

[54] LUBE OIL MANUFACTURE  
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3,652,448 3/1972 Cummins ..... 208/18  
3,380,912 4/1968 Paterson ..... 208/86  
3,281,350 10/1966 Codet et al. .... 208/66  
3,414,506 12/1968 Campagne ..... 208/309

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FOREIGN PATENTS OR APPLICATIONS

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1,006,508 10/1965 Great Britain ..... 208/18

Related U.S. Application Data

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[57] ABSTRACT

Lubricating oils are prepared by subjecting a residuum containing petroleum fraction to simultaneous deasphalting-solvent refining using a solvent, e.g., furfural or N-methyl-2-pyrrolidone. The resulting raffinate is hydrocracked and then dewaxed. N-methyl-2-pyrrolidone is superior to furfural as a deasphalting-solvent refining agent because of its greater thermal stability and solvent capacity.

[56] References Cited

UNITED STATES PATENTS

2,121,323 6/1938 Manley et al. .... 208/327  
3,458,432 7/1969 Woodle et al. .... 208/327

7 Claims, No Drawings

## LUBE OIL MANUFACTURE

This application is a continuation-in-part of our application Ser. No. 863,312, filed Oct. 2, 1969 now abandoned.

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

In the refining of crude petroleum oils, it is customary to fractionally distill the crude at atmospheric pressure to recover gasoline, naphtha, kerosene and atmospheric gas oils as overhead leaving as still bottoms an atmospheric residuum. Distillation is then continued at reduced pressure and there is obtained overhead vacuum gas oils and light lubricating oil distillates leaving a vacuum residuum. The vacuum residuum ordinarily is used as a fuel but if the crude 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 lubricating oil stocks 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 normal or isoparaffin such as propane, butane or pentane to produce a deasphalted residuum. The DA residuum is then treated with a solvent having an affinity for aromatic hydrocarbons such as furfural, phenol, dichloroethylether and the like to remove aromatics and improve the viscosity index, then with a solvent such as a mixture of methyl-ethylketone and toluene for removal of wax, to lower the pour point and is then percolated through clay to improve the color.

In each of the processing steps listed above there is a considerable loss in yield so that the final yield of refined lubricating oil actually obtained may be about 30 volume percent. Another disadvantage is that currently lubricating oils, particularly those used in automobile engines, are being subjected to use over an extended period of time. Because of the nature of the use crankcase oils must necessarily have a high viscosity index which means that in conventionally processed oils viscosity index improvers must be added to the oil. Unfortunately, when the oil is subjected to use over an extended period of time, the viscosity index improver will break down with the result that there is a considerable loss in viscosity index of the lubricating oil.

It is therefore an object of this invention to produce lubricating oils using less processing steps than conventional lubricating oil refining techniques. Another object of the invention is to produce high yields of lubricating oils from residuum-containing materials. Another object is to provide lubricating oils commercially having a viscosity index which ordinarily is obtained in commercial production only by the addition of viscosity improving agents. These and other objects will be obvious to those skilled in the art from the following disclosure.

I have now found that good yields of high viscosity index lubricating oils can be obtained while reducing the number of processing steps conventionally required for the production of high quality lubricating oils. According to my invention a residuum containing lubri-

cating oil stock is subjected to simultaneous deasphalting and solvent refining to produce a substantially residuum-free lubricating oil stock of high viscosity index which is particularly adapted to further processing by hydrocracking. In a specific embodiment of my invention the residuum is simultaneously deasphalted and solvent extracted, the highly paraffinic raffinate is subjected to hydrocracking 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 paraffinic 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 the lubricating oil fraction of the hydrocracking product is dewaxed.

The charge stocks used in the process of the invention are those containing materials boiling within the lube oil range and also containing at least 5 percent Conradson Carbon Residue. 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. Suitable charge stocks include atmospheric and vacuum residua obtained from West Texas, Mid Continent, Arabian or other paraffin base crude oils and in some cases whole crudes such as San Ardo crude.

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 so 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 concurrently or countercurrently.

The contacting is carried out at a temperature above about 50°F. 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 percent may be used, a range between 100 and 200 percent 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 percent, preferably 75-200 percent, may be used. Furfural and N-methyl-2-pyrrolidone are the preferred agents for the deasphalting-solvent refining, N-methyl-2-pyrrolidone being particularly preferred because of its superior thermal stability and its greater solvent pow-

ers, NMP surprisingly having about twice the solvent capacity of furfural.

After removal of solvent, the raffinate is then subjected to catalytic hydrocracking at a temperature between about 600° and 900°F., a pressure between about 800 and 5,000 psig, a space velocity of about 0.1 to 5.0 volumes of oil per volume of catalyst per hour with a hydrogen 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 upwardly or downwardly or the flow of hydrogen may be countercurrent to the flow of oil. Particularly suitable catalysts are those containing from 3–10 percent cobalt or nickel and 10–30 percent molybdenum or tungsten. Preferred catalysts are those containing about 6 percent nickel and 20 percent tungsten or those containing about 5 percent cobalt and 15 percent molybdenum on a support composed for the most part of alumina and having a surface area of at least 250 m<sup>2</sup>/g, a pore volume of at least 0.6 cc/g and a silica content of at least 2 wt. percent, preferably 2–30 wt. percent. Although the catalyst may be subjected 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.

After hydrocracking, the oil is subjected to dewaxing. In one embodiment of our invention, the entire effluent from the hydrocracking zone is passed directly without intermediate treatment 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 ion. Advantageously, the synthetic mordenite is treated with acid to the extent that a portion of the alumina is leached out to produce a mordenite of increased silica:alumina ratio and increased dewaxing activity. The catalytic dewaxing may be carried out at a temperature of at least 450°F., a pressure of at least 100 psig, and a space velocity of 0.2–5.0 v/v/hr. Naturally when the hydrocracker effluent is introduced directly into the catalytic dewaxing zone, the hydrogen rate in the catalytic dewaxing zone subject to hydrogen consumption in the hydrocracker is substantially the same as the hydrogen rate in the hydrocracking zone. Preferred conditions in the catalytic dewaxing zone are a temperature of 450°–950°F., a pressure of 100–1,500 psig and a space velocity of 0.2–1.0.

In another embodiment, the hydrogen and light hydrocarbons may be separated from the hydrocracking zone effluent and the lube oil then contacted with a dewaxing agent such as a mixture of ketone such as acetone, methyl ethyl ketone or normal butyl ketone and an aromatic hydrocarbon 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 –10°F. depending on the desired pour point and the waxy components removed by filtering or centrifuging. The filtrate or supernatant liquid is then subjected to flash distillation and stripping to remove residual solvent.

The following examples, which are given for illustrative purposes only, show the processing of a raw residuum by simultaneous deasphalting-extracting, hydrocracking the deasphalted raffinate and then dewaxing the resulting lube oil using a mixture containing equal parts of methyl ethyl ketone and toluene.

#### EXAMPLE I

Data and information on the residuum charge stock, operating conditions and product are tabulated below:

|                         |      |      |      |
|-------------------------|------|------|------|
| Charge Stock            |      |      |      |
| Gravity, °API           |      |      | 21.0 |
| Viscosity, SU at 210°F. |      |      | 226  |
| Viscosity Index         |      |      | 89   |
| Carbon Residue, wt. %   |      |      | 5.2  |
| Deasphalting-extraction |      |      |      |
| Solvent                 |      |      | NMP  |
| Temperature, °F.        |      |      | 155  |
| Dosage, vol. %          |      |      | 110  |
| Product Yield, vol. %   |      |      | 77   |
| Viscosity Index         |      |      | 97   |
| Carbon Residue, wt. %   |      |      | 2.3  |
| Pour Point, °F.         |      |      | 110  |
| Hydrocracking           |      |      |      |
| Run No.                 | 1    | 2    | 3    |
| Temperature, °F.        | 732  | 770  | 800  |
| Pressure, psig          | 1500 | 1500 | 1500 |
| Space velocity, v/v/hr. | 0.27 | 0.25 | 0.26 |
| Hydrogen rate, SCFB     | 5400 | 5160 | 5040 |
| Yield, vol. %           | 90   | 73   | 13   |
| Pour Point, °F.         | 50   | 105  | 110  |
| Carbon Residue, wt. %   | 0.74 | 0.21 | 0.15 |
| Dewaxed Product         |      |      |      |
| Viscosity Index         | 97   | 118  | 135  |
| Pour Point, °F.         | –5   | 0    | 0    |

#### EXAMPLE II

In this example, the same raw residuum of Example I is used as the charge. Processing conditions and data are tabulated below:

|                         |      |      |      |      |
|-------------------------|------|------|------|------|
| Deasphalting-extracting |      |      |      |      |
| Solvent                 |      |      | NMP  |      |
| Temperature, °F.        |      |      | 181  |      |
| Dosage, Vol. %          |      |      | 186  |      |
| Product                 |      |      |      |      |
| Yield, vol. %           |      |      | 51   |      |
| Viscosity Index         |      |      | 91   |      |
| Pour Point, °F.         |      |      | 120  |      |
| Carbon Residue, wt. %   |      |      | 1.3  |      |
| Hydrocracking           |      |      |      |      |
| Run No.                 | 1    | 2    | 3    | 4    |
| Temperature, °F.        | 733  | 763  | 781  | 805  |
| Pressure, psig          | 1475 | 1475 | 1475 | 1500 |
| Space velocity, v/v/hr. | 0.27 | 0.26 | 0.26 | 0.24 |
| Hydrogen rate, SCFB     | 4410 | 5150 | 5090 | 6100 |
| Yield, vol. %           | 90   | 74   | 60   | 30   |
| Dewaxed Product         |      |      |      |      |
| Viscosity Index         | 108  | 122  | 133  | 135  |
| Pour Point, °F.         | –5   | –10  | 0    | +20  |

In each example the catalyst is in the form of a fixed bed of 1/16 inch pellets containing 2.1 percent cobalt, 9.8 percent molybdenum, 0.53 percent sulfur, 79.7

percent alumina and 3.9 percent silica. The pellets have a surface area of 270 m<sup>2</sup>/g and a pour volume of 0.63 cc/g.

