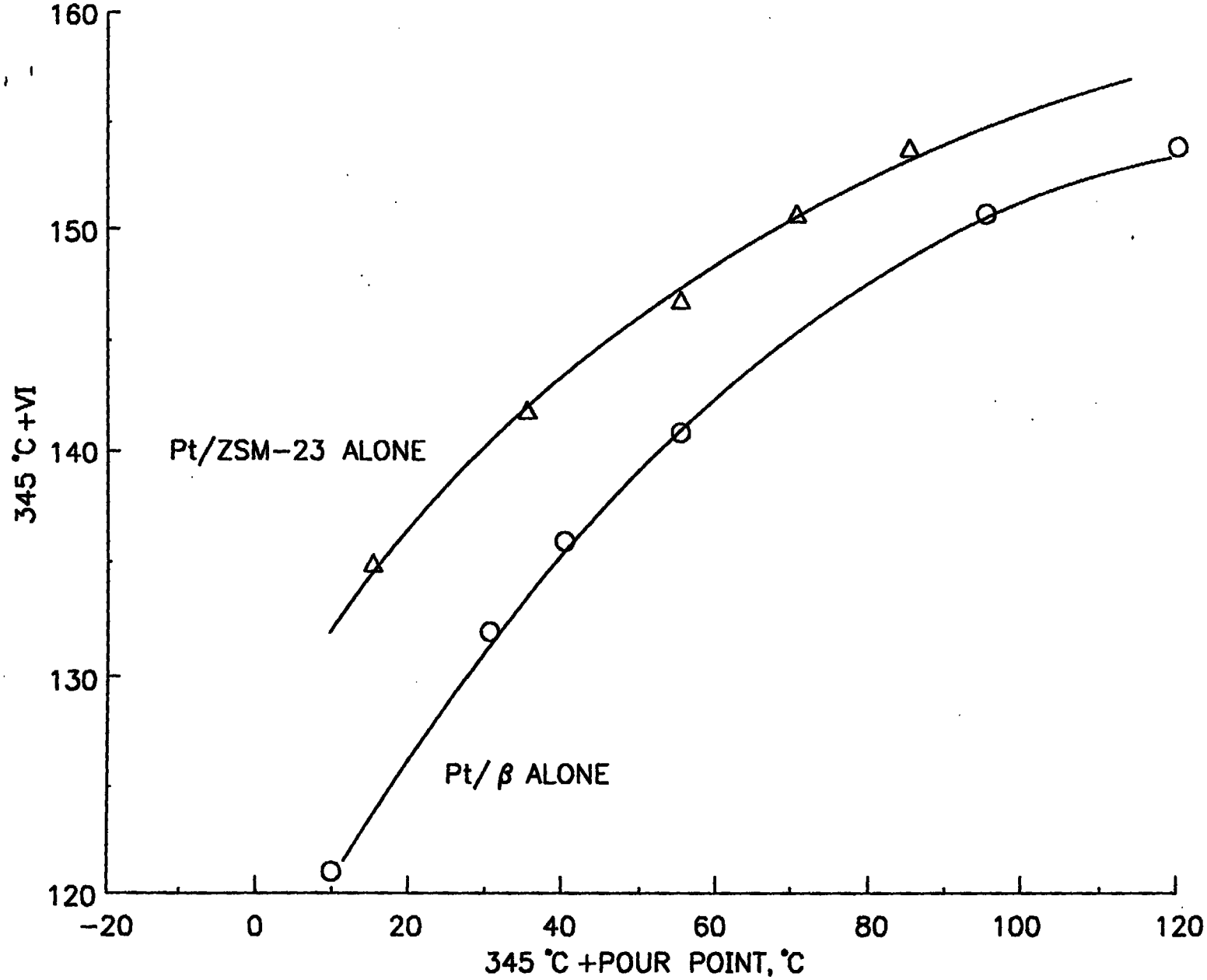

160
150
140
130
120
345 °C +VI
Pt/ZSM-23 ALONE
Pt/β ALONE
−20
0
20
40
60
80
100
120
345 °C +POUR POINT, °C

FIG. 1

