SOLVENT DEASPHALTING OF RESIDUAL OILS WITH WASH OIL TO REMOVE METAL CONTAMINANTS

Fig. 1.

Fig. 2.

Fig. 3.

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BY

Attorney.
FIG. 6.
The present invention is directed to a method of removing metal contaminants from petroleum fractions. More particularly, the present invention is concerned with the deasphalting of residual petroleum fractions and the removal of metals during said deasphalting operation. In its more specific aspects, the invention is concerned with the removal of metal contaminants from residual fractions charged to a catalytic cracking operation.

The present invention may be briefly described as a method for treating a petroleum fraction containing a major portion of components boiling above about 900° F. and which is contaminated by substantial amounts of metal contaminants in which the feed stock is introduced into a deasphalting zone and there contacted with liquefied, normally gaseous hydrocarbon and a fraction of catalytic cycle stock as hereinafter defined under conditions wherein a deasphalted oil substantially free from metal contaminants and an asphalt phase containing substantially all of the metal contaminants of the feed stock. The two phases are separately withdrawn, the liquefied, normally gaseous hydrocarbon removed therefrom as desired and the deasphalted oil phase is then used as a feed stock to a catalytic cracking operation.

In the practice of the deasphalting step of the present invention a liquefied, normally gaseous hydrocarbon such as those well known in the deasphalting art is employed. Specific examples of liquefied, normally gaseous hydrocarbons which may be used may be mentioned ethane, propane, propylene, butylene, butane, including iso and normal butane and mixtures thereof. The ethane under some conditions may contain ethylene and be used suitably in the present invention. Because of pressure limitations in operating equipment, it is preferred to use butane, propane, propylene, butylene, butanes or mixtures thereof with a desirable commercial mixture consisting of about 30% butanes and about 70% propane.

The amount of liquefied, normally gaseous hydrocarbon employed as a solvent in the deasphalting operation of the present invention is within the range of about 2 to about 10 volumes of the solvent per volume of residual petroleum fraction employed as a feed stock to the deasphalting zone. As a specific example, it has been found that about 3.2 volumes of liquefied, normally gaseous hydrocarbon solvent by volume of residual oil charged is a desirable commercial ratio.

The temperature at which the deasphalting step is conducted may be within the range of 100° to 300°. There may be a temperature gradient in the deasphalting step with the highest temperature at the deasphalted oil outlet. The temperature gradient may be within the range of 0° to 60°. As a specific example a 20° temperature may be used with the top of the tower at the point where the deasphalted oil is withdrawn being maintained at 160° F. and the bottom of the tower where the asphalt is introduced with the residual oil being 160° F.

The invention may also be carried out in a plurality of stages in one vessel or in a plurality of vessels comprising the separate stages. The separate stages may be conducted with a temperature gradient and pressure gradient between the stages. For example, a temperature and pressure of about 150° F. and 550 pounds per square inch gauge may be maintained in the top of one vessel whereas the temperature and pressure in a second vessel may be from about 160° to 180° F. and from about 400 to 500 pounds per square inch gauge.

The vessels comprising the several stages, as desired, may be arranged either in the vertical or horizontal position or intermediate thereof. For example, one or more vessels may be vertically arranged and one or more vessels may be horizontally arranged or arranged at an angle with the horizontal to allow the vessel also to be used as a settling zone for separation of asphaltic materials.

The present invention is particularly useful in preparing a feed stock for catalytic cracking operations and particularly catalytic cracking operations of the fluidized solids or powder type. The catalytic cracking operation may be either of the upflow or downflow type. In the upflow operation the vaporized hydrocarbon is contacted with the fluidized solids in a suspension and the suspension flowed upwardly through a reaction zone. Likewise, in the so-called upflow operation the catalyst is regenerated by suspending the catalyst in a combustion inducing gas, such as air, and flowing the suspension through a regeneration zone where a combustion operation takes place.

In the so-called downflow operation, the catalyst is suspended in vaporized hydrocarbons and flowed into a reaction zone in which a disperse phase and a dense phase is maintained with the catalyst being removed from the disperse phase and returned to the dense phase with the reaction products flowing out of the reactor and the catalyst flowing downwardly therefrom. In the so-called downflow cracking operation, the catalyst fouled with carbonaceous material and/or coke is regenerated by suspending it in a combustion supporting gas, such as air, and flowing same into a regeneration zone wherein a disperse phase and a dense phase are maintained, the combustion products being led off from the disperse phase after separation of a major amount of catalyst therefrom and the catalyst dropped back into the dense phase and then removed therefrom for reuse in the reaction zone.

The catalytic cracking of fractions of petroleum oil is well known to the art. A description of such a catalytic cracking operation may be found in U.S. Patent 2,587,554, issued February 26, 1954, in the name of John Weikart.