When conventionally solvent refined deasphalted residuum is hydrocracked under conditions similar to those of Examples I and II, i.e., a space velocity of 0.25 and a pressure of 1,500 psig and the viscosity indexes of the hydrocracked products dewaxed to a 0°F. pour point are plotted against the hydrocracking reactor temperatures, it will be seen that the VI of the conventionally deasphalted solvent refined hydrocracked dewaxed oil is substantially equivalent to the product of Example I but inferior to the product of Example II. This indicates that equal and superior products may be prepared by the process of this invention although using one less processing step than conventional procedures.

Similarly, with respect to the yield-viscosity index relationship, when the viscosity indexes of the hydrocracked products dewaxed to a 0°F. pour point are plotted against the lube oil yields basis charge to the hydrocracker, it will be seen that the process of Example II produces greater yields of higher viscosity index lube oils than does a conventional deasphalting, solvent refining hydrocracking dewaxing procedure and that the process of Example I is superior to a conventional deasphalting hydrocracking dewaxing procedure.

The superiority of NMP as a dual agent is evidenced by a showing that when NMP is used for simultaneous deasphalting-solvent refining, the results obtained are comparable to those obtained by conventional deasphalting of the residuum followed by furfural refining.

### EXAMPLE III

This example shows a comparison between deasphalting-extracting using N-methyl-2-pyrrolidone in a single stage and deasphalting using propane on the same charge stock as used in the previous examples

|                                 | NMP   | Propane |
|---------------------------------|-------|---------|
| Dosage, vol. %                  | 181   | 800     |
| Temp., °F.                      | 186   | 160     |
| Yield, vol. %                   | 51    | 71      |
| Product                         |       |         |
| Gravity, °API                   | 26.5  | 25.5    |
| Viscosity SUS/210°F.            | 148.2 | 121.2   |
| Viscosity Index                 | 92    | 92      |
| Conradson Carbon Residue, wt. % | 1.3   | 1.5     |
| Sulfur, wt. %                   | 0.22  | 0.38    |

The above results show the superiority of NMP in that it effects deasphalting-solvent refining simultaneously. It also effects greater desulfurization. After solvent refining the propane deasphalted material with furfural under conventional conditions, the product is subjected to hydrocracking and dewaxing on a comparative basis with the NMP refined charge. Hydrocrack-

ing conditions are a space velocity of 0.25 v/v/hr., a pressure of 1,500 psig and 5,000 SCFB hydrogen using the same catalyst as in Example I at various temperatures with dewaxing of the product to a 0°F. pour point. The viscosity index for the NMP deasphalted-refined hydrocracked-dewaxed material averages 5 units higher than that of the propane-deasphalted furfural-refined hydrocracked and dewaxed material.

Although the severity of the processing conditions can be varied depending on the properties of the charge stock and the quality of the desired product, it has been found that the best VI-yield relationship is obtained with stock that has been solvent refined to a 40-60 volume percent raffinate yield.

Another feature of my invention is to be found in the viscosity-viscosity index relationship. At a given viscosity level, products prepared by my novel process have a higher viscosity index than products prepared in a conventional manner, i.e., by using a low molecular weight paraffin for the deasphalting.

I claim:

1. A process for the preparation of a lubricating oil fraction of improved characteristics which comprises subjecting a residuum containing petroleum fraction selected from the group consisting of atmospheric residua and vacuum residua which have not been deasphalted having a Conradson Carbon Residue of at least 5 percent to simultaneous deasphalting-solvent refining which consists essentially of contacting said fraction with a solvent having an affinity for aromatics, consisting essentially of N-methyl-2-pyrrolidone to produce an extract phase rich in aromatics and asphaltic materials and a raffinate phase, recovering a lubricating oil fraction from the raffinate and contacting the recovered lubricating oil fraction with a hydrocracking catalyst at a temperature between 600° and 900°F., a pressure between 800 and 5,000 psig, a space velocity between 0.1 and 5.0 v/v/hr. and a hydrogen rate between 500 and 20,000 SCFB.

2. The process of claim 1 in which the hydrocracked lubricating oil is dewaxed.

3. The process of claim 2 in which the hydrocracked lubricating oil is catalytically dewaxed.

4. The process of claim 3 in which the dewaxing catalyst comprises a hydrogenating component supported on low sodium mordenite.

5. The process of claim 2 in which the hydrocracked lubricating oil is solvent dewaxed.

6. The process of claim 1 in which the yield of raffinate is between 40 and 60 volume percent.

7. The process of claim 1 in which the temperature is between about 730° and 800°F.

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