METHOD FOR MANUFACTURING HEATING OIL

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METHOD FOR MANUFACTURING HEATING OIL

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The present invention is concerned with an improved process for the production of high quality heating oils. The invention is more particularly directed to a process whereby cracked heating oils may be effectively blended with sweet virgin heating oils to produce a satisfactory high quality blended heating oil product. In accordance with the present invention a finished heating oil of satisfactory carbon residue content is produced by blending a "mildly hydronined" sweetened virgin heating oil with a cracked heating oil which preferably has been caustic washed.

The present invention is broadly concerned with the production of improved hydrocarbon mixtures known as, "heating oils," of the nature employed in various burner systems, as diesel fuels, or as domestic and industrial heating oils. Heating oils may be derived from petroleum by a variety of methods including straight distillation from crude petroleum oil, and thermal or catalytic cracking of various petroleum oil fractions. Heretofore, in the art, heating oil blends comprised a relatively large proportion of virgin heating oil as compared to cracked heating oils. However, due to the desirability of virgin heating oils as feed stocks to various cracking operations, as for example, a fluid catalytic cracking operation the blends comprise an increasing proportion of cracked heating oil fractions as compared to virgin stocks. Virgin heating oil fractions are also very desirable as diesel oil products which further decreases their availability for heating oil blends.

It is known in the art that heating oils consisting completely or in part of catalytic cracked stocks are characterized by an undesirable instability giving rise to the formation of sediment. It is also known that when cracked heating oils are blended with virgin heating oils certain undesirable characteristics are increased due to their incompatibility. As a result, such blended fuel oils tend to cause clogging of filters, orifices, or conduits associated with the burning systems in which they are employed.

It is also known in the art that when a virgin heating oil is blended with a cracked heating oil, the carbon residue of the blend in many cases exceeds the carbon residue of either the virgin heating oil or the cracked heating oil. This carbon residue is an indication of the extent the blended heating oil will carbonize the burners, particularly a rotary burner in actual use and to some extent determines the burning characteristics and desirability of the fuel.

In order to improve the quality of blended heating oils, various processes have been practiced in the art. It is known in the art to process a virgin heating oil by a caustic wash if the oil be relatively sweet. On the other hand, if the virgin heating oil has a relatively high mercaptan content so as to render it sour, the oil is processed by a doctor treat or an equivalent sweetening operation. On the other hand, light cracked heating oils in many operations merely require a caustic wash. However, the conventional procedure is to secure the cracked heating oil from a relatively severe cracking operation in which case it is necessary to acid treat the cracked heating oil followed by a caustic wash in order to control the carbon residue. This latter operation is not desirable since acid treatment polymerizes many desirable constituents resulting in a loss in yield. Furthermore, the sludge is expensive and difficult to handle.

In accordance with the present invention, finished heating oils of a satisfactory carbon residue content are produced by blending "mildly hydronined" virgin heating oil constituents with cracked heating oil constituents which preferably have been caustic washed. This process eliminates the further treatment of the cracked stocks that would otherwise be necessary due to the serious carbon residue incompatibility that occurs when blending sweetened virgin heating oil constituents with cracked heating oil constituents. Heating oil blends which may be processed by the hydronining operation of the present invention are particularly hydrocarbon mixtures of which more than about 10%, preferably from about 15% to 60% by volume consist of stocks derived from cracking operations. More precisely still, the finished blends may be characterized as petroleum fractions containing a proportion of cracked stocks greater than 10%, preferably from about 15% to 60% by volume, and falling within A. S. T. M. specification D 396-48T for Fuel Oils (Grades No. 1 or 2). Inspections of a typical heating oil blend are for example:

Gravity, °API... 34.5
Distillation, A. S. T. M.:
Initial, B. P. ° F. ... 363
10% @ ° F. ... 348
50% @ ° F. ... 504
90% @ ° F. ... 585
Final, B. P. ° F. ... 640
Flash, ° F. ... 158
Color, Tag Robinson... 15
Viscosity, SSU/100° F. ... 34.7
Pour point, ° F. ... 0
Sulfur, wt. per cent. ... 0.37
Suspended sediment, mgs./100 ml. ... 1.0
Carbon residue on 10% residual, per cent. ... 0.8
Corrosion, 1 hr. @ 212° F. ... Pass
Dielectric index... 48.2
Aniline point, ° F. ... 140

The process of the present invention may be more fully understood by reference to the drawings illustrating one embodiment of the same. Referring specifically to the drawing, a crude oil feed stock is introduced into distillation zone 1 by means of line 2. Temperature and pressure conditions in zone 1 are adapted to remove overhead by means of line 3 normally gaseous hydrocarbons and to remove by means of line 4 hydrocarbon constituents boiling in the motor fuel and naphtha boiling ranges. A virgin heating oil fraction is removed from zone 1 by means of line 5 while a gas oil fraction is removed by means of line 6. A residuum fraction comprising the higher boiling constituents is removed as a bottoms by means of line 7. The virgin heating oil fraction removed by means of line 5 may be treated by various processes in order to refine the same. Normally this fraction is treated with a mild caustic wash, as for example sodium hydroxide.

In accordance with the present invention this virgin heating oil fraction is "mildly hydronined" as hereinafter described.

It is to be understood that distillation zone 1, treating zone 8 and sweetening zone 12 may comprise any suitable number and arrangement of stages. The gas oil fraction removed by means of line 6 is passed to cracking zone 30 which may comprise any suitable cracking operation, as
for example, a thermal or a catalytic cracking process. However, the present invention is particularly directed toward the production of a high quality virgin-cracked heating oil blend wherein the cracking process comprises a catalytic cracking operation, as for example a fluid cata-
lytic cracking operation.

A fluid catalytic cracking plant is composed of three sections: cracking, regeneration, and fractionation. The cracking reaction takes place continuously in one reactor at a temperature in the range of about 800°F to 1050°F. The spent catalyst is continuously regenerated in a separate vessel, from which it is returned to the cracking vessel, which is at a pressure below about 200 lbs, usually below about 500 lbs, per sq. in. Continuity of flow of catalyst as well as of oil is thus accomplished, and the characteristic features of fixed-bed designs involving the intermittent shifting of reactors through cracking, purging, and regeneration cycles are eliminated.

Regenerated catalyst is withdrawn from the regenerator and flows by gravity down a standpipe, wherein a sufficiently high pressure head is built up on the catalyst to allow its injection into the fresh liquid oil stream. The resulting mixture of oil and catalyst flows into the reaction vessel, in which gas velocity is intentionally low, so that a high concentration of catalyst will result. The cracking that takes place results in carbon deposition on the catalyst, requiring regeneration of the catalyst. The cracked liquid oil vapors are withdrawn from the top of the reactor after passing through cyclone separators to remove them of any entrained catalyst particles, while the spent catalyst is withdrawn from the bottom of the reactor and is injected into a stream of undiluted air which carries the combustible gases into the regeneration vessel. The regeneration of combustion results from the regeneration operation of the catalyst leave the top of this vessel and pass through a series of cyclones where the bulk of the entrained catalyst is recovered. The regenerated catalyst is withdrawn from the bottom of the vessel to complete its cycle.

The cracked products are removed from cracking zone 30 (overhead from the reactor) by means of line 28 and introduced into a distillation zone 16. Temperature and pressure conditions in zone 16 are adjusted to remove overhead products of line 17 normally gaseous constituents and to remove by means of line 18 hydrocarbon constituents in the motor fuel boiling range. A fraction boiling above the heating oil boiling range is removed by means of line 19. A fraction boiling in the heating oil boiling range is removed by means of line 20 and in accordance with the present invention may be caustic washed in zone 21. The present invention may be caustic washed in zone 21. In accordance with the present invention the caustic washed cracking and hydrogen oil is blended with the "mildly hydrodried" virgin heating oil.

In accordance with the present invention the virgin heating oil removed by means of line 5 is "mildly hydrodried" in a zone 8. It is essential in practicing the present invention that the hydrogenation operation conducted on the virgin heating oil be a "mild hydrogenation" operation. This is to be distinguished from conventional hydrogenation operations. Hydrogenation operations, hereafter practiced in the art. Such hydrogenation operations have been employed at pressures from 200 to 500 lbs. per sq. in., at feed rates of 5 to 20 volumes of feed per volume of catalyst per hour. Relatively high pressures of hydrogen and recycle have been employed as for example, 2,000 to 4,000 standard cu. ft. per barrel in order to prevent carbonization of the catalyst. Likewise, very active and carbonization of the catalyst. Likewise, very active catalysts have been used which are effective for desulfurization. Under these conditions hydrogen consumption has generally been in the range of 150 to 600 standard cu. ft. per barrel of feed. This relatively high consumption of hydrogen in the past has made the process expensive to operate, so that its application in the past has been limited to the treatment of relatively high sulfur stocks which could not be desulfurized by any other available treating operation. The catalyst heretofore employed has been a cobalt molybdate supported on a carrier, as for example silica or alumina.

Due to the fact that the sulfur content of heating oils is relatively low, since the cracking operation converts to a great extent, conventional hydrogenation operations have not been necessary in the processing of virgin heating oils. On the other hand, when conventional sweetening operations are employed in the processing of virgin heating oils for the improvement of the fuel properties, these conventional operations were found entirely unsatisfactory, since they actually increased the carbon residue and further impaired the quality of the fuel. On the other hand, when employing the mild hydrogenation process of the present invention, unexpected desirable results are secured with a higher quality blended fuel oil product.

The "mild hydrogenation" conditions of the present invention may be secured by lowering the temperature, increasing the feed rate per volume of catalyst or by using a less active catalyst. In accordance with the present invention the temperatures used are in the range from about 400°F to 500°F, preferably in the range from about 400°F to 500°F, preferably in the range from 50 to 200 lbs. per sq. in., preferably in the range from about 50 to 200 lbs. per sq. in. In accordance with the present invention the feed rate per volume of catalyst per hour. Preferred feed rates are in the range from 4 to 10 v. cu./hr. The hydrogen consumed by the gas to the hydrogenation unit may vary from 50 to 100%. This means that, for example, dilute hydrogen from a hydrogenator may be used in the process. A particularly desirable method of hydrogenating in accordance with the present process is to recycle appreciable quantities of hydrogen to the hydrogenation unit in order to completely prevent carbonization of the catalyst.

The catalyst utilized in the present invention may be a known hydrogenating catalyst, for example cobalt molybdate on a carrier such as for example silica or alumina, providing other operating conditions are adjusted to secure a "mild hydrogenating" process. The preferred catalyst, however, of the present invention comprises molybdenum oxide on a carrier preferably alumina.

The amount of molybdenum oxide employed is about 5 to 13% by weight based upon the weight of the catalyst. The catalyst is prepared by known methods, such as by impregnation of alumina with a water-soluble molybdenum salt, followed by heating to convert this salt to molybdenum oxide, or by coprecipitation of alumina and molybdenum hydroxide by addition of ammonium molybdate to an acid monohalide solution of ammonium molybdate.
preferably less than 40. Furthermore, the extent of the sulfur reduction when utilizing the mild hydrofining conditions of the present invention does not exceed about 35% and preferably does not exceed about 20%.

The process of the present invention may be more fully understood by the following examples illustrating the same.

**EXAMPLE I**

A virgin heating oil secured from a West Texas crude and boiling in the range from about 330° to 660° F. was sweetened using various conventional procedures as illustrated in operations B to G respectively.

The sweetened virgin heating oil was then blended in equal volume with a cracked heating oil. The results of these operations are illustrated in the following table:

<table>
<thead>
<tr>
<th>Comparison of Sweetening Methods on West Texas Virgin Heating Oil</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operation</td>
<td>Feed</td>
<td>PhS/S</td>
<td>Air Caustic</td>
<td>Hypochlorite</td>
<td>Unisol</td>
<td>Hydrofining</td>
</tr>
<tr>
<td>Injections on Sweetened Fred.:</td>
<td>&lt;0.03</td>
<td>&lt;0.06</td>
<td>0.12</td>
<td>0.03</td>
<td>0.20</td>
<td>0.03</td>
</tr>
<tr>
<td>Copper No.</td>
<td>32</td>
<td>0.03</td>
<td>0.12</td>
<td>0.03</td>
<td>0.20</td>
<td>0.03</td>
</tr>
</tbody>
</table>
| Carbon Residue of 50/50 Blends of Sweetened Virgin Heating Oil and Cracked Heating Oil:
  | Actual Value | 0.36 | 0.36 | 0.12 | 0.12 | 0.12 |
  | Expected Value | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 |

1 West Texas virgin heating oil had a boiling range of 330-660° F. and a sulfur content of 0.65 wt. percent.

2 Cracked heating oil was a blend of thermal and catalytic stocks with a boiling range of 365-660° F. It was treated only by caustic washing and had a carbon residue of 0.98 wt. percent and a sulfur content of 1.17 wt. percent.

From the above (operation G) it is apparent that the hydrofining-sweetening process of the present invention produces results far superior to equivalent sweetening processes.

The equivalent treating procedures used in the above operations are summarized as follows:

**Treating Procedures**

<table>
<thead>
<tr>
<th>Process</th>
<th>Doctor</th>
<th>PhS/S</th>
<th>Air-Caustic</th>
<th>Hypochlorite</th>
<th>Unisol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Premsh</td>
<td>0.5% of 15 B.E. Caustic</td>
<td>PhS/S</td>
<td>0.5% of 15 B.E. Caustic</td>
<td>0.5% of 15 B.E. Caustic</td>
<td>0.5% of 15 B.E. Caustic</td>
</tr>
<tr>
<td>Vol. Percent Treat.</td>
<td>25%</td>
<td>25%</td>
<td>25%</td>
<td>25%</td>
<td>25%</td>
</tr>
<tr>
<td>Agitating Time</td>
<td>Agitated until doctor calm</td>
<td>Paper Filtration</td>
<td>Water Wash followed by Paper Filtration</td>
<td>Paper Filtration</td>
<td>Water Wash followed by Paper Filtration</td>
</tr>
</tbody>
</table>

1 3.4 g. PhS/S of 15° B.E. caustic, 41 mg. S/100 ml. of caustic, 16 vol. percent treat.
2 Under Ni.

The hydrofining conditions for various operations are as shown in the following table:

**Hydrofining West Texas light virgin heating oil**

| Column | A | B | C | D | E | F
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Process</td>
<td>Feed</td>
<td>Hydrofining</td>
<td>PhS/S Sweetening</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feed Rate, V/V/Hr.</td>
<td>1</td>
<td>4</td>
<td>8</td>
<td>16</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Product Injections:</td>
<td>21</td>
<td>0</td>
<td>1</td>
<td>4</td>
<td>21</td>
</tr>
<tr>
<td>Copper No.</td>
<td>0.65</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.06</td>
</tr>
<tr>
<td>Total Sulfur</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Carbon Residue, Wt. Percent</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Carbon Residue of Blends of 62% Sweetened Virgin, 38% of Catalytic Heating Oil:</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Actual</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Expected</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
</tr>
</tbody>
</table>

1 Light virgin heating oil had a boiling range of 325-360° F.
2 Hydrofining was done with cobalt molybdate catalyst at 600° F. and 200 P.S.I. g. steam, using a feed rate of 10 gpm at a rate of 700 S. C. F./B. with recycle to give an excess H2 rate of 1,000 S. C. F./B.
3 The catalytically cracked heating oil had a boiling range of 420/520° F. It was treated only by caustic washing before use and had a carbon residue of 0.68% and sulfur content of about 1.3 wt. percent.