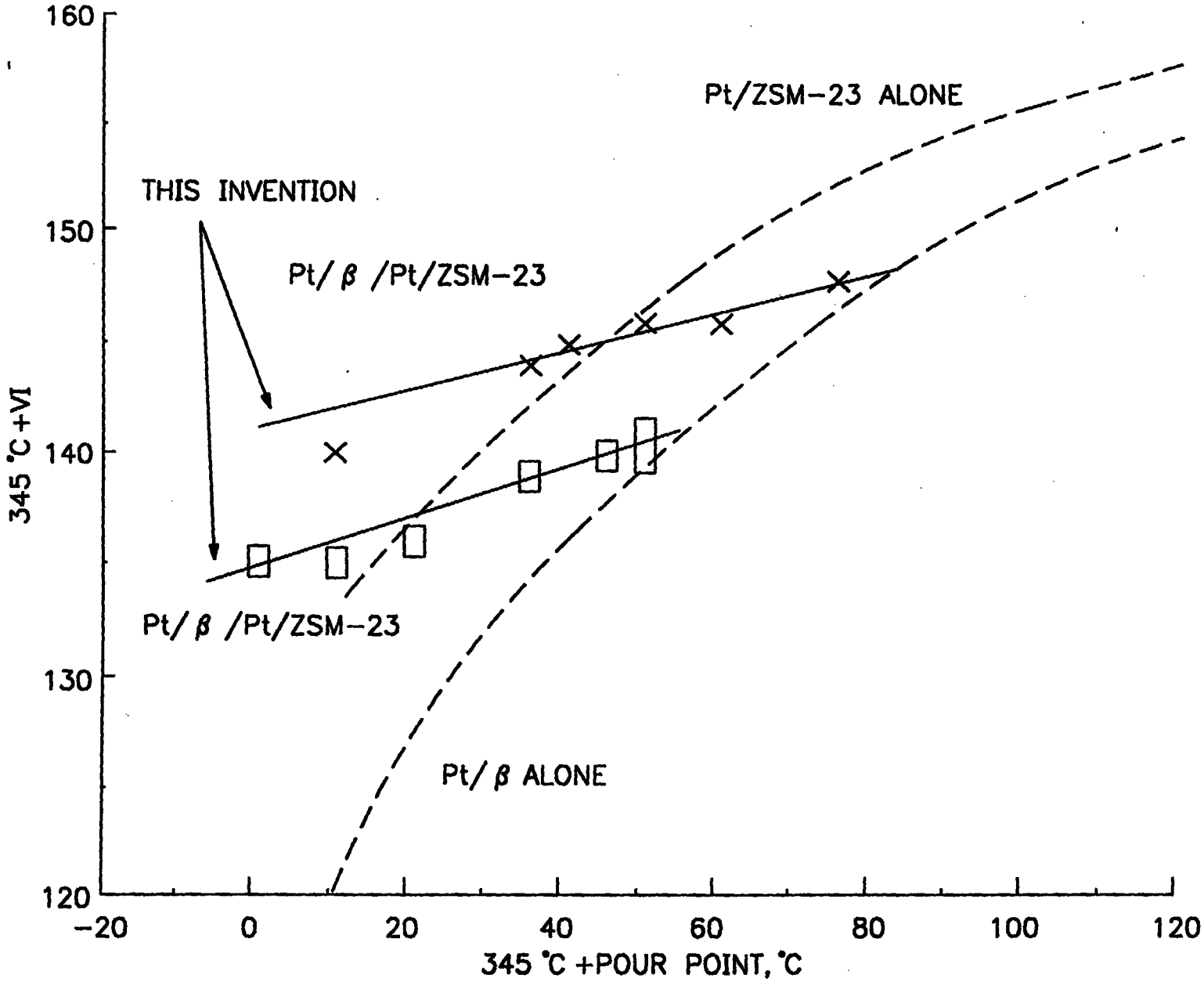

160
150
140
130
120
345 °C +VI
THIS INVENTION
Pt/ β /Pt/ZSM-23
Pt/ β /Pt/ZSM-23
Pt/ZSM-23 ALONE
Pt/ β ALONE
−20
0
20
40
60
80
100
120
345 °C +POUR POINT, °C