In such catalytic cracking operations it has been found that if the charging stock contains any metal contaminants in significant amounts, for example, as little as 1 pound of nickel or less per thousand barrels of charge stock, the catalytic cracking process is adversely affected. In general, other metal components such as vanadium and iron are undesirable in the same manner as is nickel but are less troublesome; on a weight basis it may be considered that vanadium is perhaps 5th as troublesome as nickel and iron is perhaps 1/4 as troublesome as nickel. Hereafter in the specification and claims where the expression "equivalent to 1.0 pound of nickel per thousand barrels of oil" appears, it is to be understood that this is intended to encompass the metal components nickel, vanadium and iron with nickel used at its full value, vanadium considered at 1/4th its actual weight value and iron considered at 1/5 its actual weight value.

In the practice of the present invention wherein residual petroleum fractions boiling above about 900° F. are employed which are contaminated with metals, a wash oil is employed in the deasphalting step which is a fraction of a catalytic cycle stock obtained from a catalytic crack-
is one of the fluidized solids type as mentioned supra.

This wash oil, as mentioned, is a fraction of a catalytic cycle stock which is cut from the cycle stock at a temperature above about 900° F. and preferably at a temperature in the range from about 900° F. to about 1050° F. This wash oil may have a so-called high in the range from about 100° to 125° F., a specific gravity in the range from about 1 to about 1.2 with the preferred range from 1.05 to about 1.08, a flash point in the range from about 550° to 650° F. and should remove about 85% of the nickel contaminants from the residual oil which is contaminated with the metals down to about 0.5 part per million of metallic contaminants.

The wash oil may be secured by fractionally distilling the products from a catalytic cracking operation of the type mentioned supra at a cut point of about 900° to about 1050° F. The wash oil may suitably be obtained also by precipitating a portion of the cycle stock from a catalytic cracking operation and employing the same either with or without the removal of the precipitating agent which may be a liquefied, normally gaseous hydrocarbon.

The wash oil may also be obtained from the distilled portion of the cycle stock from a catalytic cracking operation by taking a broad residual fraction from the distillation of the cracked products and subjecting it to a clarification operation to remove heavier fractions and residual catalyst contained in the products from a catalytic cracking operation of the fluidized powder type. The clarified oil may be employed as a wash oil after suitable treatment such as by solvent precipitation and/or distillation. Preferably, the wash oil is a fraction of catalytic cycle stock which is recovered by distillation.

The term "cycle stock" as employed in the present invention and in the sense used here refers to a fraction recovered as a distillate intermediate the heating oil fraction and the residual fraction resulting from distillation of the catalytically cracked products. The term "fraction of catalytic cycle stock" means a fraction which is intermediate the heating oil fraction and heavy residues remaining after the distillation of the lighter material from the cracked product from the catalytic cracking of hydrocarbons.

A desirable wash oil for use in the present invention may have the characteristics as shown in Table I.

<table>
<thead>
<tr>
<th>Table I</th>
<th>Fraction of catalytic cycle stock</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sp. Gravity, 60°/60° F.</td>
<td>1.1134</td>
</tr>
<tr>
<td>Viscosity:</td>
<td></td>
</tr>
<tr>
<td>SSU/210° F.</td>
<td>523</td>
</tr>
<tr>
<td>SSU/275° F.</td>
<td>103</td>
</tr>
<tr>
<td>O. C. Flash, ° F.</td>
<td>465</td>
</tr>
<tr>
<td>Conradson carbon, wt. percent</td>
<td>27.1</td>
</tr>
<tr>
<td>Bomb sulfur, wt. percent</td>
<td>1.98</td>
</tr>
<tr>
<td>C/H weight ratio</td>
<td>14.19</td>
</tr>
<tr>
<td>Aggregate ash:</td>
<td></td>
</tr>
<tr>
<td>Wt. percent</td>
<td>0.557</td>
</tr>
<tr>
<td>Ni by wet ash, p. p. m.</td>
<td>5570</td>
</tr>
<tr>
<td>V by wet ash, p. p. m.</td>
<td>2.8</td>
</tr>
<tr>
<td>Fe by wet ash, p. p. m.</td>
<td>—</td>
</tr>
</tbody>
</table>

The present invention will be further illustrated by reference to the drawing in which:

- Fig. 1 is in the form of a diagrammatic flow sheet illustrating a simplified preferred procedure for carrying out the desalting step of the present invention;
- Fig. 2 illustrates the employment of the present invention in a catalytic cracking operation and the preparation of the fraction of the catalytic cycle stock;
- Fig. 3 is a diagrammatic flow sheet of a modification of Fig. 2;
- Fig. 4 is a still further diagrammatic flow sheet of another mode of practicing the present invention;
- Fig. 5 is a diagrammatic flow sheet of a modified procedure for carrying out the desalting step of the present invention; and
- Fig. 6 is a diagrammatic flow sheet of another modified procedure for carrying out the process of the present invention.

