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[54] **PRODUCTION OF LUBRICATING OILS**

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[58] **Field of Search** 208/18, 86, 87

[56] **References Cited**

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[57] **ABSTRACT**

Improved lubricating oils are prepared by simultaneously solvent refining-deasphalting a vacuum residuum, hydrocracking the product and fractionating the hydrocracked oil to remove material having a viscosity SUS at 210° F of at least 300.

10 Claims, No Drawings

PRODUCTION OF LUBRICATING OILS

This invention relates to the manufacture of lubricating oils. More particularly, it is concerned with a processing sequence in which good yields of ultraviolet stable high viscosity index lubricating oils are obtained.

In the refining of crude petroleum oils, it is customary to fractionally distill the crude oil at atmospheric pressure to recover gasoline, naphtha, kerosene and atmospheric gas oils as overhead and to leave as still bottoms an atmospheric residuum. Distillation is then continued at subatmospheric pressure and there are obtained as overhead vacuum gas oils and light lubricating oil distillates and as still bottoms a vacuum residuum. The vacuum residuum ordinarily is used as a fuel but if the crude oil is of a high quality such as Pennsylvania crude which is particularly suitable for the production of lubricating oils it is more advantageous to remove the fractions boiling in the lubricating oil range from the vacuum residuum and further process them to produce lubricating oils. In fact, with the increasing demand for lube oils, even poor quality stocks are now being processed further in an effort to obtain greater production of lube oils. Conventionally the processing comprises subjecting the residuum to deasphalting by contact with a low molecular weight n-paraffin or isoparaffin such as propane, iso-butane or pentane to produce a deasphalted DA residuum. The DA residuum is then treated with a solvent having an affinity for aromatic hydrocarbons such as furfural, N-methyl-2-pyrrolidone, phenol, dichloroethylether and the like to remove aromatics and produce a raffinate of improved viscosity index. The raffinate is contacted with a solvent such as a mixture of methylethylketone and toluene for removal of wax, to lower its pour point, and is then percolated through clay to improve the color.

In each of the processing steps listed above, there is generally some loss in yield so that the final yield of refined lubricating oil actually obtained may amount to about 30 volume per cent of the residuum.

Another disadvantage is that now lubricating oils, particularly those used in automobile engines, are subjected to use over an extended period of time. Because of the nature of their use, crankcase oils must have a high viscosity index which means that in conventionally-processed oils, viscosity index improvers must be added to the oil. Unfortunately, when such an oil is subjected to use over an extended period of time, the viscosity index improver will break down resulting in a considerable loss in viscosity index of the lubricating oil.

It is therefore an object of this invention to produce lubricating oils using improved methods over conventional lubricating oil refining techniques. Another object of the invention is to produce lubricating oils from residuum-containing materials. Another object is to produce lubricating oils having a viscosity index which ordinarily may be obtained from residua by the addition of viscosity index improving agents. These and other objects will be obvious to those skilled in the art from the following disclosure.

It has now been found that good yields of high viscosity index lubricating oils of improved color can be obtained while reducing the number of processing steps conventionally required for the production of high quality lubricating oils. According to our invention, a residual lube oil stock is improved by subjecting it to

simultaneous deasphalting and solvent refining to produce a substantially asphalt-free lubricating oil stock of improved viscosity index, hydrocracking the refined deasphalted product, subjecting a selected portion of the hydrocracked oil to additional refining and dewaxing the refined product. In a specific embodiment of our invention, the residuum is simultaneously deasphalted and solvent extracted, the highly paraffinic raffinate is subjected to hydrocracking, the lighter portion thereof is refined and the product is dewaxed to produce good yields of high quality lubricating oil. More specifically, a raw residuum is contacted with furfural or N-methyl-2-pyrrolidone to yield an extract mix containing solvent, asphalt and aromatics and a parraffinic raffinate containing a minor amount of solvent. The solvent is recovered from the extract mix in a flashing operation followed by fractionation or steam stripping and from the raffinate by fractionation or steam stripping. The solvent-free raffinate is charged to a lube oil hydrocracking step and a selected portion of the lubricating oil fraction of the hydrocracking product is subjected to a second solvent extraction and is then dewaxed.

The charge stocks used in the process of the invention are those containing materials boiling within the lube oil range and also containing asphaltic components. To obtain a high viscosity index in the final product without resorting to severe processing conditions, the VI of the charge stock preferably should be at least about 75 but the process is not limited to such charge stocks. Charge stocks having VI's of 50 and lower may be used successfully to produce high viscosity index products using more severe processing conditions. Particularly suitable charge stocks include vacuum residua obtained from West Texas, Mid Continent Arabian or other paraffin base crude oils.

In the deasphalting-solvent refining step the charge stock undergoing treatment is subjected to liquid-liquid contact with a selective solvent which preferentially dissolves the more aromatic constituents of the charge. It is a characteristic of the solvent employed that it is partially miscible with the charge undergoing treatment to that during the deasphalting-solvent refining step there are formed two phases, a raffinate phase containing substantially only a solvent refined material having a reduced amount or proportion of aromatics and asphalt as compared to the charge stock and an extract phase or mix containing substantially more aromatics and asphalt than the charge. The deasphalting-solvent refining step may be carried out stagewise (combinations of mixer-settler) or continuously in a suitable contacting apparatus, e.g. packed or plate tower, rotating disc contactor either cocurrently or countercurrently.

The contacting is carried out at a temperature above the pour point but below the temperature of complete miscibility of the charge in the solvent. Ordinarily an extraction temperature of 120°250° F., preferably 150°–200° F., is employed. A solvent dosage within the range of 50–450% may be used, a range between 100 and 200% being preferred for the deasphalting-refining of paraffin base charges. When the charge is of the naphthenic type, temperatures of 50°–200° F., preferably 75°–150° F., and dosages of 50–300%, preferably 75–200%, may be used. Furfural and N-methyl-2-pyrrolidone are the preferred agents for the deasphalting-solvent refining, N-methyl-2-pyrrolidone being par-

ticularly preferred because of its superior thermal stability and its greater solvent powers, N-methyl-2-pyrrolidone surprisingly having about twice the solvent capacity of furfural.

After removal of solvent, the raffinate is then subjected to catalytic hydrocracking by, in a preferred embodiment, being passed downwardly through a fixed bed of particulate catalyst at a temperature between about 600° and 900° F., a pressure between about 800 and 5,000 psig, a space velocity of from about 0.1 to 5.0 volumes of oil per volume of catalyst per hour with hydrogen at a rate of between about 1,500 and 20,000 SCFB of charge. Preferably the temperature is maintained within the range of 650°–850° F., the pressure between 1,300 and 3,000 psig, the space velocity between 0.15 and 1.5 v/v/hr., and the hydrogen rate between 3,000 and 10,000 SCFB.

Suitable hydrocracking catalysts for use in the process of our invention comprise metals or compounds of metals of Group VI and Group VIII of the Periodic Table. Examples of such components are chromium, molybdenum, tungsten, iron, cobalt, and nickel and mixtures thereof. Generally, these components are supported on a base comprising a refractory inorganic oxide material such as alumina, silica, magnesia, zirconia, titania, and the like and mixtures thereof, optionally in conjunction with a crystalline aluminosilicate of reduced alkali metal content and having uniform pore openings of 6–15A. The catalyst may be used in the form of a slurry, a fluidized bed or a fixed bed. When used in the form of a fixed bed, the reactant flow may be either upward or downward or the flow of hydrogen may be countercurrent to the flow of oil. Particularly suitable catalysts are those containing from 2–10% cobalt or nickel and 10–30% molybdenum or tungsten. Preferred catalysts are those containing about 4–8% nickel and 15–25% tungsten or those containing about 2–4% cobalt and 12–15% molybdenum on a support composed for the most part of alumina, having a surface area of at least 250 m^2/g, a pore volume of at least 0.6 cc/g and having a silica content of at least 2 wt. per cent, preferably 2–30 wt. per cent. Although the catalyst may be subject to chemical change in the reaction zone due to the presence of hydrogen and sulfur therein, the catalyst is ordinarily in the form of the oxide or sulfide when first brought into contact with the charge. Preferably the catalyst is used as a fixed bed of b ⅛– 1/16 inch pellets.

The invention contemplates then fractionating the lubricating oil portion of the effluent from the hydrocracking zone to remove as overhead 80–90% of the lubricating oil portion and to leave 10–20% as still bottoms. The latter may be recycled to the initial deasphalting zone or to the hydrocracking zone or may be removed from the system for other purposes such as use as a low sulfur fuel oil. Surprisingly, it has been found that although hydrocracked lubricating oils ordinarily have a substantially constant viscosity index throughout the heavier portion of the lube oil fraction, lubricating oils prepared by the simultaneous refining-deasphalting of a vacuum residuum using furfural or N-methyl-pyrrolidone and then hydrocracking show a considerable drop in viscosity index at the heavy end of the lubricating oil fraction. By removing the 10–20% bottoms of unexpectedly low viscosity index, not only is the viscosity index of the hydrocracked oil improved but in addition, the color of the final product is improved and this treatment also serves to remove the undesirable high viscosity portion of the hydrocracked lube oil having a viscosity SUS at 210° F. of more than 300.

The 80–90% overhead of the hydrocracked lube oil product is then subjected to a solvent refining step for improvement of the viscosity index and for stability to ultraviolet light. Suitable solvents are furfural, nitrobenzene, dimethyl formamide, liquid SO_2 and the like. However, because of its chemical stability and its superior solvent capacity N-methyl-2-pyrrollidone is the preferred solvent. The solvent may generally be used at a dosage of about 100–600% and at a temperature between about 120°–250° F., preferred conditions being dosages of 100–300% and temperatures between 120° and 180° F. It has been found that oils produced by hydrocracking are unstable to ultraviolet light. To improved the stability of the oil solvent refining is necessary but it must follow hydrocracking. Solvent refining prior to hydrocracking is not sufficient to render the oil UV stable and therefore if the solvent refining precedes the hydrocracking then for a product oil stable to ultraviolet light, the oil should be solvent refined again after hydrocracking. When two solvent refining steps are used, one before and one after the hydrocracking, the conditions for the second solvent refining step need not be as severe as those for the first.

The raffinate from the solvent refining of the hydrocracked oil may then be subjected to dewaxing to reduce its pour point. This can be done by passing the raffinate from the solvent refining into contact with a catalyst comprising a hydrogenating component, such as is used in the hydrocracking catalyst, supported on a decationized mordenite. Preferably, the mordenite support is prepared by treating a synthetic mordenite with dilute acid such as 6N HCl 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. and a pressure of at least about 100 psig. In a preferred embodiment the catalytic dewaxing is effected by passing the oil through a fixed bed of particulate catalyst with hydrogen introduced at a rate between 1,000 and 10,000 scfb of oil, the oil being introduced into the reactor at a space velocity of from 0.2 to 5.0 volumes of oil per volume of catalyst per hour. Preferred conditions are a temperature between 450° and 800° F., a pressure between 100 and 1,500 psig, a space velocity between 0.2 and 2.0 and a hydrogen rate between 1,500 and 5,000 scfb.

Alternatively, the dewaxing may be effected by contacting the oil with a dewaxing agent such as a mixture comprising from about 40–60% by volume of a ketone such as acetone, methylethyl ketone or normal butyl ketone and about 60–40% of an aromatic compound such as benzene or toluene using about 3–4 parts of solvent per part of oil by volume. The mixture is cooled to from about 0° to −30° F. depending upon the desired pour point and the solidified waxy components are removed by filtering or centrifuging. The clear liquid is then subjected to flash distillation for removal of the solvent. The resulting product has an improved viscosity index, has improved color and has good stability towards ultraviolet light.

The following examples are submitted for illustrative purposes only and it should not be construed that the invention is limited thereto.

EXAMPLE I

This example serves to show that contrary to expectations a hydrocracked lube oil obtained by the simultaneous deasphalting-refining of a vacuum residuum has a relatively low viscosity index at each end of its boiling range. In Table 1 below, A is produced by propane deasphalting a vacuum residuum and hydrocracking the deasphalted residuum over a cobalt molybdate on alumina catalyst. B is derived by simultaneously deasphalting-refining the same vacuum residuum and hydrocracking the product under the same conditions as A. The products are fractionated and the viscosity indices of the separate fractions on a waxy basis are reported below:

TABLE 1

Overhead Fraction, cumulative vol.%	A	B
5	—	95
15	62	91
25	100	109
35	94	110
45	110	113
55	109	113
65	108	110
75	106	114
85	109	92

EXAMPLE II

In this example the charge, the same as that used in Example I, is a vacuum residuum having the characteristics listed in column 1. Column 2 shows the characteristics of the residuum after treatment with N-methyl-2-pyrrolidone at a dosage of 180% and a temperature of 185° F. for removal of asphalt.

