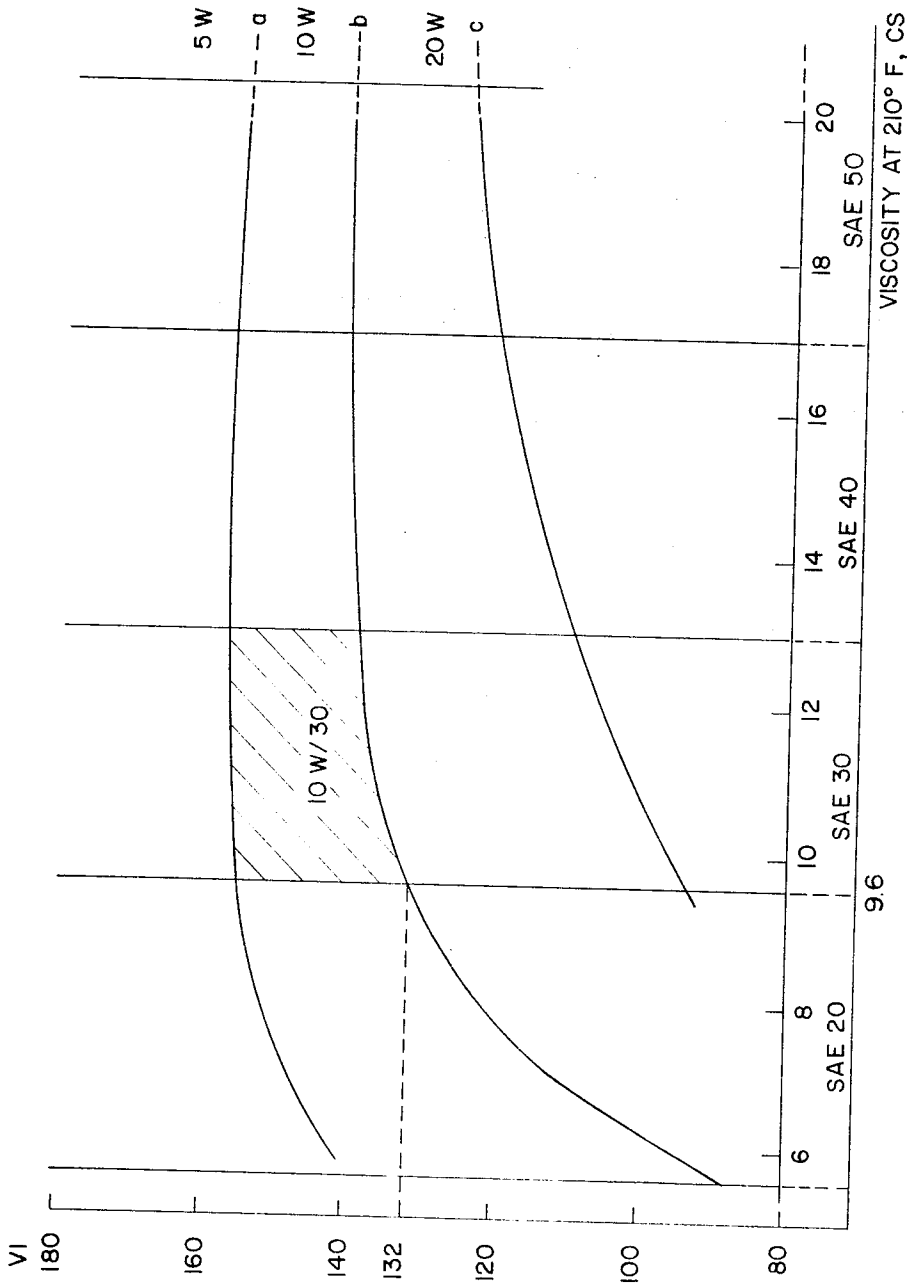


May 16, 1972

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PROCESS FOR THE PRODUCTION OF VERY HIGH
VI LUBRICATING OILS BY HYDROTREATING
Filed Aug. 28, 1969

3,663,422



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3,663,422

PROCESS FOR THE PRODUCTION OF VERY HIGH VI LUBRICATING OILS BY HYDROTREATING**Peter W. Dun and Formijn J. van Hemert, Amsterdam, Netherlands, assignors to Shell Oil Company, New York, N.Y.**