FIG. 2

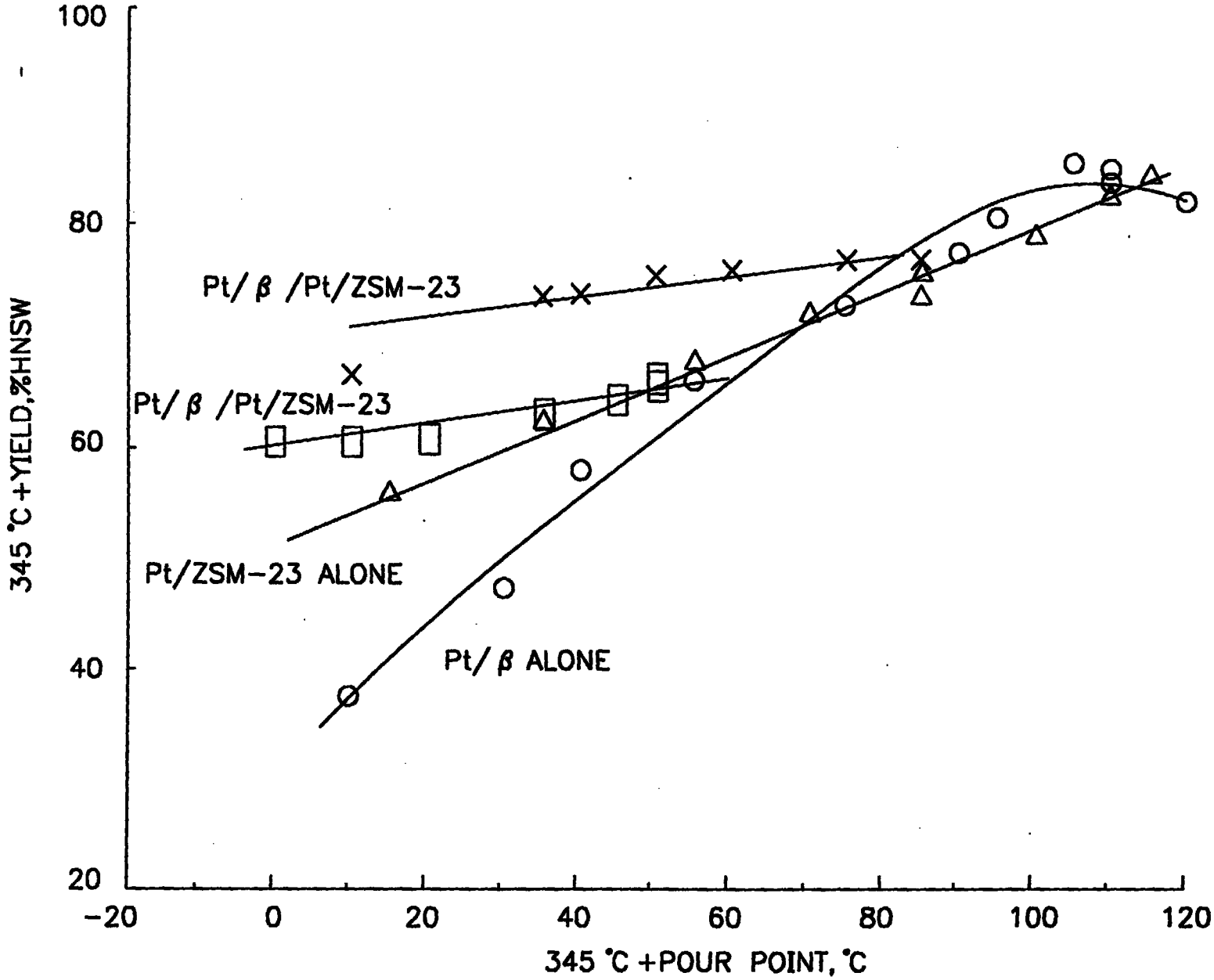

100
80
60
40
20
345 °C +YIELD,%HNSW
Pt/ β /Pt/ZSM-23
Pt/ β /Pt/ZSM-23
Pt/ZSM-23 ALONE
Pt/ β ALONE
-20
0
20
40
60
80
100
120
345 °C +POUR POINT, °C