In various operations the virgin heating oil was hydrofining using a cobalt molybdate on alumina catalyst wherein the concentration of the cobalt molybdate was about 10 to 15% by weight based upon the alumina. In other operations the catalyst comprised molybdenum oxide on alumina wherein the concentration of the molybdenum oxide by weight based upon the alumina was in the range of about 8 to 10%.

The data presented above demonstrate the fact that a satisfactory reduction in copper number, which is indicative of mercaptan content, can be secured by mildly hydrofining the virgin fraction. The data further show that when the hydrofined virgin oil was mixed with a cracked oil which had been treated only by caustic washing, a product with a satisfactorily low carbon residue was obtained. While satisfactory results can be obtained with cobalt molybdate catalyst, operated at 600° F. and 8 to 16 v/v/hr., the preferred operating conditions include the use of the MoOs on Al catalyst at 600° F. with a feed rate of 4 to 16 v/v/hr. Satisfactory operation can also be obtained at 500° F. with either catalyst at lower feed rates.

As discussed, severe hydrofining for desulfurizing oil products is known in the art. The process generally
been used on high sulfur stocks. It has now been found, however, that mild hydrofining is useful for treating products which require no reduction in sulfur, other than mercaptan sulfur which is the type contributing to bad odor in heating oils. The present invention is concerned with an application of hydrofining to this type of operation.

The hydrofined virgin constituents, after removal from the hydrofining zone may be further refined or treated as desired.

For example, it may be desirable to remove small traces of dissolved H₂S which constituents may be removed either by steam stripping or by caustic washing. If caustic washing is utilized, a caustic solution having a strength from 2–10% sodium hydroxide may be employed.

In accordance with the present process, a virgin heating oil is sweetened by hydrofining under relatively mild conditions whereby mercaptan sulfur in the oil is converted to hydrogen sulfide, which is separated from the oil by conventional means. The virgin heating oil is then blended with cracked heating oil components which have been treated only by caustic washing to obtain a heating oil blend which is satisfactory with respect to requirements for carbon residue, as well as other inspections for heating oil. This is to be contrasted with other sweetening methods where considerably more severe conditions would of necessity have to be utilized on the cracked stock than if the virgin oil were not hydrofined as described in accordance with the present operation.

What is claimed is:

1. A process for improving the quality of virgin heating oil which comprises subjecting virgin heating oil constituents to a temperature in the range of 400° to 700° F., and pressure in the range of 50 to 250 pounds per square inch in the presence of extraneously generated hydrogen and a hydrofining catalyst comprising molybdenum oxide on a carrier at feed rates in the range of 1 to 16 v./v./hr. so that there is a consumption of hydrogen not in excess of about 60 standard cubic feet per barrel and so that the sulfur reduction does not exceed about 35%.

2. The process defined by claim 1 in which the said hydrogen consumption does not exceed about 40 standard cubic feet of hydrogen per barrel and the said sulfur reduction does not exceed about 20%.

3. A process for the preparation of a high quality heating oil blend comprising virgin fractions and cracked fractions, which comprises segregating virgin hydrocarbon constituents boiling in the heating oil boiling range and cracked hydrocarbon constituents boiling in the heating oil boiling range, subjecting said virgin constituents to a temperature in the range of 400° to 700° F., and pressure in the range of 50 to 250 pounds per square inch in the presence of extraneously generated hydrogen and a catalyst consisting of cobalt molybdate on a carrier at feed rates in the range of 1 to 16 v./v./hr. so that there is a consumption of hydrogen not in excess of about 60 standard cubic feet per barrel and so that the sulfur reduction does not exceed about 35%, and thereafter blending said treated virgin constituents with said cracked constituents to produce a high quality heating oil blend.

4. The process defined by claim 3 wherein said cracked hydrocarbon constituents are caustic treated prior to the said blending.

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