Referring now to the drawing in which identical numerals will be employed to designate identical parts, Fig. 1, a desalting tower, such as 11, is provided into which a crude residue is introduced at approximately a central part thereof through line 12 and through a spider or distributing means 13. Propane or other liquefied, normally gaseous hydrocarbon is introduced into the tower 11 by way of line 14 for adjusting the temperature of the residual fraction introduced by line 12. A wash oil which is a fraction of catalytic cycle stock is introduced into the upper portion of tower 11 through line 15 and flows downwardly therein after being distributed through a spider or distributing means 16.

Desalinated oil in propane solution is removed from the upper portion of the tower 11 by way of line 17 and after stripping of dissolved propane may be introduced as a feed stock into a catalytic cracking operation. Asphalt is removed from the bottom of the tower by way of line 18 and this asphalt contains substantially all of the metal contaminants present in the crude residue introduced by line 12. The conditions in desalting tower 11 are those exemplified supra.

In Fig. 2 another mode of operation is performed in which crude oil which contains metal contaminants, such as nickel, vanadium, iron, and the like, is introduced into the system by way of line 20 and charged to a fractional distillation zone 21 which may be a plurality of fractional distillation towers, each equipped with internal vapor-liquid contacting means, such as bell cap trays. Zone or tower 21 is provided with a heating means as illustrated by a steam coil 22 for adjustment of the temperatures and pressures therein. In distillation zone 21 light fractions including gasoline may be removed by line 23, kerosene fractions by line 24, and heating fractions by line 25 and a gas oil fraction by line 26. Crude residue may be discharged from zone 21 by line 27 for further processing as will be described.

The gas oil fraction is then charged by line 26 into a catalytic cracking zone 28 of the type illustrated supra wherein catalytic cracking takes place at temperatures, for example, from about 800° to about 1150° F. The cracked products issue from zone 28 which is shown as a block in the flow diagram by line 29 and is introduced thereby into a distillation tower or zone 30 which, like zone 21, is provided with internal vapor-liquid contacting means and with a heating means illustrated by steam coil 31.

In zone 30 conditions of temperature and pressure are adjusted to take overhead a light fraction through line 32, gasoline components through line 33 and heating oil through line 34. A residual fraction including finely divided catalyst which may have carried over from zone 28 by line 29 is discharged by line 33a. A fraction of catalytic cycle stock cut at a temperature of about 900° to 1050° F. is withdrawn from zone 30 by line 33b and charged into zone 11 through spider or distributing means 16.

The crude residue withdrawn from zone 21 by line 27 controlled by valve 34a is introduced into line 12 and thence through spider 13 into zone or desalting tower 11 where it is contacted with liquefied, normally gaseous hydrocarbons, such as propane and the like, introduced by line 14. Like in Fig. 1 asphalt containing the metal contaminants is discharged by line 18 while the desalinated oil is removed by line 17. In this particular instance, the desalinated oil in solution in the light hydrocarbon is introduced into a stripping zone 35 provided with a heating means 36 for removal of light hydrocarbons by way of line 37 for reuse in the process. The
2,853,426

5 deasphalted oil substantially free of liquefied, normally
gaseous hydrocarbons is removed from stripper 35 by
line 38 and introduced thereby into line 26 for charging
in the catalytic cracking unit 28 in admixture with the
hydrocarbons in line 26 or alone as may be desired.

It may be desirable not to charge the crude residue
from zone 21 into zone 11 and under these
circumstances the crude residue in line 27 may be withdrawn
from the system through line 39 controlled by valve
or only operated at the boilup temperature of
line 27 may be charged to line 12. Likewise, other crude residue may be introduced
to zone 11 by opening valve 41 in line 12 connect-
ing to a source of other crude residue which are
contaminated with metals.

A still further mode of the present invention may be illustrated with respect to Fig. 3. In this particular mode, the feed stock to catalytic zone 28 is introduced by line 26 and submitted to cracking operations therein to form a product which is withdrawn by line 29 into distillation zone 30. In this particular instance, a broader fraction may be obtained through line 33a than with respect to Fig. 2 by omitting the sidestream withdrawal by line 34 by closing off line 34 by valve 34b. Under these conditions, the fraction in line 33a may suitably be admixed with a liquefied, normally gaseous hydrocarbon, such as one of the type mentioned before, introduced by line 50 and the admixture flowed into a precipitation zone 51 which is preferentially to deasphalting zone 11 to obtain a fraction of the catalytic cycle stock, the oil solution of liquefied, normally gaseous hydrocarbon removed from the catalytic cycle stock being discharged from zone 51 by line 52 while the precipitated material is discharged from zone 54 by line 53 into line 54 which is controlled by valves 55 and 56. By closing valve 55
the material from zone 51 flows into a stripping zone
57 provided with a heating means 58 for removal of liquefied,
normally gaseous hydrocarbon by line 50 for re-
introduction into line 33a, the oily material free of nor-
mally gaseous hydrocarbon then being introduced by line 59 controlled by valve 60 into deasphalting tower 11 through spider 16.

