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CATALYTIC PRODUCTION OF LOW POUR POINT LUBRICATING OILS

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ABSTRACT OF THE DISCLOSURE

In a process for reducing the pour point of heavy lubricating oils without physically dewaxing the oils or diluting them with low-boiling products, which comprises denitrifying and hydroisomerizing the oils under specified conditions, it has been found that the hydroisomerization is made much more selective and the concurrent hydrocracking significantly reduced if the denitrified oil is hydrogenated to substantially eliminate the aromatic compounds prior to hydroisomerization. The hydroisomerized oil may be further hydrogenated, if desired, to improve the stability of the oil.

CROSS REFERENCES

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

BACKGROUND OF THE INVENTION

This invention relates to processes for lowering the pour points of hydrocarbon oils and to processes involving treating lubricating oils with hydrogen in the presence of catalysts.

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

Normal paraffins and waxes present in virtually all high-boiling portions of crude petroleum impart a high pour point to the oil fractions as obtainable directly by distillation, and accordingly the oils must be treated to meet the low pour point specifications. Treating procedures of two kinds have been described in the prior art. One type of procedure involves combining low-boiling materials (i.e., materials boiling below about 550° F.) with the high-boiling portions or, if the initial oil contains both high- and low-boiling portions, leaving both portions in the finished product. This procedure is unsatisfactory, for it produces wide-boiling range end products, which have components boiling below 550° F. and are thus unsatisfactory for use as lubricants. Another procedure which is described in the art is one in which the high-boiling portions are dewaxed. The dewaxing procedures heretofore used have all required at least one step of physically separating wax from the oil, though a variety of procedures have been developed. Thus the oil may be cooled to a low temperature sufficient to crystallize out hard, normal paraffin wax; and the wax can then be physically separated by filtration, centrifugation, or like methods. More commonly, solvent dewaxing is employed wherein a solvent, such as a mixture of methylethylketone and benzene is added, which preferentially dissolves the non-waxy hydrocarbons and lowers the oil viscosity without appreciably lowering the crystallization temperature of the wax, but the wax must still be separated physically as before. In addition, it is frequently necessary to use mechanically complicated, internally scraped, heat exchangers in the chilling procedures. Other methods have been devised involving forming complexes with the wax molecules, such as in the urea adduction process; but again a physical separation of the wax or wax adduct or complex is needed.

The dewaxing methods heretofore used are quite costly to build and to operate because of the large amount of equipment needed for the mechanical handling, which must be done at low throughputs to accomplish the physical wax separation. Thus in a typical process for producing lubricating oils comprising several steps—including, for example, solvent extraction, acid treating, hydrofining, clay contacting, and solvent dewaxing—the dewaxing step is the most costly treating step. There have been some indications in the art that certain oils need only "preferentially" be dewaxed. However, examination of data disclosed in this art makes clear that the oils in question are produced by processes in which only a few degrees' reduction in pour point of the product oils is achieved or in which the product oils contained some quantity of low-boiling materials; and the latter served to reduce the pour point of the product oils. It would, therefore, be highly desirable to be able to minimize or eliminate completely the need for dewaxing by physical separation of wax, which would require that some means be found for lowering the pour points of the available oils other than by dilution of the high-boiling oils with low-boiling materials.

SUMMARY

As disclosed in our aforementioned copending applications, it has been found that the pour points of heavy waxy oils can be lowered sufficiently to meet the low pour point specifications of lubricating oils and similar products without recourse to any step involving physically separating wax. In accordance with the process disclosed in said copending application Ser. No. 477,597, the pour point of a heavy oil is lowered by first substantially eliminating organic nitrogen compounds present in the oil and then contacting the nitrogen-free oil with a reforming catalyst in a hydrocracking-hydroisomerization zone. The pour point lowering results from hydroisomerization of high pour point paraffins contained in the oil, and the conditions used in the hydroisomerization are such that the pour point lowering is accompanied by hydrocracking. The hydrocracking lowers the yield of the desired high-boiling oil products.

It has now been unexpectedly found that hydroisomerization of the nitrogen-free oil at temperatures in the

range of 750°–900° F. over a naphtha reforming catalyst having no more than two weight percent halide is made much more selective for effecting a greater lowering of the pour point with less hydrocracking if aromatic compounds are substantially eliminated from the nitrogen-free oil prior to the contacting with the hydroisomerization catalyst. Thus in accordance with the present invention, the aromatics are eliminated from the nitrogen-free oil by contacting with an active hydrogenation catalyst in the presence of hydrogen at mild temperature conditions of 200°–650° F. and elevated pressures of 1,000–5,000 p.s.i.g.

DETAILED DESCRIPTION OF THE INVENTION

To illustrate the nature of the improvements which can be accomplished by means of the present invention, the following example presents a comparison of the results obtained by (1) the two-stage process of first subjecting a heavy waxy oil to hydrocracking-denitrification to substantially eliminate organic nitrogen compounds and then hydroisomerizing the high-boiling portion of the nitrogen-free oil, and by (2) the process of the invention wherein an aromatics hydrogenation step is interjected between the nitrogen removal step and the hydroisomerization step. In addition, there are shown for comparison the results obtainable by conventional solvent dewaxing of the nitrogen-free oil.

EXAMPLE

The residuum from vacuum distillation of mixed California crude oils was subjected to propane deasphalting to obtain a metal-free residual oil in a yield of 57 percent, containing 7,400 p.p.m. organic nitrogen, 1.06 weight percent sulfur, and having a gravity of 16.1° API. The deasphalted oil is quite waxy, as a yield of only 88 percent oil is obtainable by solvent dewaxing to 0° F. pour point. The undewaxed solvent-deasphalted oil was contacted with a nickel sulfide-molybdenum sulfide-alumina-silica sulfactive hydrogenation catalyst at 800° F., 2,400 p.s.i.g., and 0.5–0.65 LHSV, in the presence of about 5,000 standard cubic feet of recycled hydrogen per barrel. The effluent oil was freed of H_2S and NH_3 and then distilled to recover a bottoms fraction boiling entirely above 750° F., obtained in a yield of 45 weight percent from the deasphalted oil. The hydrocracked oil boiling above 750° F. contained 2 p.p.m. nitrogen and 12 p.p.m. sulfur and had a pour point of 105° F. This heavy nitrogen-free oil was separated into three portions which were separately treated as follows:

(A) A portion was subjected to conventional solvent dewaxing with a methylethylketone solvent to a pour point of 0° F., and the dewaxed oil was then distilled into fractions with boiling ranges of 750°–900° F., representing a 140 neutral lubricating oil; 900°–1,000° F,. representing a 400 neutral lubricating oil; and 1,000+ ° F. bottoms representing a bright stock.

(B) Another portion was contacted with a platinum-on-alumina reforming catalyst containing 0.4 weight percent platinum, 0.2 weight percent chloride, and 0.5 weight percent fluoride, at 800° F., 2,800 p.s.i.g., 0.4 LHSV, and about 10,000 standard cubic feet of recycled hydrogen per barrel. The oil effluent of this contacting was distilled to obtain distillate fractions and a bottoms fraction boiling entirely above 750° F., which bottoms fraction was then further distilled into the fractions corresponding to the 140 neutral, 400 neutral, and bright stock.

(C) The third portion of nitrogen-free heavy oil was contacted with a hydrogenation catalyst comprising 2 weight percent palladium on 87/13 silica/alumina cracking catalyst support at a low temperature ranging between 250° F. and 300° F., at 2,300 p.s.i.g., 0.5 LHSV, with 6,300 standard cubic feet of hydrogen per barrel. The hydrogenated oil was then contacted with the platinum-alumina reforming catalyst in the same manner as just described in (B) above, at a lower temperature of 756° F. isomerized oil was then separated into the 140 neutral, 400 neutral, and bright stock fractions.

