The invention accordingly consists in a method of preparing a petroleum material of greater naphthenic content than the original feedstock which comprises contacting a naphthenic feedstock boiling above 350° C. and having at least 30% n-paraffin content with a gas under super-critical conditions of temperature and pressure, removing the gas phase product, and separating therefrom a material enriched in naphthenes. Subject to the above requirements the feedstock may be a crude petroleum or a fraction derived therefrom. The fraction treated may be derived from the crude petroleum by conventional distillation, or super-critical means may be employed. In the latter case the crude petroleum may be separated into light and heavy fractions and the latter contacted with super-critical gas at lower pressure and higher temperature than in the initial separation.

The choice of gas used in a super-critical separation process, and the temperature and pressure at which it is used, will depend on the components to be separated. Thus, the gas must be inert with respect to the components to be separated. Since absorbability is greater the nearer the process temperature is to the critical temperature of the gas and the greater is the process pressure, it is desirable that a gas be chosen whose critical temperature is near, but below, the desired working temperature, and whose critical pressure is, as far as possible, much below the desired working pressure. The working temperature should not be more than 100° C. above the critical temperature. In addition it is preferable that the working temperature should be within the range —100° C. to +300° C., and that the boiling point of the feedstock should be at least 100° C. above the critical temperature of the gas. Taking these, and other criteria, into account, suitable gases for use in the method of the present invention include the lower alkanes and alkenes and their halo- generated derivatives, and inorganic gases such as carbon dioxide and ammonia. Mixtures of one or more of these gases may be used provided that they are inert with respect to the feedstock. For the separation of hydrocarbon mixtures such as are envisaged in the present application the gases ethane, ethylene, propane, and propylene are especially preferred.

The experimental work on which this invention was based was carried out in the apparatus shown diagrammatically in the drawing. This comprises a visual cell 1 of 180 mL capacity which is a flanged stainless steel cylinder capable of withstanding pressures of up to 10,000 p.s.i., and fitted with a sight glass along its entire length, connected at its top via nylon tubing and a valve 3 to a small glass graduated receiver 4, fitted with a side arm and a valve 5. The side arm is connected to a gas meter 13, the gas from which is vented to atmosphere, or compressed and recirculated to the system. The bottom of the cell is connected by high pressure small bore tubing via a valve 2 and another valve 8 to the top of a gas cell 7 containing mercury. The gas cell is connected via a valve 9 to a mercury pump 10 fitted with a pressure gauge 11. Gas is supplied from cylinder 12. The pump is an electrically driven positive displacement device of conventional design. The visual cell and the receiver, together with the associated valves 2, 3 and 5, are located in an electrically heated and thermostatically controlled air oven 6 fitted with a window and means for applying slight agitation to the cell.

In carrying out the work, 50 mL of the feedstock was charged to the visual cell through the charge top. The top flange was then replaced and the cell evacuated with a vacuum pump so as to deaerate the system as much as possible. The temperature of the air oven was then set at the desired value, and gas, compressed as desired by the mercury pump to the degree indicated by the pressure
gauge was introduced into the visual cell from the gas cell by opening valve 2 slightly, valves 8 and 9 being open and valves 3 and 5 being closed. The introduction of gas was kept at a low rate, valve 2 being opened gradually until fully opened, the pressure in the gas cell being kept constant during this period by operation of the mercury pump. When valve 2 was fully open valves 8 and 9 were closed and the visual cell was agitated to promote equilibrium between the gas and liquid phases. More gas was introduced as found necessary to maintain a constant pressure. The procedure was repeated until the pressure has been stabilized.

Gas was now allowed to bubble through the liquid in the visual cell by opening valve 3 so as to permit a flow rate of 2 to 3 litres per minute as measured by the gas meter. The pressure of the gas in the tubing connecting valve 3 to the product receiver under these circumstances fell to atmospheric, and any material which has been taken up into the gas phase was thereby precipitated and carried by the gas to the receiver. The required quantity of material was allowed to accumulate in the receiver and the flow of gas then stopped. A short time was allowed to elapse for liquid in the tubing to drain into the receiver. The fraction thus collected was removed for examination and further fractions obtained by resuming the gas flow and repeating the procedure described.