Filed Aug. 28, 1969, Ser. No. 853,719

Claims priority, application Great Britain, Sept. 5, 1968, 42,311/68

Int. Cl. C10g 41/00

U.S. Cl. 208—28

5 Claims

ABSTRACT OF THE DISCLOSURE

Very high viscosity index (VI >125) lubricating oils are produced by hydrotreating solvent-refined, asphalt-free waxy hydrocarbons in the presence of a suitable catalyst under specific hydrotreating conditions. A true SAE 10W/30 multigrade oil is produced which does not require the addition of VI improvers or thickeners.

BACKGROUND OF THE INVENTION**Field of the invention**

The present invention relates to a process for the production of very high viscosity index (VHVI) lubricating oils from a hydrocarbon feedstock by means of hydrotreating. It particularly relates to a process in which solvent-refined, asphalt-free waxy hydrocarbon oils are hydrotreated at specific temperatures and pressures in order to obtain lubricating oils meeting the SAE 10W/30 specification for multigrade oils.

Description of the prior art

Lubricating oils for automotive purposes, both for diesel and gasoline engines, are classified according to a scheme introduced by the Society of Automotive Engineers, in which ranges of viscosities measured in seconds Saybolt Universal (SSU) at 210° F. are indicated by SAE numbers. Originally seven categories were proposed, the lightest three SAE 5W, 10W and 20W oils being known as winter or W-grades. These winter-grade oils have the same viscosity requirement at 210° F. but have also to meet viscosity requirements at 0° F. increasing from the 5W to the 20W oils. The other four grades SAE 20, SAE 30, SAE 40 and SAE 50 oils have increasing viscosities at 210° F. but no requirement at 0° F. In recent years, however, multigrade oils have been developed which are lubricating oils for automotive purposes falling within more than one SAE category. They cover in one oil both a winter grade and a normal grade, thus ensuring both good lubrication at high temperatures and sufficient fluidity at low ones. They are designated by the appropriate two-grade numbers e.g., 5W/20, 10W/20, 20W/20, 5W/30, 10W/30, 20W/30, and so on.

In Table I the viscosities of some multigrade oils as required by the SAE specification are given in SSU units. Preference has been given herein to kinematic viscosities expressed in centistokes (cs.) instead of SSU. As is known, these viscosities may easily be converted into each other

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or the corresponding values may be taken from viscosity conversion tables. Reference is made to the table in the Handbook of Chemistry and Physics (43rd ed.) of The Chemical Rubber Publishing Company, p. 2210.

TABLE I

	Viscosities in SSU		
	At 210° F.		
	At 0° F., Maximum	Minimum	
Multigrade oil:			
5W/20.....	4,000	45	<58
10W/20.....	12,000	45	<58
10W/30.....	12,000	58	<70
10W/40.....	12,000	70	<58
20W/30.....	48,000	58	<70
20W/40.....	48,000	70	<85

Pure mineral lubricating oils do not usually fulfill the requirements set and in order to obtain the desired multigrade oil it is customary to add viscosity-index (VI) improvers for improving the viscosity-temperature characteristics and/or thickeners for increasing the viscosity. In addition thereto, other oil additives such as pour point depressors, antioxidants, corrosion inhibitors, detergents and the like may further be added, so that the multigrade oils on the market are generally oil formulations. Particularly preferred multigrade oil formulations are a 10W/30 and a 10W/40 grade.

It is a well-known fact that in continued use the lubricating oil deteriorates through many causes, one of which is that the VI improver and the thickener it contains—which are high-molecular-weight polymers—are gradually broken down by shearing in the engine, resulting in a permanent drop in viscosity index and viscosity. Finally, the oil has to be replaced by fresh multigrade oil. Moreover the multigrade oil formulation also shows a temporary loss in viscosity when in use, because under the influence of shear the polymers align themselves—leading to a reduced internal friction—as a result of which the viscosity falls. This phenomenon is sometimes called “temporary depolymerization.” As the rate of shear increases the apparent viscosity of the oil formulation approaches the viscosity of the lubricating base oil.

In view of the above it would be highly advantageous if multigrade oils could be provided which contain little or no VI improvers or thickeners at all, because such oils will perform their duty in engines for a much longer time, without without showing a temporary loss of viscosity under working conditions. Although for certain SAE grades it has been shown possible to produce mineral lubricating oils directly which fulfill the requirement of a particular multigrade oil according to the SAE classification, it has up to now been impossible to produce a true 10W/30 multigrade oil from a hydrocarbon feedstock.

It has been proposed in the prior art to produce lubricating oils with a VI of at least 125 by hydrotreating of a raffinate obtained by solvent-extracting a hydrocarbon

feedstock to an aromatic content of less than 5% of carbon atoms occurring in aromatic rings. The hydrotreating conditions applied are, however, less severe and the lubricating oils obtained have a viscosity at 210° F. far below 9.0 centistokes (cs.) (Vosser et al., Br. 1,006,508).

Furthermore it has also been proposed to hydrotreat deasphalted oils at a pressure of at least 175 kg./cm.² and a temperature between 390° and 440° C. and to recover lubricating oils having a VI of at least 115 from the hydrotreated product. The lubricating oils so obtained have a VI of less than 125 and do not classify as a 10W/30 multigrade oil; they may, however, be used as 10W/20, 20W/30, or 20W/40 oils (Beuther et al., U.S. 2,960,458).

SUMMARY OF THE INVENTION

The present invention relates to a process for the production of very high-viscosity-index lubricating oils, which comprises hydrotreating a solvent-refined, asphalt-free waxy hydrocarbon oil in the presence of a sulfided catalyst comprising a Group VI and/or Group VIII metal supported on a substantially non-acidic refractory oxide base, at a temperature in the range of from 420 to 460° C. and a pressure of from 165 to 225 kg./cm.², and recovering a dewaxed lubricating oil having a viscosity index of at least 125 and a viscosity at 210° F. of at least 9.0 centistokes from the hydrotreated waxy oil by means of fractionation and dewaxing.

Preferably, a true 10W/30 multigrade lubricating oil, i.e., an oil having a viscosity index of at least 132 and a viscosity at 210° F. of at least 9.6 centistokes is recovered from the hydrotreated waxy oil.

The process of the present invention has the advantage that in addition to the 10W/30 multigrade oil a substantial yield of light and medium machine oils of very high viscosity index (VHVI) is obtained as by-products, while the remainder of the hydrocarbon feedstock is converted into valuable fuel materials substantially boiling below 375° C.

The advantages of the VHVI lubricating oils produced according to the invention are that a VI improver is not generally required and, with regard to the 10W/30 lubricating oil, viscosity improvers or thickeners are usually not required either. If it is, however, desired to formulate multigrade oils meeting the 5W/30, 10W/40 or 10W/50 specification which require higher viscosity indices and/or viscosities, only minor amounts of the compounds mentioned are required. Additional oil additives such as pour-point depressants, antioxidants, corrosion inhibitors, detergents and the like may be added, if desired, to obtain multigrade oil formulations meeting requirements set in other specifications.

From the above it follows that a 10W/30 oil formulation based on a true 10W/30 lubricating oil of the invention does not suffer a permanent loss of viscosity under shearing, nor is there a temporary loss of viscosity. If a 10W/30 multigrade oil has been formulated on the basis of the oil produced according to the invention using a minor amount of thickener, the multigrade oil will never drop out of its SAE classification, since the base oil is a true 10W/30 oil. Moreover, the multigrade oils so obtained will show a measured viscosity at 0° F. which is substantially the same as the extrapolated viscosity at 0° F. because of the virtual absence of polymers in the multigrade formulation.

BRIEF DESCRIPTION OF DRAWING

In the drawing, multigrade oils have been graphically represented using kinematic viscosities (cs.) on the horizontal axis. The viscosity range of oils belonging to a particular SAE number has also been indicated on the horizontal axis. On the vertical axis the VI as determined

by ASTM D-567 is given, 80 being the minimum value for high-viscosity-index oils. On the right-hand side of the drawing the SAE W-grades have been indicated, the area above line *a* being the 5W-grade, between lines *a* and *b* 10W-grade and between lines *b* and *c* the 20W-grade. The shaded area represents the 10W/30 oils which are produced by the process of the invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

In the present specification the viscosity indices mentioned refer to values as determined by means of the ASTM method D-567, unless stated otherwise.

In order to obtain the desired multigrade oil it is essential to use a solvent-refined and asphalt-free hydrocarbon oil as the feed. The oil should moreover be a waxy oil. The hydrocarbon oil may be a waxy distillate obtained by vacuum or similar distillation of a crude oil, a reduced crude oil, or a fraction thereof, which has been solvent-refined.

The hydrocarbon oil is preferably a residual oil obtained by deasphalting a vacuum-reduced crude, i.e., a petroleum residuum resulting from a vacuum or similar distillation of a petroleum crude oil, or a topped crude oil or fraction thereof, with a low-boiling hydrocarbon such as propane, and solvent-refining the deasphalted oil to remove aromatic compounds. The solvent-refined asphalt-free waxy hydrocarbon oil may also be a synthetic oil derived from shale oil.

Although any of the usual solvents which selectively remove aromatic hydrocarbons may be used, it is preferred to use as the feed a furfural raffinate, i.e., a furfural-refined waxy oil. Other solvents that are selective towards aromatic hydrocarbons such as liquid sulfur dioxide, phenol, cresol and the like may also be used, however. The deasphalting may be carried out by using any suitable solvent. Preferred solvents are the lower-boiling paraffinic hydrocarbons such as ethane, propane, butane or pentane or mixtures thereof, propane being preferred. If it is desired to obtain a high yield of deasphalted oil, pentane is the most suitable solvent. As deasphalting solvents, mixtures of the above lower-boiling hydrocarbons with alcohols such as methanol and isopropanol may be used as well.

Deasphalting and solvent-refining as such are known in the art. Conditions applied during these feed preparation steps for producing the desired starting material for the process of the invention, i.e., temperature, solvent/oil ratio, and so on, are conventional and need not be elaborated further.

The severity of the hydrotreating operation is chosen such that a dewaxed lubricating oil is obtained finally with a viscosity index in the range of from 130 to 160 and with a kinematic viscosity at 210° F. in the range of from 9.5 to 13.0 cs. Preferably, however, the severity is adjusted such that a dewaxed lubricating oil is recovered with a VI of at least 132 and a viscosity at 210° F. of at least 9.6 cs., thus satisfying the requirements of the 10W/30 SAE specification.

The temperature and pressure applied during hydrotreating of the waxy raffinate are preferably in the range of from 430 to 445° C.—these temperatures being average reactor temperatures—and from 170 to 185 kg./cm.², respectively. The weight hourly space velocities applied are preferably rather low in order to increase the severity of the operation. Particularly preferred space velocities are in the range of from 0.4 to 1.7 kg.l.⁻¹.h⁻¹. The hydrogen gas rate may, however, vary within a wide range and is generally between 500 and 5000 NL. of hydrogen per kg. of feed.

The catalyst employed in the process must have a substantially non-acidic refractory base in order to avoid excessive cracking at the reactor conditions specified. Acidity

of the base promotes those hydrocarbon conversions which involve the formation of carbonium ions, e.g., dealkylation and hydrocracking. For the purpose of the present invention suitable non-acidic bases are the metal oxides of certain metals such as alumina, boria, silica, magnesia and zirconia. Mixtures of certain of these oxides may be used as well, such as alumina-magnesia or magnesia-zirconia mixtures, but mixtures of metal oxides comprising silica are unsuitable. Alumina is particularly preferred as a base. The alumina base may comprise minor amounts of alkali or alkali-earth metal in order to ensure the non-acidity of the base. Preferred amounts are from 0.05 to 1.5% w. expressed as metal oxide. Commercial aluminas comprising silica in an amount of more than 5 w., and/or halogens such as fluorine and/or chlorine, are unsuitable.

Preferred Group VI and Group VIII metals are molybdenum, tungsten, cobalt, nickel and platinum. The non-noble metals may be present on the base either as the sulfide or as the oxide. The catalysts comprising these metals are, however, used in the sulfided form. Catalyst sulfiding may be carried out according to any technique or procedure known in the art. Particularly suitable catalysts for the present invention are the commercially available hydrodesulfurization catalysts comprising from 1 to 5% of nickel and from 3 to 20% of molybdenum on an alumina carrier.

The hydrotreating effluent will contain lower-boiling reaction products such as gasoline, kerosene and gas oil. These lower-boiling non-lubricating products have to be separated from the lubricating oil. Generally, the products boiling above 375° C. will be recovered as the lube-oil fraction. This lube-oil fraction will be further fractionated into different lubricating base oils. The VHVI base oils forming the subject matter of the present invention will usually be obtained as the fraction boiling above 480° C. The lower cut point of these VHVI oils may, however, vary in the range of from 460 to 515° C.

Finally, the wax present is removed by dewaxing. Dewaxing is accomplished by any treatment conventionally used for dewaxing oils. Preferably the lubricating oils are dewaxed to a pour point that is below 10° F. and more preferably to a pour point below 5° F. As the lubricating oil is dewaxed at a lower temperature there is an increasing yield loss which may be as high as 30% for the oil fraction boiling above 480° C. There is a corresponding VI loss of about 2 to 3 points. In a typical satisfactory dewaxing process the oil is dissolved in a solvent such as propane, methyl ethyl ketone or toluene or mixtures of the two latter solvents, the oil solution is cooled and subsequently filtered. The dewaxing solvent may be removed by distillation.

The 10W/30 multigrade oil of the invention may be formulated to multigrade lubricating oil compositions comprising a major amount of a true 10W/30 multigrade oil and a minor amount of one or more lubricating oil additives as mentioned hereinbefore. Usually these additives are applied in an amount of from 1-10% w.

Examples of additives which may be incorporated in the 10W/30 oil are the known VI improvers such as isobutylene polymers, polyacrylate and -methacrylates and the like, detergents including those of the class of metal sulfonates, metal phenates, and metal naphthenates and polymer dispersants such as polyethylene glycol substituted polymethacrylates and so on. The antioxidants include such compounds like zinc dithiophosphates, alkylated phenols and an example of the known corrosion inhibitor is the class of amine-derived succinic anhydrides.

The present invention will be further illustrated by means of the following examples. In the experiments described, the lubricating oil fractions have been dewaxed to a pour point as low as -19° C. in order to demonstrate that the results obtained in accordance with the process of the invention are not dependent on the dewaxing temperatures applied.

EXAMPLE I

This example demonstrates the importance of hydrotreating temperature. A propane-deasphalted oil from a Middle East crude was solvent-refined with furfural at a temperature of about 120° C. and a solvent/oil ratio of 5/1. The bright stock waxy raffinate obtained (60% on deasphalted oil) was used as feedstock for the production of lubricating base oils by means of hydrotreating. The bright stock waxy raffinate had the following properties:

Specific gravity, 70/4° C.	0.8594
Sulfur, percent w.	1.23
Total nitrogen, percent w.	0.03
Carbon, percent w.	85.27
Hydrogen, percent w.	13.28
UOP distillation:	
3% v. recovered, ° C.	478
5% v. recovered, ° C.	491
10% v. recovered, ° C.	504

The bright stock waxy raffinate was contacted with hydrogen in a bench-scale reactor with a total capacity of 250 ml., in the presence of a commercially available hydrodesulfurization catalyst. The catalyst was used in the form of 1.5 mm. extrudates and had the following composition: 17.6 p.b.w. (parts by weight) of MoO₃ and 4.0 p.b.w. NiO on 100 p.b.w. of Al₂O₃.

The liquid reactor effluent was fractionated and the material boiling above 480° C. recovered as waxy lube oil. This waxy lube oil was dewaxed at -30° C. with a mixture of methyl ethyl ketone/toluene (50/50 volume ratio) to give a pour point of -19° C. (-2.2° F.).

The catalyst was presulfided by means of a cold start-up using a gas oil from a Middle East crude (1.6% w. of sulfur) as the sulfiding agent. The bright stock waxy raffinate was converted at two different reactor temperatures. The results are given below in Table II.

TABLE II

Experiment	1	2
Conditions:		
Total pressure, kg./cm. ²	175	175
Space velocity, kg.l. ⁻¹ h. ⁻¹	1.0	1.0
Average temperature, ° C.	413	423
H ₂ gas rate, Ni/kg.	2,000	2,000
Yield, percent w. on feed:		
Total material <375° C.	14.0	21.0
Yield of waxy lube oil >480° C.	69.8	60.2
Yield of dewaxed lube oil.	40.3	31.3
Lube oil properties:		
Pour point, ° C.	-19	-19
Viscosity at 210° F., cs.	18.0	15.3
VI (ASTM D 567)	107	112
VI _E (ASTM D 2270)	108	116

Although a furfural-refined hydrocarbon oil was used as the feed, the lubricating oils obtained had a low VI.

EXAMPLE II

The experiments of Example I were repeated under more severe treating conditions on a pilot-plant scale, using the same feedstock and catalyst. The reactor had a capacity of about 7 liters and allowed operation with recycle of the hydrogen gas. The catalyst was presulfided for 21 hours with a gas oil (1.6 percent w. S) applying a cold start-up procedure. The reactor effluent was processed as described for the experiments 1 and 2. The results are given below in Table III. This table also records the lube oil fractions boiling between 375° and 480° C., which fractions are obtained in addition to the lube oils boiling above 480° C.

TABLE III

Experiment.....	3	4	5
Conditions:			
Total pressure, kg./cm. ²	175	175	175
Space velocity, kg.l. ⁻¹ .h. ⁻¹	1.0	0.75	0.50
Average temperature, ° C.....	431	348	435
Recycle gas rate, NI/kg.....	2,700	2,700	2,700
Yield, percent w. on feed:			
Total material <375° C.....	56.9	59.8	67.1
Waxy lube oil >480° C.....	19.7	16.8	9.7
Dewaxed lube oil.....	8.2	8.8	5.0
Dewaxed lube oil properties:			
Pour point, ° C.....	-19	-19	-19
Viscosity at 210° F., cs.....	10.5	9.9	9.8
VI (ASTM D 567).....	127.5	130	132.5
VI _E (ASTM D 2270).....	139.5	145	148.5
Lube oil fraction, ° C.....	375-440	440-480	375-440
Yield, percent w. on feed.....	13.7	9.4	14.9
Yield of dewaxed lube oil, percent w.....	12.0	7.3	12.8
Dewaxed lube oil properties:			
Viscosity at 210° F., cs.....	3.4	5.2	3.4
VI (ASTM D 567).....	124.5	137	132
VI _E (ASTM D 2270).....	120.5	138	128.5

The oil obtained in experiment 5 is a true 10W/30 multigrade oil satisfying the SAE requirements with respect to viscosity and viscosity index. The data show that under the conditions applied a lubricating oil with a VI above 125 and a viscosity at 210° F. higher than 9.0 can be obtained from a furfural-extracted deasphalted oil. The by-products include large quantities of light and medium machine oils of a high viscosity index (fractions 375-440° C. and 440-480°) which make the process of the invention a viable commercial proposition.

EXAMPLE III

This example demonstrates the importance of solvent refining in order to obtain a 10W/30 oil.

The deasphalted oil of Example I was used as the hydrotreating feedstock, the solvent-refining step with furfural being omitted. The hydrotreating step was carried out at three different temperatures, using the same catalyst as in Example I. The conditions applied were a pressure of 200 kg./cm.², a WHSV of 1.0 kg.l.⁻¹.h.⁻¹ and a hydrogen-to-oil ratio of 3000 NI./1.

The results obtained are given below in Table IV.

TABLE IV

Experiment.....	6	7	8
Conditions: temperature, ° C.....	420	430	440
Yield, percent w. on TLP:			
Total material <375° C.....	29.5	41.0	61.7
Waxy lube oil >375° C.....	70.5	59.0	38.3
Dewaxed lube oil.....	56.7	45.8	28.8
Dewaxed lube oil properties:			
Viscosity at 210° F., cs.....	11.73	8.98	6.93
VI (ASTM D 567).....	108	117	128

The lube oil fraction boiling above 375° C. of the experiments Nos. 6 and 8 was further fractionated into

three separate lube oil fractions, such as a fraction 400-440° C., a fraction 440-480° C. and a fraction boiling above 480° C. The fractions obtained after dewaxing, their viscosities and VI are mentioned below in Table V.