The following table summarizes the results obtained in the above comparisons, and shows the yields of the respective products which are obtainable from a given amount of solvent deasphalted oil feed by the respective techniques of the runs (A), (B), and (C) just described.

TABLE

Lube oil products from SDA oil feed	A Hydrocracking plus solvent dewaxing	B Hydrocracking plus hydroisomerization	C Hydrocracking plus hydrogenation plus hydroisomerization
140 Neutral:			
Yield, bbls.	2,900	2,700	2,500
Viscosity, SUS at 210° F.	42	41	41
V.I.	100	118	112
Pour point, ° F.	0	+20	−5
400 Neutral:			
Yield, bbls.	1,240	600	1,100
Viscosity, SUS at 210° F.	60	57	57
V.I.	108	118	115
Pour point, ° F.	0	+30	−30
Bright Stock:			
Yield, bbls.	1,100	350	400
Viscosity, SUS at 210° F.	97	90	102
V.I.	115	114	115
Pour point, ° F.	0	+20	
Micro solid pt., ° F.			−56

As shown, the largest yield of the respective lubricating oil fractions is obtained by solvent dewaxing the hydrocracked nitrogen-free oil. But besides being the most expensive technique, this system also has the disadvantage that the viscosity index of the 140 neutral, and of the 400 neutral, is lower than obtained in the other runs. If the solvent dewaxing is carried further so as to obtain a lower pour point than shown, the viscosity index is even lower. Particularly to be noted is that the hydrocracking+hydroisomerization process of column B is substantially improved by the interjected hydrogenation step, as shown in column C. In particular, a higher yield of 400 neutral distillate and a higher yield of bright stock are obtained, with only slightly lower yield of 140 neutral; and the pour points of all the respective fractions are much lower than obtained by the isomerization without the prehydrogenation.

Further, the improved process shown in column C permits operation of the hydroisomerization step at a temperature more than 45° F. lower than that required by the process of column B. This results in longer catalyst life, lower fouling rates, and lower costs for construction and maintenance of equipment. Thus the prehydrogenation unexpectedly caused a marked increase in the selectivity of the hydroisomerization step such that a greater reduction in pour point could be obtained at the same or a lower temperature with less hydrocracking. It had already been established that, without the prehydrogenation, higher temperatures of hydroisomerization causing even more hydrocracking would have to be used to obtain the low pour points.

In the hydrogenation with the palladium on silica-alumina catalyst, the concentration of aromatics in the nitrogen-free oil was lowered from about 11 weight percent to less than 1 weight percent. Specifically, the aniline point of the nitrogen-free oil boiling above 750° F. recovered from the first hydrocracking-denitrification was 246° F.; and the aniline point of the hydrogenated oil fed to the hydroisomerization with the platinum-alumina catalyst was 263° F. The hydrocracking-denitrification step itself can be effective in lowering the aromatics content of the heavy oil feed to less than about 5 percent, if the temperature used is not too high; but it is not possible

thereby to obtain the very low aromatics concentrations contemplated in the practice of this invention. It is considered that for best results the aromatics concentration should be lowered to below 1 weight percent, which requires the use of a lower temperature than used in the denitrification and the use of an active hydrogenation catalyst.

The catalyst used in the hydrogenation step of the present invention comprises an active hydrogenating metal component associated with a solid inorganic oxide carrier. The hydrogenating metal component is preferably a noble metal of the platinum-palladium group, but nickel may also be used if higher concentrations of the metal are provided in the catalyst. Usually the catalyst will contain from 0.1 to 10 weight percent noble metal, with amounts in the range 0.3–3 weight percent being preferred in view of the cost of these metals. The balance of the catalyst, as mentioned, is a refractory inorganic oxide carrier lending high porosity and surface area to the composite. Carriers having pore diameters of about 100 Angstroms or more are preferred. Alumina is an eminently suitable carrier, but mixed oxides, such as silica-alumina, can also be employed; and these can be of the acidic, high silica content, type used as cracking catalysts or of the lower silica content type, having only moderate or low acidity and cracking activity.

The catalysts can be prepared by conventional impregnation, coprecipitation, or coagulation techniques. They are invariably sensitive to nitrogen compounds and also, to a lesser extent, to sulfur compounds. Accordingly, the hydrogenation step is to be applied to the oil only after any organic nitrogen compounds present have been substantially removed. Preferably the nitrogen content does not exceed 10 p.p.m., and the sulfur content does not exceed 50 p.p.m. More preferably, the nitrogen content is less than 1 p.p.m., and the sulfur content will be correspondingly lower. The catalyst employed in the above-described example for the hydrogenation step—i.e., the palladium on silica-alumina catalyst—is more resistant to deactivation by sulfur compounds than most platimum catalysts, and can accordingly be used to great advantage.

Conditions used in the hydrogenation step for substantially eliminating aromatics includes temperatures of 200°–650° F. and pressures of 1,000–5,000 p.s.i.g., preferably at least 1,500 p.s.i.g. Low temperatures, preferably 250°–450° F., are used with catalysts comprising acidic carriers whereas temperatures of 500°–600° F. are preferred if the catalyst has only low or moderate acidity, low enough to prevent hydrocracking occurring to any substantial extent. At the high pressure and low temperature, with adequate contact time the aromatic compounds present can be essentially completely saturated with practically no splitting or hydrocracking even if the catalyst used is of a type which would have substantial hydrocracking activity at higher temperatures of 700° F. or above for example. The space velocity used will be in the range of 0.2–10 LHSV, preferably 0.3–3 LHSV, depending on the concentration of aromatics in the nitrogen-free oil; and the throughput of hydrogen-rich gas, which may be recycled, should be at least 1,000 s.c.f./bbl. with larger amounts in the range 2,000–20,000 s.c.f./bbl. being preferred even though hydrogen consumption may be less than 500 s.c.f./bbl.

The hydrogenation catalyst could in some cases be provided as a separate bed in the inlet portion of a single reactor, the lower or downstream portion of which contains the isomerization catalyst. The necessity to operate at greatly different temperatures in the respective reaction zones, however, frequently makes it more desirable to use separate reaction vessels, which is also more advantageous where large quantities of oil are to be treated. Also the hydrogenation catalyst may tend to lose activity more rapidly than the isomerization catalyst because exposed to the nitrogen compounds still remaining in the oil and protecting the isomerization catalyst from them. Thus it may be desired to regenerate or replace the hydrogenation catalyst more often than the others.

Feedstocks which may be successfully treated in accordance with the invention include high pour point heavy oils, which must boil at least partly above 700° F. More desirably, the oil feed boils mostly above 800° F. and at least partly above 900° F. A preferred feed is at least as heavy as a straight-run vacuum gas oil, and the most preferred feed is a deasphalted residual oil. The residual oil is required to be nonasphaltic because the asphaltenes, being polynuclear aromatic-type compounds, interfere with the conversion of paraffins in the process of the invention and also tend to rapidly reactivate the catalysts used. The deasphalting treatment applied in preparing the preferred feed may be the type of deasphalting used in preparing heavy catalytic cracker feedstocks; i.e., treatment with a light hydrocarbon solvent, such a propane, butane, pentane, or mixtures thereof, at near the critical point of the solvent. The treatment may be such as to recover as feed the entire so-called maltene fraction, comprising oil and resins, rejecting only the asphaltenes. The deasphalted oil feeds treated in accordance with the invention will have high pour points of above +35° F., and more usually of at least +50° F. Thus a deasphalted oil feed will contain sufficient high melting paraffins such that at least about 10 weight percent of the feed would have to be separated as wax to obtain a pour point of 0° F. by prior art solvent dewaxing methods.

As the first stage of the process, nitrogen compounds in the oil are substantially eliminated. This is best done by hydrogenation, wherein the impure high pour point oil feed and hydrogen are passed at elevated pressure above 1,000 p.s.i.g. through a reaction zone to contact therein a sulfactive hydrogenation catalyst having hydrocracking and denitrification activity until organic nitrogen and sulfur compounds inherently present in the raw feed are substantially eliminated. At the conditions required to accomplish the substantially complete conversion of organic nitrogen to ammonia, substantial hydrocracking of the oil to lower boiling distillates occurs. While it would appear desirable to minimize such hydrocracking conversion so as to maximize the yield of high-boiling product, it appears that at least about 20 percent conversion of the feed to distillates lower boiling than the feed is needed to obtain a high overall pour point reduction and to improve the viscosity index of the product. With residual oil feeds the most preferred conversion range appears to be from about 30 percent to about 60 percent to distillates boiling below 700° F. The conversion is accompanied by the consumption of substantial amounts of hydrogen, amounting usually to about 500 standard cubic feet or more per barrel of oil.

Conditions used in the first stage hydrocracking-denitrification include temperatures of 650°–900° F., more desirably 700°–850° F. The pressure should be at least about 1,000 p.s.i.g. and may range upwards of 5,000 p.s.i.g., with the preferred range being 1,500–4,000 p.s.i.g. The throughput of hydrogen-rich gas, which may be recycled, should be at least 1,000 s.c.f./bbl. of feed, more usually 2,000–20,000 s.c.f./bbl., with the preferred range being 4,000–10,000 s.c.f./bbl. The contact time between oil and catalyst is sufficiently long to accomplish the desired nitrogen removal and hydrocracking, which can generally be accomplished at space velocities of 0.2–10 volumes of oil per hour per volume of catalyst (LHSV), preferably 0.3–3 LHSV.

The catalyst used in the first step may be of the sulfactive hydrogenation type commonly used for desulfurization and denitrification. Suitable catalysts include combinations of the Group VI and Group VIII metals, oxides, or sulfides, associated with porous refractory oxide carriers. Most suitable metals are nickel or cobalt in combination with molybdenum or tungsten as sulfides. The refractory oxide may be alumina, or combinations of alumina with silica, magnesia, zirconia, titania, and like

materials, or combination of such other oxides, for example silica-magnesia. Such catalysts can be prepared in a variety of ways, including preparing the porous carrier first and then impregnating it with solutions of the metal compounds which are later converted to metal oxides by calcining. Particularly good catalysts for use in the first stage hydrocracking can be prepared by coprecipitation techniques wherein all of the components are initially supplied as dissolved compounds in aqueous solutions and coprecipitated together.

The conditions in the first stage hydrocracking should be such as to substantially eliminate organic sulfur compounds by conversion to H_2S in addition to substantially eliminating organic nitrogen compounds by conversion to NH_3. Usually the nitrogen conversion is the more difficult to accomplish, and accordingly if the organic nitrogen content has been reduced to satisfactory levels, the organic sulfur concentration will also have been sufficiently reduced. In some rare cases, however, as where the impure oil feed has an unusually high sulfur content and unusually low nitrogen content, it may be possible to achieve a satisfactorily low nitrogen concentration without having removed sufficient sulfur. In those cases the contacting should be continued until the sulfur concentration has been lowered to below about 50 p.p.m.

Some pour point reduction may occur during the hydrocracking with the denitrification catalyst, but not sufficient to lower the pour point of the highest boiling portion of the oil feed from above +35° F. to below +15° F. unless the conversion is continued far beyond what is needed in accordance with the present invention, thereby greatly reducing product yield. There is evidence that, in the first stage hydrocracking, normal paraffins are cracked and isomerized to moderately branched isoparaffins which, however, still impart a high pour point to the oil. These isoparaffins are removable by solvent dewaxing techniques, and they would have to be so removed in accordance with prior art techniques to obtain an acceptable low pour point product from the oil effluent of the first stage hydrocracking.