When necessary the product rate was increased by raising the pressure in the visual cell progressively. In this case the gas flow was interrupted and the system allowed to reach equilibrium at the higher pressure.

At the end of each experiment valve 2 was closed and valve 3 gradually opened so as to bring the pressure in the visual cell down to atmospheric. In the cases where the residue remaining in the cell was liquid it was drained through valve 2 after disconnecting from valve 8. Otherwise the top flange of the visual cell was removed and the material dissolved in a low boiling hydrocarbon solvent and removed. With this material was combined material, if any, which had collected in the receiver during de-presurisation of the visual cell. The solvent was stripped off conventionally in a stream of nitrogen.

A material balance for each experiment was made by weighing the quantity of feedstock charged to the cell, and also each of the gas phase fractions and the residue.

The product rate was expressed as the weight of material vaporised per unit volume of gas measured at NTP.

For comparison a conventional vacuum distillation was carried out on the same feedstock as was treated in the above manner, a Vacuum Engler apparatus being used.

**EXAMPLE**

Using the apparatus and technique described above, a Bachauqua 76.95% wt. residue boiling above 350° C., prepared by distillation in a 14-plate laboratory column was contacted with ethane at a temperature of 176° F. (80° C.) and a pressure of 5000 p.s.i.g. The critical temperature of ethane is 32° C. and the critical pressure is 732 p.s.i.g.

The results obtained are shown in Table 1 below, Table 2 below shows the results obtained by Vacuum Engler distillation of an identical feedstock.

---

**TABLE 1**

<table>
<thead>
<tr>
<th>Fraction No.</th>
<th>Product yield, percent wt on feed</th>
<th>Cumulative Mfd. percent yield on feed</th>
<th>Product rate, g./1000 lb. total</th>
<th>Specific gravity 60° F.</th>
<th>Sulphur content, percent</th>
<th>Kineimetric viscosity, cent at—</th>
<th>Wax content, percent wt</th>
<th>Asphaltenes, percent wt</th>
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<td>8.7</td>
<td>4.3</td>
<td>8.5</td>
<td>0.943</td>
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<td>2</td>
<td>5.8</td>
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<td>0.794</td>
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<td>470 50.0 43.7 18.7</td>
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<td>15</td>
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<tr>
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<td>469 105.6 45.1 15.1</td>
<td>21</td>
<td>15</td>
</tr>
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<td>20.8</td>
<td>8.6</td>
<td>0.577</td>
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<td>405 118.0 60.0 25.9</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>8.8</td>
<td>8.9</td>
<td>4.2</td>
<td>0.596</td>
<td>2.83</td>
<td>590 172.6 61.0 25.5</td>
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<td>16</td>
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<td>Residue</td>
<td>55.7</td>
<td>71.7</td>
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<td>&gt;129</td>
<td>1.2</td>
<td>10</td>
</tr>
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<td>10.8</td>
<td>1.1</td>
<td>0.943</td>
<td>2.12</td>
<td>88.7 14.1 8.9 4.19</td>
<td>4.09</td>
<td>1.7</td>
</tr>
</tbody>
</table>