TABLE 2

	1	2
Gravity, °API	17.6	23.4
Viscosity, SUS 170°F.	1413	520
Viscosity, SUS 210°F.	474	213
Carbon residue	7.3	2.8

The deasphalted residuum of column 2 is then hydrocracked as in Example I by being passed downwardly with hydrogen through a fixed bed of pellets of cobalt molybdenum or alumina catalyst having the following specifications under the tabulated conditions:

TABLE 3

Cobalt, wt. %	2.2
Molybdenum, wt. %	10.5
Silica, wt. %	4.9
Surface area, m^2/g	289.7
Pore volume, cc/g	0.55
Conditions	
Temperature, °F.	780
Pressure, psig	1500
Space velocity, v/v/hr.	0.3
Hydrogen rate, scfb	6130

The lube oil portion of the effluent is solvent refined with N-methyl-2-pyrrolidone at 175° F. and a dosage of 100% and then dewaxed to a 0° F. pour point using a mixture composed of equal parts by volume of methyl ethyl ketone and toluene. Properties of the products are reported below:

TABLE 4

	Solvent refined	Dewaxed
Gravity, °API	30.4	27.7
Viscosity, SUS, 100°F.	440	555
Viscosity, SUS, 210°F.	65.1	67.7
Viscosity Index	127	103
ASTM color*	14.5	—
UV Stability	—	poor

*double diluted

EXAMPLE III

This example is a substantial duplicate of Example II with the exception that the lube oil portion of the effluent from the hydrocracking zone is fractionated, only the 80% overhead is sent to solvent refining and then dewaxed. Properties of the products are reported below:

TABLE 5

	Solvent refined	Dewaxed	20% bottoms
Gravity, °API	32.6	29.5	20.3
Viscosity,SUS,100°F.	244	302	—
Viscosity,SUS,210°F.	52.1	53.3	467
Viscosity Index	129	105	—
ASTM color	12.5	—	—
UV stability	—	good	—
Sulfur, wt. %	0.011	0.015	0.21

Obviously, various modifications of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore, only such limitations should be made as are indicated in the appended claims:

We claim:

1. A process for the production of a lubricating oil which comprises simultaneously solvent refining-deasphalting a vacuum residuum which has not been deasphalted to produce an asphalt-rich extract and an asphalt-poor raffinate containing viscous material having a viscosity SUS at 210° F. of at least 300 by contacting said residuum with an agent consisting essentially of a member of the group consisting of N-methyl-2-pyrrolidone and furfural, contacting said raffinate with a hydrocracking catalyst under hydrocracking conditions and fractionating the product to recover as overhead a hydrocracked lubricating oil and to leave as still bottoms a highly viscous material having a viscosity SUS at 210° F. of at least 300.

2. The process of claim **1** in which the hydrocracked lubricating oil is fractionated to remove 80–90% thereof as overhead.

3. The process of claim **1** in which the solvent refining-deasphalting agent is furfural.

4. The process of claim **1** in which the solvent refining-deasphalting agent is N-methyl-2-pyrrolidone.

5. The process of claim **2** in which the overhead fraction is subjected to a solvent refining by contact with a solvent selected from the group consisting of furfural and N-methyl-2-pyrrolidone.

6. The process of claim **2** in which the overhead fraction is dewaxed.

7. The process of claim **1** in which the hydrocracking catalyst comprises a compound of an iron group metal and a compound of a group VI metal on a support comprising a low alkali metal zeolite having uniform pore openings of from 6–15A.

8. The process of claim **1** in which the hydrocracking catalyst comprises a compound of an iron group metal and a compound of a Group VI metal on a support comprising an amorphous refractory inorganic oxide selected from the group consisting of alumina, silica, magnesia, titania and zirconia.

9. The process of claim **1** in which the hydrocracked lubricating oil is solvent refined by extracting the aromatics therefrom with a solvent having an affinity for aromatic hydrocarbons.

10. The process of claim **9** in which the solvent extracted lubricating oil is dewaxed.

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