In another mode of the present invention, the material from line 53 and line 54 without removal of normally gaseous hydrocarbon would be flowed directly into line 59 by opening valve 55. Under these circumstances, the material introduced into line 59 by way of line 54 will supply at least part of the liquefied, normally gaseous hydrocarbon which are may be supplied by liquefied, normally gaseous hydrocarbon introduced by line 14 for treatment of crude residue introduced by line 12 through spider 13, the precipitated asphalt being withdrawn by line 18 and the deasphalted oil free of metallic contaminants then being also withdrawn by tower 11 by line 17 and introduced
into stripper 35 for removal of liquefied, normally gaseous hydrocarbon by way of line 37 and to recover deasphalted oil by line 38 for introduction into line 26. It is to be noted that line 26 is provided with a valve 26a so as to regulate the amount of extraneous feed introduced by line 26.

A still further mode of the present invention is illustrated in Fig. 4 wherein two catalytic cracking zones are employed. In this mode, a catalytic cracking zone 70 which may be of the upflow type and a catalytic cracking zone 71 which may be of the downflow type are employed.

Feed stock, such as gas oil, is introduced into zone 70 by way of line 72 and submitted to cracking in a fluidized powder operation to form a cracked product which is discharged from zone 70 by line 73 and introduced thereby into a distillation zone 74 which, like zones 30 and 21, is provided with suitable internal vapor-liquid contacting means to allow a sharp separation among the products. Heat and pressure in zone 74 by a heating means, such as steam coil 75. Light fractions are removed from zone

74 by line 76, intermediate boiling fractions by lines 77 and 78 and a rather broad cycle stock fraction which contains catalyst carried over with the cycle stock withdrawn by line 74 by line 73 is withdrawn by line 79 into a clarifier, such as a Dorr thick-
ener 80, wherein a separation is made between the catalyst and heavier fractions and the clarified oil, the heavier fractions being discharged from thickeners 80 by line 81 while the clarified oil is withdrawn by line 82 controlled by valve 84 for further treatment as will be described. A feed stock, such as a gas oil, is introduced into catalytic cracking zone 71 by way of line 85 and cracked as a suspension to form a product which is withdrawn from zone 71 by line 86, the clarified oil in line 82 being admixed with the cracked products either in line 86 or in distillation zone 87 into which the clarified oil and the cracked products are introduced. Zone 77 is provided with suitable internal vapor-liquid contacting means to make a separation of the lighter products from the cata-
lytic cycle stock and to recover the desirable fractions of the cracking operation. Light fraction products are removed from zone 87 by line 88 and intermediate boiling fractions are removed by lines 89 and 90. A fraction of the clari-

cified oil and cycle stock from zones 70 and 71 is discharged from zone 87 by line 91 controlled by valve 92 and intro-
duced through spider or other distributing means 16 into de-
asphalting tower or zone 11 wherein it contacts the con-


taminated crude residue introduced by line 12 and spider

13 and propane introduced by line 14 to precipitate as-
phalt containing the metal contaminants which is removed by line 18.

The deasphalted oil in propane solution is withdrawn by line 17 into stripper 35 and the propane removed by line 37, the deasphalted oil free of propane being withdrawn by line 38 and introduced into line 85 for cracking in zone 71.

It is to be understood that the deasphalted oil in line 38 may be charged to zone 70 or zone 71 or to both of them as may be desired.

It is to be noted that the clarified oil in line 82 may be routed at least in part as may be desired into a precipita-
tion zone such as 81 by opening valve 94 in branch line
95 for recovery of wash oil by line 52 for use in zone 11.

While the present invention, has been described with respect to Fig. 4 with the clarified oil from thicker 80 being directed into zone 87, it is understood that the clarified oil from zone 80 and the cycle stock from either or both of zones 74 and 87 may be combined and dis-

tilled or subjected to treatment for recovery of a fraction of the cycle stock in a separation distillation zone. Subsequently, the cycle stocks and clarified oil in admixture may be subjected to a solvent precipitation treatment as desired either with or without subsequent distillation.

In Fig. 5, a modified procedure for the deasphalting operation is described. Specifically, Fig. 5 refers to the employment of a plurality of stages with a temperature and pressure gradient between the stages. In Fig. 5, the tower 11 may comprise a plurality of stages and the incorpora-
tor 100 and settler 101 comprise an additional stage.

Wash oil of the type described supra and derived from catalytic cycle stock is introduced into the system by line 102 which connects into line 103 by way of which the wash oil is introduced into the top of deasphalting tower or zone 11 by way of spider or distribution means 16.

The deasphalted oil in propane-butane solution leaves the tower 11 by line 17 for removal of propane-butane and for subsequent use as a catalytic cracking stock. As described previously, the crude residue is introduced into tower 11 by line 12 and through spider 13 while propane-
butane solvent is introduced by line 14, the asphalt con-
taining metal contaminants being discharged by line 18.