FIG. 3

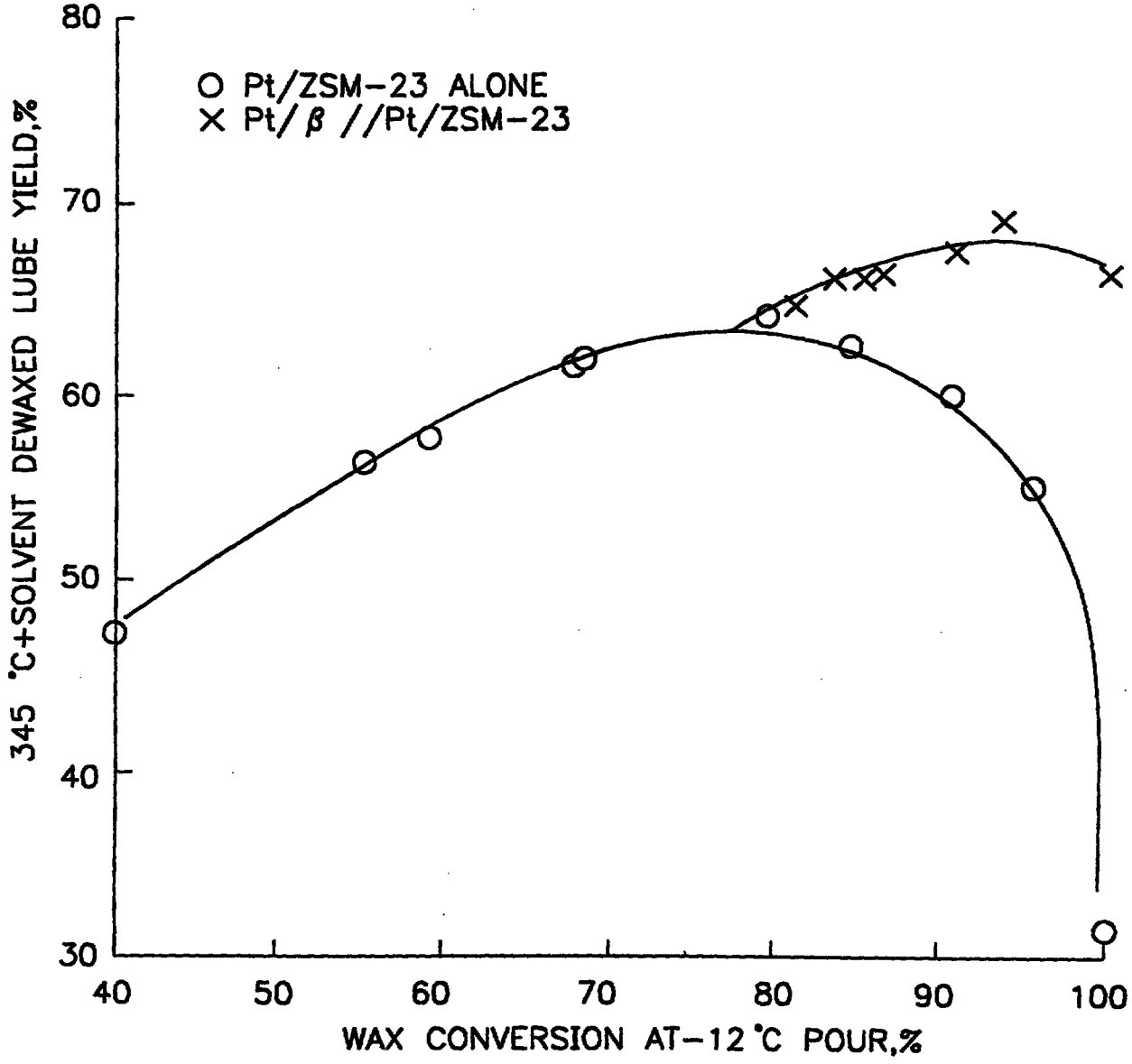

80
70
60
50
40
30
345 °C+SOLVENT DEWAXED LUBE YIELD,%
O Pt/ZSM-23 ALONE
× Pt/β //Pt/ZSM-23
40
50
60
70
80
90
100
WAX CONVERSION AT-12 °C POUR,%

FIG. 4