In accordance with the invention, the hydrocracked oil effluent of the first stage is not dewaxed; but instead at least a high-boiling portion of the oil effluent and hydrogen is passed at elevated pressure above 1,000 p.s.i.g. through the hydrogenation zone and then through a pour point reducing reaction zone, which may also be referred to as a hydroisomerization zone or a hydrocracking-hydroisomerization zone. The oil effluent of the pour point reducing reaction zone is distilled directly into fractions including a highest boiling portion having a low pour point which is at least 30° F. lower than the pour point of the high pour point purified oil effluent of the hydrocracking-denitrification reaction zone.

Conditions used in the pour point reducing reaction zone include temperatures of 750°–900° F., preferably 750°–850° F.; pressures of 500–5,000 p.s.i.g.; more usually 1,000–3,000 p.s.i.g.; hydrogen-rich gas throughput rates greater than 1,000 s.c.f./bbl. of oil, generally 2,000–20,000 s.c.f./bbl., and preferably 4,000–10,000 s.c.f./bbl. The contact time in terms of liquid hourly space velocity is from 0.2–10, preferably 0.3–3 LHSV. Variation of any of the reaction conditions outside these ranges means that some or all of the other process variable must be set at or beyond their stated limits. Thus, for instance, if a lower temperature than 750° F. is used, an LHSV which is unreasonably high from an operational standpoint must be maintained. Further, operation outside the stated ranges produces products with high pour points and/or other undesirable characteristics which make them unsuitable as lubricants. The required conditions are such that at least 10 weight percent of the oil entering this final reaction zone is hydrocracked to lower boiling distillates, and usually at least about 20 percent hydrocracking conversion is accomplished. The higher the percent conversion to lower boiling distillates, the greater the pour point reduction that is achieved. When the oil is prehydrogenated in accordance with the present invention prior to hydroisomerization, the desired pour point reduction is achieved with substantially less conversion to lower boiling distillates than is the case without prehydrogenation. Nevertheless, with residual oils it still appears desirable that the conversion be at least about 30 weight percent, especially if the pour point of the nitrogen-free oil recovered from the first stage is above about 90° F.

The catalyst employed in the pour point reducing hydroisomerization zone is described as a naphtha reforming catalyst having no more than moderate acidity. A catalyst which has only "moderate acidity" is herein defined to mean one that is less acidic than a cafalyst supported on alumina containing more than two weight percent halide or a catalyst supported on a silica-alumina support which contains more silica than alumina. Such a catalyst typically comprises a Group VI metal oxide or a Group VIII metal hydrogenation-dehydrogenation component, desirably a noble metal, preferably platinum or palladium, associated with a porous refractory oxide carrier, such as alumina, and which may be inherently moderately acidic or moderately acidified with no more than about two weight percent of halide. The reforming catalyst is an active isomerization catalyst. Nitrogen and sulfur compounds may deactivate such a catalyst, and accordingly these heteroorganic compounds are substantially excluded from the oil. Thus a typical preferred catalyst comprises essentially alumina promoter with a small amount, 0.1–2 percent of platinum metal and a small amount, less than 1 percent, of chloride and/or fluoride. This is a well-known platinum reforming catalyst, but its action is quite different at the conditions used in the pour point reducing zone. There is a net consumption of hydrogen, and instead of forming aromatics from naphthenes, the essential reaction occurring appears to be one of hydrocracking and isomerizing moderately branched isoparaffins to highly branched isoparaffins. Instead of pure alumina or halided alumina as the carrier or support, there may be used a moderately acidic alumina-silica cogel or coprecipitate containing more alumina than silica. For example, good results have been obtained using a 2 percent palladium catalyst on 82 percent alumina-18 percent silica. Other analogous carriers and supports suitable for use will suggest themselevs to those skilled in the art. The silica-alumina materials containing more silica than alumina, such as cracking catalysts, do not appear to be good supports for the catalysts because they are too strongly acidic and adversely affect selectivity for the isomerization of isoparaffins.

We have obtained best results in the hydroisomerization step per se using a platinum-alumina reforming catalyst containing only a small amount of halides, from 0 to 1 weight percent total. The known noble metal isomerization catalysts containing upwards of 2 weight percent halide appear to be too acidic and have low selectivity at the conditions employed in the process of this invention, accomplishing less isomerization and more hydrocracking and tending to become deactivted more rapidly. It is known from the art that, as halogen level increases, the yield of lubricating oil product of a given pour point decreases. Conversely, in order to obtain a large pour point reduction with a high halide content catalyst, a substantial loss of product oil yield must be taken. For instance, the reduction in pour point achieved by a catalyst containing 0.4 weight percent platinum and 0.7 weight percent halide is approximately twice that achieved at the same yield of a 800°–1,000° F. lubricating oil by a catalyst containing the same amount of platinum but 3.9 weight percent halide. At higher halide levels, the superiority of the low halide catalyst would be even more marked. Further, the low halide catalyst as used in the present process has been shown to have an order of magnitude greater pour point reducing ability than the same catalyst as used in prior art processes. Thus in one com-

parison, in a prior art process the catalyst containing 0.7 weight percent halide produced a 5° F. pour point reduction; while in the process of this invention a similar catalyst produced a 55° F. pour point reduction. The hydrogenation step of this invention is accordingly used to greatest advantage in conjunction with a process wherein there is employed hydroisomerization catalysts of no more than moderate acidity.

It will be recognized that the contacting of the oil and hydrogen with the catalyst in the respective reaction zones may be carried out in a variety of well-known ways including the use of fixed beds of catalyst particles in high pressure reactors through which the hydrogen and oil flow concurrently or countercurrently. This appears to be the most practical and convenient method, but other known techniques can be used such as those involving the use of fluidized circulating catalyst particles, catalyst slurries, and gravitating catalyst masses.

The metal hydrogenation-dehydrogenation components of the catalysts employed in the hydrogenation and hydroisomerization stages should be used and maintained in the non-sulfided state. Noble metals of the platinum group are preferred in both of these latter stages because their sulfides are unstable, and the catalysts can accordingly tolerate a small amount of sulfur in the feed without becoming irreversibly sulfided. For example, the palladium catalyst used in the hydrogenation step of the example herein declined in activity during use while treating the 12 p.p.m. sulfur oil. Most of the lost activity could be regained by flowing H_2 over the catalyst for a few hours at temperatures above 750° F. Nickel is less advantageous in these catalysts because it forms a stable sulfide, and its use would require that sulfur compounds be virtually completely excluded. In the denitrification stage, wherein sulfided catalysts are used to greatest advantage, highly branched isoparaffins are not readily formed so that an excessively high hydrocracking conversion would be needed to obtain a substantial lowering of the pour point. By nuclear magnetic resonance it has been shown that the ratio of $-CH_3$ groups to $-CH_2-$ groups is about 30 percent greater in a low pour point oil product of the hydroisomerization stage than in a low pour point (solvent dewaxed) sample of the corresponding oil product of the hydrocracking-denitrification stage. The higher ratio shows that the isoparaffins are more highly branched. Thus further branching of both high pour point and low pour point isoparaffins is accomplished in the isomerization stage, which could not be accomplished in the first stage with the sulfided catalyst.

The low aromatics content of the hydrogenated oil passed to the hydroisomerization zone in the practice of this invention is usually reflected in a very low aromatics concentration in the final oil products. In some cases this can be undesirable as many of the additives conventionally put into lubricating oil products as ultimately sold depend on the oil having some aromatics to aid in dissolving the said additives. In such cases, a small amount of aromatics can be added to the hydroisomerized oil, as the purpose of removing the aromatics by hydrogenation was to improve the selectivity in the hydroisomerization step; and it is not essential to most lubricating oils that they be absolutely free of aromatics.

In some instances, possibly because of the presence of small amounts of condensed aromatic species, the oils produced by the process of this invention may exhibit some instability to oxidation in the presence of light. This can be corrected by known low cost treatments including treating with sulfuric acid or clay contacting. A finishing hydrogenating, at low temperature conditions and with a catalyst such as used in the intervening hydrogenation, has been found particularly effective in stabilizing the low pour point oils produced by the method of this invention. Thus in some cases a four-stage hydrogen treating process is contemplated comprising: first, a denitrification at temperatures above about 700° F. using a sulfactive catalyst; second, a hydrogenation at temperatures below about 650° F. using a nitrogen-sensitive catalyst; third, a hydroisomerization at temperatures above about 750° F. using a reforming catalyst; and fourth, a hydrogenation at temperatures below about 650° F. using any suitable hydrogenation catalyst; all at elevated hydrogen partial pressure. Catalysts and conditions used in the final hydrogenation are preferably like those previously described herein as usable in the prehydrogenation.

For example, a solvent deasphalted oil was denitrified by contact with a nickel-tungsten sulfide catalyst at 0.4 LHSV, 785° F., 2,400 p.s.i.g. and 5,000 s.c.f./bbl. hydrogen. The 750° F.+ product was hydrogenated by contact with a 2 percent palladium on acidic silica-alumina catalyst at 0.2 LHSV, 350° F., 3,000 p.s.i.g. and 6,400 s.c.f./bbl. hydrogen. The hydrogenated product was hydroisomerized and then hydrogenated for stabilization by contact first with a 0.4 percent platinum on alumina catalyst at 0.4 LHSV, 754° F., 2,600 p.s.i.g. and 5,000 s.c.f./bbl. hydrogen and then with a 2 percent palladium on silica-alumina catalyst, containing less silica than the similar catalyst used in the prehydrogenation, in the lower part of the same reactor at 0.8 LHSV, 500° F., 2,600 p.s.i.g. and 5,000 s.c.f./bbl. hydrogens. The 750° F.+oil from the above process is stable to air and sunlight for longer than 20 days. Comparable samples of oils not subjected to the final hydrogenation with the palladium catalyst show evidence of instability in less than 3 days.

It is apparent that many different embodiments of this invention may be made without departing from the scope and spirit thereof, and therefore it is not intended to be limited except as indicated in the appended claims.

We claim:

1. A process for reducing the pour point of a heavy oil containing aromatics and organic nitrogen compounds without physically dewaxing said oil or diluting said oil with low boiling materials, comprising first substantially eliminating organic nitrogen compounds present in said heavy oil and simultaneously converting at least 20 percent of said heavy oil to distillates lower boiling than said heavy oil, and then substantially eliminating aromatics in the essentially nitrogen-free oil by contacting said essentially nitrogen-free oil with an active hydrogenation catalyst in the presence of hydrogen at a temperature in the range of 200°–650° F., and a pressure in the range of 1,000–5,000 p.s.i.g., followed by simultaneous hydrocracking and hydroisomerization of the essentially nitrogen- and aromatics-free oil over a naphtha reforming catalyst comprising a noble metal associated with alumina and containing no more than two weight percent halide in the presence of hydrogen at a temperature of 750°–900° F. and a pressure of 1,000–5,000 p.s.i.g., whereby said elimination of aromatics makes said hydroisomerization more selective for lowering the pour point of said essentially nitrogen- and aromatics-free oil with less simultaneous hydrocracking, permitting recovery of a product oil with a pour point at least 30° F. lower than the pour point of said essentially nitrogen-free oil.

2. The process of claim 1 wherein said hydrogenation catalyst comprises a noble metal associated with a porous carrier.

3. The process of claim 1 wherein said naphtha reforming catalyst comprises a noble metal associated with a porous alumina carrier containing 0–1 weight percent halide.

4. The process of claim 1 wherein said substantial elimination of organic nitrogen compounds reduces the nitrogen content of the oil to less than 10 p.p.m.

5. The process of claim 1 wherein the aromatics content of said essentially nitrogen-free oil is reduced to less than 1 percent.

6. The process of claim 1 further characterized in that said product oil is subjected to a finishing hydrogenation catalyst comprising contacting said product oil with a hydrogenation catalyst at an elevated pressure and a

temperature below about 650° F. in the presence of hydrogen, and recovering a lubricating oil of improved stability.

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