1. Calculated.

---

**TABLE 2—VACUUM ENGLER DISTILLATION OF BACHAUQUA 76.95% WT. RESIDUE**

<table>
<thead>
<tr>
<th>Fraction No.</th>
<th>TBP Temperature, °F</th>
<th>Yield yield, percent wt on feed</th>
<th>Cumulative Mfd. yield on feed</th>
<th>Product rate, g./1000 lb. total</th>
<th>Specific gravity 60° F.</th>
<th>Sulphur content, percent</th>
<th>Kineimetric viscosity, cent at—</th>
<th>Wax content, percent wt</th>
<th>Asphaltenes, percent wt</th>
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<td>88.7 14.1 8.9 4.19</td>
<td>4.09</td>
<td>1.7</td>
<td>7.8</td>
</tr>
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<td>422</td>
<td>6.3</td>
<td>9.6</td>
<td>0.947</td>
<td>2.25</td>
<td>48 23.0 19.8 8.82</td>
<td>+5</td>
<td>6</td>
<td>&lt;1</td>
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<td>449</td>
<td>6.4</td>
<td>15.9</td>
<td>0.937</td>
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<td>721 33.0 18.7 8.73</td>
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<td>5</td>
<td>&lt;1</td>
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<td>20</td>
<td>&lt;1</td>
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<tr>
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<td>6.4</td>
<td>28.6</td>
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<td>2.59</td>
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<td>+9</td>
<td>30</td>
<td>&lt;1</td>
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<td>6.5</td>
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<td>&lt;1</td>
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<td>552</td>
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<td>30.5</td>
<td>0.994</td>
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<td>2500 597.4 177.2 51.8</td>
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<td>70</td>
<td>&lt;1</td>
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<td>2.98</td>
<td>&gt;129</td>
<td>1.2</td>
<td>10</td>
<td>7.8</td>
</tr>
<tr>
<td>Feed</td>
<td>1.08</td>
<td>10.8</td>
<td>1.1</td>
<td>0.943</td>
<td>2.12</td>
<td>88.7 14.1 8.9 4.19</td>
<td>4.09</td>
<td>1.7</td>
<td>7.8</td>
</tr>
</tbody>
</table>

1. Calculated.

---

It will be seen that the fractions obtained with super-critical ethane are considerably more naphthenic in character than the corresponding distillates. This is revealed by the substantially higher viscosity indices of the former than of the latter, as to which, on a calculated basis, the calculated viscosity indices for the bulk super critical gas phase fractions and the Vacuum Engler distillates are +16 and —17, respectively.

The super-critical gas phase products have slightly lower sulphur contents than the corresponding distillates and they also have low asphaltene contents. In addition, and although not shown in Table 1, their colour was better than that of the distillate fractions. All these characteristics are desirable in a lubricating oil base stock, and such a stock can be obtained as has been described without the need to use large quantities of liquid solvents or catalytic methods using relatively arduous conditions.

We claim:

1. A method of obtaining naphthenic lubricating oil base stock having a greater naphthenic content than the original feedstock from a naphthenic feedstock having a low n-paraffin content in one stage without any need for further processing which comprises contacting the naphthenic feedstock boiling above 300° C. and having a low n-paraffin content and a cloud point of less than —30° F., with a gas selected from the group consisting of lower alkanes, lower alkenes, and halogenated derivatives thereof at a working temperature and a working pressure above the critical temperature and the critical pressure of said gas, said working temperature being within the range —100° C. to 300° C. and not more than 100° C. above.
the critical temperature of said gas and said working pressure being greater than the critical pressure of said gas, said gas being inert with respect to the components to be separated, removing a gas phase product, and separating therefrom a lubricating oil base stock enriched in naphthenes.

2. A method of obtaining naphthenic lubricating oil base stock having a greater naphthene content than the original feedstock from a naphthenic feedstock having a low n-paraffin content in one stage without any need for further processing which comprises contacting the naphthenic feedstock boiling above 300° C. and having a low n-paraffin content and a cloud point of less than —30° F., with a gas selected from the group consisting of ethane, ethylene, propane, propylene, carbon dioxide, ammonia, and their inert mixtures thereof at a working temperature and a working pressure above the critical temperature and the critical pressure of said gas, said working temperature being within the range —100° C. to 300° C. and not more than 100° C. above the critical temperature of said gas and said working pressure being greater than the critical pressure of said gas, said gas being inert with respect to the components to be separated, removing a gas phase product, and separating therefrom a lubricating oil base stock enriched in naphthenes.

References Cited

UNITED STATES PATENTS
2,391,576 12/1945 Katz et al. 208—366
2,391,607 12/1945 Whaley 208—356

HERBERT LEVINE, Primary Examiner

U.S. Cl. X.R.

208—309, 366
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,516,928 Dated June 23, 1970

Inventor(s) William Ronald King and William Llewelyn Thomas

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 18 for "-30°F" read --30°F--;

Column 3, Table 2, column headed "Specific Gravity 60°F./60°F." line 3 for "9.957" read --0.057--; line 4 for "9.972" read --0.972--;

Column 5, line 13 for "colud" read --cloud--.

SIGNED AND SEALED
DEC 1-1970

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents