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PRODUCTION OF IMPROVED LUBRICATING OILS BY HYDROCRACKING AND SOLVENT EXTRACTION

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ABSTRACT OF THE DISCLOSURE

Lube oils of improved ultraviolet stability, color and viscosity index are obtained by hydrocracking a lube oil fraction and subjecting the product to solvent refining the then dewaxing. The preferred solvent is N-methyl-2-pyrrolidone. The feed may be a wax distillate, a deasphalted residuum and may be subjected to pre-hydrocracking solvent refining step.

This application is a continuation-in-part of my copending application Ser. No. 837,930, filed June 30, 1969.

This invention relates to the production of improved lubricating oils. More particularly it is concerned with a process sequence for the production of hydrocracked lubricating oils of high viscosity index having good stability towards ultraviolet light. In one of its more specific aspects, it is concerned with the production of high viscosity index lubricating oils of good color and ultraviolet stability from low grade lubricating oil charge stocks using a process sequence which includes in a preferred embodiment hydrocracking, solvent refining and then dewaxing.

Various steps for the refining of lubricating oils such as distillation, solvent refining, solvent dewaxing, acid treating and clay contacting are well known. When residual type oils are being processed, a preliminary step of deasphalting is also generally required.

In the processing steps listed above, distillation is employed as a means of separating a crude oil into fractions of various viscosities, solvent refining with, for example, furfural, sulfur dioxide or phenol is ordinarily used as a means of removing aromatic compounds and thereby improving the viscosity index, solvent dewaxing using for example a mixture of methyl ethyl ketone and toluene is used to improve low temperature properties by lowering th pour point of the oil and clay contacting is used generally as a final step to further improve the color and to neutralize the oil after acid treating.

In a typical operation, a crude oil is topped under atmospheric pressure to produce light distillates and an atmospheric reduced crude which is then vacuum distilled to produce lube oil distillates and the residue from the vacuum distillation is deasphalted to yield residual lubricating stocks. Conventionally the various lube oil fractions are then further processed by solvent refining, dewaxing, acid treating and clay contacting.

In conventional lube oil refining the solvent extraction step is carried out first to recover about 45–90% of the charge as solvent refined oil and to reject about 10–55% of the charge as dark colored viscous extract. Since the extract amounts to a relatively high percentage of the charge and is not suitable for up-grading by dewaxing and clay contacting to a satisfactory quality level for use as a lube oil, solvent extraction has, up to the present been the most logical and economical step to apply first. Conventionally the solvent refined oil is contacted with clay

to improve its color and then dewaxed alhtough in some instances it may be desirable to dewax prior to clay contacting.

Because of the increasing demand for the lighter grade lubricating oils it has been found advantageous to convert the heavier grade oils to the more valuable lighter products by hydrocracking. Not only does this result in an increase in yield of desired lube oil fractions but because of the high hydrogen pressures involved, hydrocracking, like hydrotreating has been proposed as a replacement for solvent refining. However, for not completely known reasons, oils prepared by hydrocracking are not stable to ultraviolet light, and form a flocculent precipitate upon prolonged exposure to ultraviolet light. It is therefore a principal object of this invention to produce by hydrocracking lubricating oils with improved stability to ultraviolet light.

Another object is to improve the color of a hydrocracked lube oil. Still another object is to increase the viscosity index of a hydrocracked lube oil.

According to my invention a lubricating oil which has been derived from a hydrocracking process is subject to solvent refining and if desired the solvent refined product is dewaxed to lower the pour point.

The process of the invention may be applied to a variety of feedstocks. For example, the feed may be obtained by subjecting a vacuum residuum to deasphalting with a low molecular weight hydrocarbon such as propane or butane. The deasphalted residuum can then be hydrocracked and solvent refined. It is also possible to feed a wax distillate to the hydrocracking stage. The feed whether obtained by vacuum distillation or by deasphalting a vacuum residuum may be subjected to a preliminary solvent refining before being subjected to hydrocracking. It is also possible to use as the feed a lubricating oil fraction which has been obtained from a residuum such as atmospheric residuum or vacuum residuum by a simultaneous deasphalting-solvent refining procedure in which the residuum is treated not with the conventional low molecular weight hydrocarbon deasphalting agents but with a solvent such as furfural or N-methyl-2-pyrrolidone and the raffinate of reduced aromatic and asphalt content is charged to the hydrocracking zone.

The reaction conditions for the hydrocracking may be varied depending on the amount of hydrocracking desired and on the charge stock. Typical reaction conditions include a temperature of about 700–900° F., preferably 750–850° F. The pressure may range between about 500 and 5000 p.s.i.g., a preferred range being from 1000 to 2500 p.s.i.g. Space velocities may vary between about 0.1 and 10.0 v./v./hr. with a preferred range being 0.3–1.5. Hydrogen rates of from 1000–10,000 s.c.f.b. have been found satisfactory although rates of 3000–10,000 s.c.f.b are preferred.

Hydrogen from any suitable source such as electrolytic hydrogen, hydrogen obtained from the partial combustion of hydrocarbonaceous material followed by shift conversion and purification or catalytic reformer by-product hydrogen may be used. The hydrogen should have a purity of between about 50 and 100% with hydrogen purities of 75–95 volume percent being preferred.

The oil and hydrogen are brought into contact in the presence of a catalyst. The catalyst may be in the form of a fixed bed, a moving bed, a fluidized bed or may be slurried with the oil. Hydrogen flow may be upward or downward through the reactor as may be the flow of the oil. In a specific embodiment, both the oil and a portion of the hydrogen are introduced at the top of a reactor containing a fixed bed of the catalyst, the balance of the hydrogen being introduced at intermediate points in the reactor for cooling purposes.

The catalyst for the hydrocracking step preferably comprises a compound of a Group VI metal such as molybdenum, chromium or tungsten or a compound of a Group VIII metal such as cobalt, iron or nickel and mixtures thereof. Ordinarily the catalyst is charged to the reactor in oxide form although it can be expected that some reduction and some sulfidation take place during the course of the process so that after being on stream for some time the catalyst is probably a mixture of the metal, the metal sulfide and perhaps the oxide. If desired, the catalyst after being charged to the reactor but prior to the institution of the on stream period may be converted at least in part to the sulfide form for example by contact with a gas such as a mixture of hydrogen and a sulfiding agent, e.g. hydrogen sulfide, methyl mercaptan or carbon disulfide. The Group VIII metal may be present in an amount varying from 1 to 20% by weight of the total catalyst composite, preferably 2–15% and the Group VI metal may be present in an amount ranging from about 5–40%, preferably 7–25%.

The metal components are supported on a refractory inorganic oxide such as decationized zeolite, alumina, zirconia, silica or magnesia and mixtures thereof optionally promoted with an acidic material such as boron oxide or a halogen.

Advantageously, the catalyst has a surface area of at least 150 $m.^2/g.$, and a pore volume of at least 0.5 cc./g. The upper limit of the surface area and pore volume is governed by the hardness and ruggedness of the catalyst. As a practical matter, for commercial installations where the catalyst is used in units capable of processing several thousand barrels of charge per day, the surface area probably should not exceed about 800 $m.^2/g.$ and the pore volume should not exceed about 0.8 cc./g.

The catalyst may be prepared by any of the methods well known in the art, such as by impregnating the support with a solution of a salt of one of the metals, filtering, drying and then if desired impregnating with a solution of a salt of another metal, filtering, drying and calcining in a manner well known in the art.

The effluent from the hydrocracker is cooled and hydrogen-rich gas separated therefrom and recycled to the hydrocracking zone. Optionally, the hydrogen-rich stream is scrubbed with water to remove any ammonia contained therein or a portion thereof may be bled from the system to prevent the buildup of ammonia and/or low molecular weight hydrocarbons. Hydrogen is added to the recycle stream to replace that consumed in the hydrocracking reaction and if necessary to replace any hydrogen purged from the system. Lubricating oil fractions are recovered from the balance of the hydrocracker effluent by distillation, if necessary, at reduced pressure.

The hydrocracked oil is then subjected to a solvent refining step. Suitable solvents are furfural, nitrobenzene, dimethyl formamide, liquid SO_2, and the like. However, because of its chemical stability, the improved ultraviolet stability of the product and its superior solvent capacity, N-methyl-2-pyrrolidone is the preferred solvent. Solvents are generally used at dosages of 100–600%, at temperatures between 120–250° F., preferred conditions being dosages of 100–300% and temperatures between 120 and 180° F. The unusual feature of this invention is that solvent refining prior to hydrocracking alone is not sufficient to render the oil stable to ultraviolet light but a solvent refining after hydrocracking particularly when the solvent is N-methyl-2-pyrrolidone, results in an improved oil. When two solvent refining steps are used, one before and one after hydrocracking, the solvent refining conditions for the second solvent refining need not be as severe as those for the first although in commercial installations it may be advantageous to use the same conditions.

After solvent refining of the hydrocracked oil, the oil may be subjected to dewaxing to reduce its pour point. In one embodiment of our invention, the raffinate from the solvent refining is passed into contact with a catalyst comprising a hydrogenating component, such as is used in the hydrocracking catalyst, supported on a decationized mordenite. Preferably the support is made by treating a synthetic mordenite with acid to replace the sodium ions with hydrogen ions. Advantageously, the synthetic mordenite is treated with acid to the extent that a portion of the alumina is leached out to produce a mordenite having a silica:alumina mol ratio of at least 20 and having increased dewaxing activity. The catalytic dewaxing may be carried out at a temperature of at least 450° F., a pressure of at least 100 p.s.i.g., a space velocity of 0.2–5.0 v./v./hr. and a hydrogen rate of 1000–10,000 s.c.f.b. Preferred conditions in the catalytic dewaxing zone are a temperature of 450–800° F., a pressure of 100–1500 p.s.i.g. and a space velocity of 0.2–2.0.

Alternatively, the oil may be contacted with a dewaxing agent such as a mixture containing 40–60 volume percent of a ketone such as acetone, methyl ethyl ketone or normal butyl ketone and 60–40 volume percent of an aromatic compound such as benzene or toluene in a ratio of about 3–4 parts by volume of solvent per volume of oil, the mixture cooled to a temperature of about 0 to −20° F. and the waxy components removed by filtering or centrifuging. The filtrate is then subjected to flash distillation and stripping to remove the solvent. The resulting product is a lubricating oil of high viscosity index and good stability towards ultraviolet light.

The following examples are submitted for illustrative purposes only.

EXAMPLE I

The charge in this example is an oil obtained by distillation from a deasphalted vacuum residuum and then furfural refined. It is hydrocracked over a catalyst containing 2.8% nickel and 9.6% molybdenum as the sulfides supported on silica-alumina base (73% silica) having a pore volume of 0.72 cc./g. and a surface area of 349 $m.^2/g.$, at 750° F. 1800 p.s.i.g., 0.4 v./v./hr. and 6000 s.c.f.b. hydrogen. Table 1 column 1 shows the characteristics of the hydrocracked oil, column 2, the dewaxed hydrocracked oil, column 3 the characteristics of an oil obtained by refining the hydrocracked oil with N-methyl-2-pyrrolidone at 180° F. and a dosage of 300% and column 4 the oil of column 3 after dewaxing. In both cases the dewaxing solvent is a mixture of equal parts by volume of toluene and methyl ethyl ketone. This example shows that the floc formation of the hydrocracked oil in ultraviolet light is reduced by the mild solvent refining treatment. Additionally the viscosity index of the oil is improved 12 VI units. It also shows that solvent refining only prior to hydrocracking does not yield an oil stable to ultraviolet light but does show that when the solvent refining follows the hydrocracking the product oil shows the desired stability.

TABLE I

	1	2	3	4
Gravity, °API	33.1			32.4
Viscosity:				
SUS/100° F.	225	256	260	289
SUS/210° F.	50.8	50.8	53.7	54.1
Viscosity index	129	107	140	119
Pour, ° F.	+95	0		
U.V. stability, 48 hours		Floc		(1)

[1] No. floc.

EXAMPLE II

In this example the charge, an oil obtained by propane deasphalting a vacuum residuum, is hydrocracked at 785° F., 2300 p.s.i.g., 0.4 v./v./hr. and 6000 s.c.f.m. hydrogen over a fixed bed of pelleted catalyst containing 5.9% nickel and 18.3% tungsten on an alumina support having a surface area of 171 $m.^2/g.$ and the hydrocracked product is then dewaxed using a 50:50 mixture of methyl ethyl ketone and benzene at a 3:1 dilution and a temperature of −30° F.

In Table 2 below column 1 lists the characteristics of the dewaxed hydrocracked oil, column 2 those of the raffinate obtained by batch furfural refining the dewaxed hydrocracked oil at a dosage of 300% at 150° F. and column 3 those of the raffinate obtained by batch solvent refining the dewaxed hydrocracked oil at a dosage of 300% at 150° F. with N-methyl-2-pyrrolidone.

TABLE II

	1	2	3
Viscosity:			
SUS/100° F.	434	513	481
SUS/210° F.	60.4	66.2	64.7
Viscosity index	100	104	107
Pour, ° F.	0	−5	0
U.V. Stability, 48 hours	Floc	(1)	(2)

[1] No flock but haxy.
[2] No floc clear.

Example II shows the superiority of N-methyl-2-pyrrolidone over furfural for producing a product having stability towards ultraviolet light. It also shows that the hydrocracked oil which has not been treated with a solvent having an affinity for aromatics has very poor U.V. stability. In addition to improved ultraviolet stability, the solvent refining of the hydrocracked oil results in an oil with improved viscosity index.

EXAMPLE III

The hydrocracked deasphalted vacuum residuum used in Example II is solvent refined with N-methyl-2-pyrrolidone on a mixer-settler countercurrent extractor with 176 vol. percent solvent dosage, 209° F. extraction temperature and a refined oil yield of 79 vol. percent. The properties of the dewaxed charge and dewaxed refined oil are shown in columns 1 and 2 respectively of Table III. The improvement in ultraviolet stability and viscosity index are again evident.

TABLE III

	1	2
Viscosity:		
SUS/100° F.	466	469
SUS/210° F.	61.9	64.5
Viscosity index	98	110
Pour, ° F.	−20	+5
U.V. stability, 48 hours	Floc	(1)

[1] No floc.

EXAMPLE IV

In this example, the vacuum residuum obtained from a sweet Louisiana crude is treated with butane as a deasphalting agent and the deasphalted residuum is hydrocracked as in Example II. Solvent refining of the hydrocracked oil is conducted on a 12 stage mixer-settler countercurrent extractor using 105 vol. percent N-methyl-2-pyrrolidone at 120° F. extraction temperature. The refined oil is produced in 82 vol. percent yield. Properties of the hydrocracked oil before and after solvent refining are shown in columns 1 and 2 respectively of Table IV.

TABLE IV

	1	2
Gravity,° API	31.1	35.2
Viscosity:		
SUS/100° F.	62.7	67.6
SUS/210° F.	35.5	36.7
Viscosity index	106	130
Color, Lovibond	130/½	⅝

[1] No floc.

These results show the vast improvement in color obtained by solvent refining the hydrocracked oil using N-methyl-2-pyrrolidone as the solvent.

I claim:

1. A process for the production of a lubricating oil of improved viscosity index and ultraviolet stability which comprises contacting a lubricating oil fraction wth a hydrocracking catalyst comprising a Group VI metal and a Group VIII metal or compounds thereof on a support consisting essentially of alumina having a surface area between 150 m.²/g. and 800 m.²/g. and a pore volume between 0.5 and 0.8 cc./g. under hydrocracking conditions including a temperature between 750 and 850° F. and extracting the hydrocracked oil with N-methyl - 2 - pyrrolidone to produce a lubricating oil raffinate of improved viscosity index and ultraviolet stability.

2. The process of claim 1 in which the lubricating oil fraction is a wax distillate.

3. The process of claim 1 in which the lubricating oil fraction is a deasphlated residuum.

4. The process of claim 1 in which the catalyst comprises nickel and molybdenum or compounds thereof.

5. The process of claim 1 in which the catalyst comprises nickel and tungsten or compounds thereof.

6. The process of claim 4 in which the catalyst comprises sulfided nickel and molybdenum supported on a mixture of silica and alumina.

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