To increase the removal of metals a portion of the de-
asphalted oil may be routed into settler 101 by closing valve 104 in line 17 which causes the deasphalted oil in propane solution to flow by line 105 through an orifice-
type or other mixing device 100 and thence through heat;
exchanger or heating means 106 into settler 101 whereby a separation is made between a further asphalt phase and a deasphalted oil in propane-butane solution which is discharged back into line 17 through line 107. The settler 101 allows separation of the asphalt phase which is withdrawn by line 103 and returned to the zone 11 with the wash oil.

It is desirable that a portion of the asphaltic phase including wash oil introduced by line 102 be admixed with the deasphalted oil in propane-butane solution in line 105. To this end line 108 controlled by valve 109 is provided which allows the material in line 103 to be discharged into line 105 for admixing with the deasphalted oil solution.

It may be desirable to close off valve 109 and introduce wash oil directly into line 108 and into line 105 and this may be accomplished by closing valve 110 or throttling same and bypassing at least a portion of the wash oil from line 102 by line 111 into line 108 as may be desired.

In operations according to Fig. 5, a temperature of 150°F, and 550 pounds per square inch gauge may be maintained in the top of tower 11, whereas the mixture introduced in settler 101 may be at a pressure of 450 pounds per square inch gauge and at a temperature of 170°F. This is accomplished by passing the mixture through the heat exchanger 106 and by suitable adjustment of controls. By providing a pressure differential of 50 to 70 pounds per square inch gauge across the incorporator 100 or other mixing device, complete mixing is obtained. By providing a small temperature rise after mixing, the asphalt will precipitate more readily on the wash oil droplets increasing their size and permitting adequate settling in settler 101. The mixture of precipitated asphalt from settler 101 may be pumped as shown to the tower 11 which improves distribution due to the larger volume of the material recycled. By maintaining a 15° to 20°F temperature gradient across the top of the tower 11, the deasphalted oil yield is adjusted to a desired level ahead of the stage comprising mixer 100 and settler 101 which reduces the amount of nickel or other metal contaminants to be removed from the deasphalted oil. This operation also serves to decrease the amount of wash oil which might be carried over into the deasphalted oil solution.

In Fig. 6 a further modification of the present invention is shown. In accordance with this modification there is provided a suitable distillation zone 120, such as a so-called "vacuum still zone" which is operated at pressures of about 25 mm. to 250 mm. of mercury. A metals-contaminated petroleum feed stock fraction containing a major portion of components boiling about 900°F. is introduced into the distillation zone 120 by line 121, the feed stock being heated at a suitable temperature such that the lighter portions thereof are "flushed" off under the pressure conditions given and ascend the zone 120 in vapor form for withdrawal through an upper discharge line 122. The heavier portions of the feed stock descend to the bottom of the zone 120 for withdrawal through a lower discharge line 123. It will be understood that, if desired, the zone 120 may be provided with one or more side discharge lines (not shown). A suitable wash oil of the type described above is charged to the distillation zone 120 by line 124. The wash oil contacts the feed stock in zone 120 and affects a substantial removal of metal contaminants from the vaporized lighter components of the feed stock.

The vaporized lighter components of the feed stock withdrawn by line 122 are then passed through a suitable cooler 125 for liquefaction and thence to a tower deasphalted zone 126 through a suitable distributing means 127. Propene or other liquefied, normally gaseous hydrocarbon is introduced to the tower 126 by way of a line 128 to flow countercurrently to the feed stock fraction. Deasphalted oil in solution is removed from the upper portion of the tower 126 by way of a line 129 and after being stripped of normally gaseous hydrocarbon may be introduced as a feed stock into a catalytic cracking operation. Asphaltic components are withdrawn through the bottom of the tower 126 through a line 130.

If desired, and sometimes preferably, a still further reduction of metal contaminants may be obtained by charging a suitable wash oil of the type described above to the deasphalted tower through a distributing means 131 fed by a line 132 controlled by a valve 133. The conditions in the deasphaltating tower 126 are those exemplified supra.

It is to be emphasized that in conducting operations in accordance with the procedure exemplified by Fig. 6 the wash oil should not be brought into contact with the crude residue to be decontaminated in the distillation zone 120 while such residue is in liquid form for in this situation the wash oil may become dissolved in the crude residue and metal contaminants-removal may not be effected.

In general, it may be stated that the wash oil should be brought into contact with the metals-contaminated crude residue while such crude residue is in a non-solubilizing condition with respect to the wash oil (i.e. catalytic cycle stock). This may be accomplished, for example, by introducing the wash oil 105 as shown in the presence of a liquid, normally gaseous hydrocarbon (Figs. 1-5) or by adding the wash oil to vaporized crude residue or to a vaporized lighter portion thereof (Fig. 6).

From the foregoing description of the several modes of practice of the invention, it is clear that the invention may be practiced in several ways and the fraction of the catalytic cycle stock may be obtained by any one of several ways from the cracked products. The fraction may be obtained by distillation, solvent precipitation, precipitation by mechanical means with subsequent distillation and/or solvent precipitation or by other reducing operations which will remove fractions boiling below 900°F.

In order to illustrate the invention further, runs were made comparing the deasphalting of crude residue from West Texas crude without employing a wash oil and while employing a fraction of catalytic cycle as a wash oil. The operations are presented in Table II:

<table>
<thead>
<tr>
<th>Wash Oil Used</th>
<th>Fraction of Catalytic Cycle Stock</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>Actual DAO Yield Vol. Per. 47.5</td>
<td>None</td>
</tr>
<tr>
<td>DAO Inspection</td>
<td>60.4</td>
</tr>
<tr>
<td>Sp. Gr. 0.895 F.</td>
<td>0.989</td>
</tr>
<tr>
<td>Con. Carbon, Wat. Per. 3.77</td>
<td>3.09</td>
</tr>
<tr>
<td>Avg.Ash, p. p. m. 5.5</td>
<td>5.9</td>
</tr>
<tr>
<td>NI Cont., p. p. m. 1.74</td>
<td>0.39</td>
</tr>
<tr>
<td>V Cont., p. p. m. 2.12</td>
<td>0.28</td>
</tr>
<tr>
<td>Fe Cont., p. p. m. 1.71</td>
<td>1.01</td>
</tr>
<tr>
<td>Percent NI Reduction 88.1</td>
<td></td>
</tr>
</tbody>
</table>

It will be seen that 88% and 75% nickel reductions were obtained, respectively, at deasphalted yields of approximately 50% and 67% with substantially all of the nickel, which is the contaminant having the major effect, being removed.

The crude residue employed as a feed stock of the present invention is the residue obtained as exemplified by distilling crude oil to remove the valuable components thereof. The crude oil and its residues by virtue of being in contact with earth formations, processing equipment, tanks, pipe lines, and the like, will contain various metals, such as nickel, vanadium, iron and numerous others too numerous to mention here, which deleteriously affect the catalytic activity of the catalyst.
in catalytic cracking operations. Since the metal contaminants eventually end up in the crude residue, it is desirable, as illustrated in the practice of the present invention, to remove metal contaminants from the desirable fractions of the crude residue before using same in catalytic cracking operations. Other metal-containing compounds such as the naturally occurring porphyrins of nickel, vanadium, iron, and the like are present as contaminants in crude petroleum and its residues and may be removed in accordance with this invention. The present invention, therefore, has great utility in allowing valuable components of crude residue to be catalytically cracked which heretofore could not be cracked sufficiently to obtain maximum yields of desired products without formation of undesirable products, such as gas and coke.

As illustrative of crude residues suitable for treatment in the practice of the present invention and for recovery of fractions suitable for catalytic cracking, the following inspections are presented in Table III.

<table>
<thead>
<tr>
<th>Table III.—Feed inspections</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.9% West Texas residuum</td>
</tr>
<tr>
<td>Sp. gravity, 60°/60° F.</td>
</tr>
<tr>
<td>Viscosity:</td>
</tr>
<tr>
<td>SSF/210° F.</td>
</tr>
<tr>
<td>SSF/275° F.</td>
</tr>
<tr>
<td>O. C. Flash, F.</td>
</tr>
<tr>
<td>Creosote, wt. percent</td>
</tr>
<tr>
<td>Bomb sulfur, wt. percent</td>
</tr>
<tr>
<td>C/H weight ratio</td>
</tr>
<tr>
<td>Aggregate ash:</td>
</tr>
<tr>
<td>Wt. percent</td>
</tr>
<tr>
<td>P. by wet ash, p. m.</td>
</tr>
<tr>
<td>V by wet ash, p. m.</td>
</tr>
<tr>
<td>Fe by wet ash, p. m.</td>
</tr>
</tbody>
</table>

From the inspections of a typical crude residue, it will be seen that this particular residuum is contaminated with relatively large quantities of nickel, vanadium, and iron which deleteriously affect the catalytic cracking operation.

The present invention has wide utility and is being used commercially in removing anywhere from about 30% to 75% or more of the nickel from approximately 25,000 barrels of crude residue being charged to a deasphaltizing tower in which about 1,600 barrels per day of a fraction of the catalytic cycle stock obtained by distilling a mixture of clarified oil and a fraction of the catalytically cracked products at a cut point of 900° to 1050° F. The procedure removes the metal contaminants down to about 0.5 part per million. The efficiency of removal of nickel and other metals and compounds thereof may be increased still further by increasing the number of stages in the deasphaltizing tower.

The nature objects of the present invention having been completely described and illustrated, what I wish to claim as new and useful and to secure by Letters Patent is:

1. A method for treating a petroleum fraction feed stock containing a major portion of components boiling above 900° F. and contaminated by a substantial amount of metal contaminants which comprises countercurrently contacting said feed stock in a deasphaltizing zone with a liquefied normally gaseous hydrocarbon in simultaneous countercurrent contact with a separately introduced fraction of catalytic cycle stock under conditions to form a deasphalted oil phase substantially free from metal contaminants and an asphalt phase containing substantially all of the metal contaminants of the feed stock and separately withdrawing said phases, said fraction of catalytic cycle stock having a specific gravity within the range of about 1.05 to 1.2.

2. A method in accordance with claim 1 in which the fraction of the catalytic cycle stock is obtained by distillation.

3. A method in accordance with claim 1 in which the fraction of the catalytic cycle stock is obtained by deasphalting.

4. A method in accordance with claim 1 in which the petroleum fraction contains as little as the equivalent of 1 pound of nickel metal contaminant per thousand barrels.

5. A method for treating a crude petroleum residue containing a major portion of components boiling above 900° F. and contaminated with metal contaminants which comprises deasphalting said residue in countercurrent contact with a liquefied normally gaseous hydrocarbon in a deasphaltizing zone while simultaneously countercurrently contacting said residue with a separately introduced fraction of catalytic cycle stock under conditions to form a deasphalted oil phase and an asphalt phase, and recovering said deasphalted oil phase, said catalytic cycle stock being obtained by catalytic cracking of a gas oil fraction of crude petroleum and said deasphalted oil phase, said fraction of catalytic cycle stock having a specific gravity within the range of about 1.05 to about 1.2.

6. A method in accordance with claim 6 in which the fraction of the catalytic cycle stock is obtained by distillation.

7. A method in accordance with claim 6 in which the petroleum fraction contains as little as the equivalent of 1 pound of nickel metal contaminant per thousand barrels.

8. A method in accordance with claim 6 in which the fraction of the catalytic cycle stock is obtained by deasphalting.

9. A method in accordance with claim 6 in which the fraction of the catalytic cycle stock is obtained by a clarification and distillation operation.

10. A method in accordance with claim 6 in which the petroleum fraction contains as little as the equivalent of 1 pound of nickel metal contaminant per thousand barrels.

11. A method in accordance with claim 6 in which the crude petroleum residue is obtained from the crude petroleum from which the gas oil fraction is obtained.

12. A method for treating a petroleum fraction feed stock containing a major portion of components boiling above 900° F. and contaminated by a substantial amount of metal contaminants which comprises introducing said feed stock into a deasphaltizing zone comprising a plurality of stages and there countercurrently contacting said feed stock with a liquefied normally gaseous hydrocarbon in simultaneous countercurrent contact with a separately introduced fraction of catalytic cycle stock under conditions to form a deasphalted oil phase substantially free from metal contaminants and an asphalt phase containing substantially all of the metal contaminants of the feed stock and separately withdrawing said phases, said conditions encompassing a temperature gradient between said stages with the highest temperature at the stage adjacent the point of withdrawal of said deasphalted oil phase, said fraction of catalytic cycle stock having a specific gravity within the range from about 1.05 to about 1.2.

13. A method for treating a petroleum fraction feed stock containing a major portion of components boiling above 900° F. and contaminated by a substantial amount of metal contaminants which comprises vaporizing at least a portion of said feed stock, countercurrently contacting said vapors with a fraction of catalytic cycle stock to substantially extract metal contaminants from said vapors, collecting and liquefying the thus contacted vapors, deasphalting the thus collected liquid by countercurrently contacting the same with a liquefied normally gaseous hydrocarbon under conditions to form a deasphalted oil phase and an asphalt phase and recovering the deasphalted oil phase, said fraction of catalytic cycle stock having a specific gravity within the range of about 1.05 to about 1.2.

14. A method for treating a petroleum fraction feed stock containing a major portion of components boiling...
above 900° F. and contaminated by a substantial amount of metal contaminants which comprises vaporizing at least a portion of said feed stock, countercurrently contacting said feedstock with a fraction of catalytic cycle stock to substantially extract metal contaminants from said vapors, collecting and liquefying the thus contacted vapors, deasphalting the thus collected liquid by contacting the same with about 2 to 10 volumes per volume of collected liquid of a liquefied normally gaseous hydrocarbon and a further quantity of said catalytic cycle stock under conditions to form a deasphalting oil phase and an asphalt phase, and recovering the deasphalting oil phase, said fraction of catalytic cycle stock having a specific gravity within the range of about 1.05 to about 1.2.

15. A method for treating a petroleum fraction feed stock containing a major portion of components boiling above 900° F. and contaminated by a substantial amount of metal contaminants which comprises introducing said feed stock into a deasphalting zone and there countercurrently contacting said feed stock with about 2 to 10 volumes per volume of feed stock of a liquefied normally gaseous hydrocarbon and also simultaneously countercurrently contacting said feed stock in said deasphalting zone with a separately introduced fraction of catalytic cycle stock under conditions to form a deasphalting oil phase substantially free from metal contaminants and an asphalt phase containing substantially all of the metal contaminants of the feed stock and separately withdrawing said phases, said fraction of catalytic cycle stock having a specific gravity within the range of about 1.05 to about 1.2.

16. A method for treating a petroleum fraction feed stock containing a major portion of components boiling above 900° F. and contaminated by a substantial amount of metal contaminants which comprises introducing said feed stock into a deasphalting zone and there countercurrently contacting said feed stock with about 2 to 10 volumes per volume of feed stock of a liquefied normally gaseous hydrocarbon and also simultaneously countercurrently contacting said feed stock in said deasphalting zone with a separately introduced fraction of catalytic cycle stock under conditions to form a deasphalting oil phase substantially free from metal contaminants and a solvent phase contacting said fraction of catalytic cycle stock having a specific gravity within the range of about 1.05 to about 1.2.

17. A method for treating a petroleum fraction feed stock containing a major portion of components boiling above 900° F. and contaminated by a substantial amount of metal contaminants which comprises introducing said feed stock into a deasphalting zone comprising a plurality of stages and there countercurrently contacting said feed stock with about 2 to 10 volumes per volume of feed stock of a liquefied normally gaseous hydrocarbon and also simultaneously countercurrently contacting said feed stock in said deasphalting zone with a separately introduced fraction of catalytic cycle stock under conditions to form a deasphalting oil phase substantially free from metal contaminants and an asphalt phase containing substantially all of the metal contaminants of the feed stock and separately withdrawing feed phases, said catalytic cycle stock being obtained by catalytic cracking of a mixture of a gas oil fraction of crude petroleum and said asphalt phase, said fraction of catalytic cycle stock having a specific gravity within the range of about 1.05 to about 1.2.

18. A method for treating a petroleum fraction feed stock containing a major portion of components boiling above 900° F. and contaminated by a substantial amount of metal contaminants which comprises vaporizing at least a portion of said feed stock, countercurrently contacting said feed stock with a fraction of catalytic cycle stock to substantially extract metal contaminants from said vapors, collecting and liquefying the thus contacted vapors, deasphalting the thus collected liquid by contacting the same with about 2 to 10 volumes per volume of collected liquid of a liquefied normally gaseous hydrocarbon and a further quantity of said catalytic cycle stock and an asphalt phase and recovering the deasphalting oil phase, said fraction of catalytic cycle stock having a specific gravity within the range of about 1.05 to about 1.2.

19. A method for treating a petroleum fraction feed stock containing a major portion of components boiling above 900° F. and contaminated by a substantial amount of metal contaminants which comprises vaporizing at least a portion of said feed stock, countercurrently contacting said feed stock with a fraction of catalytic cycle stock to substantially extract metal contaminants from said vapors, collecting and liquefying the thus contacted vapors, deasphalting the thus collected liquid by contacting the same with about 2 to 10 volumes per volume of collected liquid of a liquefied normally gaseous hydrocarbon and a further quantity of said catalytic cycle stock and an asphalt phase and recovering the deasphalting oil phase, said fraction of catalytic cycle stock having a specific gravity within the range of about 1.05 to about 1.2.

20. A continuous method for treating a metals contaminated petroleum fraction feed stock containing a major portion of components boiling above 900° F. in a deasphalting tower which comprises the steps of continuously introducing a liquefied normally gaseous hydrocarbon into said tower adjacent the lower end thereof, continuously introducing said feed stock into said tower above the point of introduction of said liquefied hydrocarbon, continuously introducing into said tower above the point of introduction of said feed stock a primary asphalting material, said primary asphalting material being obtained by continuously withdrawing a first solution of deasphalted oil in said liquefied hydrocarbon from the top of said deasphalting tower, continuously adding a wash oil to at least a portion of said first solution and intimately mixing said wash oil with said portion of said first solution in a mixing zone; and into said second solution, continuously resolving said second solution into an asphalt phase and a solution of deasphalted oil in said liquefied hydrocarbon in a settling zone and continuously recycling said asphalt phase from said settling zone to said deasphalting tower as said primary wash material, withdrawing an asphalt phase from the bottom of said deasphalting tower and recovering a solution of deasphalted oil in said liquefied hydrocarbon from said settling zone, said wash oil consisting of a fraction of catalytic cycle stock having a specific gravity within the range of about 1.05 to about 1.08.

21. A method as in claim 20 wherein said deasphalting tower is operated to provide for a pressure of about 450 p. s. i. g. and a temperature of about 170° F. at the top thereof, and wherein a pressure differential within the range of about 50 to 70 p. s. i. g. is maintained across said mixing zone, with the lower pressure being at the outlet end of said mixing zone.

22. A method for treating a petroleum fraction feed stock containing a major portion of components boiling above 900° F. and contaminated by a substantial amount of metal contaminants which comprises contacting said feed stock in a deasphalting zone with a liquefied normally gaseous hydrocarbon and forming an asphalt phase and a solution of deasphalted oil in said solvent, contacting said solution of deasphalted oil with a fraction of catalytic cycle stock and recovering
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a deasphalted oil substantially free from metal contaminants from said solution, said fraction of catalytic cycle stock having a specific gravity within the range of about 1.05 to 1.2.

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