TABLE V

Boiling range, ° C.	Experiment 6			Experiment 8		
	Dewaxed oil, percent w. on TLP*	Viscosity at 210° F., cs.	VI	Dewaxed oil, percent w. on TLP	Viscosity at 210° F., cs.	VI
400-440.....	8.5	4.6	94	9.1	4.2	132
440-480.....	8.2	6.9	104	6.8	5.9	127
>480.....	34.9	16.7	105	11.4	12.1	120

*TLP = total liquid product.

The results show that the fraction boiling above 480° C. of experiment 8 has the required viscosity of more than 9.6 cs. but that its viscosity index is far below 132; thus, it does not meet the requirements for a 10W/30 lubricating oil.

EXAMPLE IV

In a long-uration experiment a large batch of a true 10W/30 lubricating oil was produced. The feedstock and the catalyst were the same as those used in Example I. The pilot-plant reactor had a catalyst inventory of 15,120 g. The catalyst was presulfided by a cold start-up procedure, followed by a running-in period under hydrodesulfurization conditions with a sulfur-containing gas oil. The conditions applied during the long-duration experiment remained fairly constant. Table VI, below, gives the results obtained at the beginning and towards the end of the run (about 600 hours). The lube oil fractions were dewaxed to a pour point of -19° C. (-2° F.).

TABLE VI

Pressure, kg./cm. ²	175	175
Average temp., ° C.....	429	434
WHSV, kg. l. ⁻¹ .h. ⁻¹	0.68	0.67
Recycle gas rate, NI/kg.....	2,700	2,700
Product:		
Fraction, ° C.....	400-440	440-480
Yield on feed, percent w.....	9.6	9.3
Viscosity at 210° F., cs.....	3.87	5.21
Dewaxed lube oil:		
Yield, percent w. on fraction.....	81.8	70.4
Viscosity at 210° F., cs.....	3.94	5.36
VI (ASTM D 567).....	134.5	137
VI _E (ASTM D 2270).....	127.5	140

The fractions boiling above 480° C. do not completely satisfy the 10W/30 specification. However, by slightly changing the cut point during fractionation the fraction >480° will yield such a multigrade oil. After the run had been terminated, the lube oil fractions 440-480 and >480 were collected and redistilled under laboratory conditions. A 10W/30 lubricating oil with a viscosity at 210° F. of 9.6 cs. and a VI of 133.5 was obtained in a yield of about 6.2 on waxy raffinate.

We claim as our invention:

1. A process for the production of very high viscosity index lubricating oils which comprises hydrotreating a solvent-refined asphalt-free waxy hydrocarbon oil in the presence of a sulfided catalyst consisting essentially of nickel and molybdenum on a non-acidic alumina at a temperature in the range of from 420 to 460° C., a pressure of from 165 to 225 kg./cm.² and a weight hourly space velocity of from 0.25 to 2.25 kg. of said oil per liter of catalyst per hour, and recovering a dewaxed lubricating oil having a viscosity index in the range of from 130 to 160 and a kinematic viscosity at 210° F. in the range of from 9.5 to 13.0 centistokes from the hydrotreated waxy oil by means of fractionation and dawaxing.

2. The process of claim 1 in which the asphalt-free waxy hydrocarbon oil is a residual oil obtained by propane-deasphalting a vacuum-reduced crude.

3. The process of claim 1 in which the waxy hydrocarbon oil is a wax-containing distillate oil.

4. The process of claim 1 in which a dewaxed 10W/30

multigrade lubricating oil is recovered having a viscosity index of at least 132 and a kinematic viscosity at 210° F. of at least 9.6 centistokes without viscosity index improves or thickeners.

5. The process of claim 1 in which the temperature is in the range of from 430° to 445° C., the pressure is in the range of from 170 to 185 kg./cm.², the weight hourly space velocity is in the range of from 0.4 to 1.7 kg./l.-¹, h.-¹, and the hydrogen gas rate is between 500 and 5000 Nl. of hydrogen per kg. of feed.

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HERBERT LEVINE, Primary Examiner

U.S. Cl. X.R.

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