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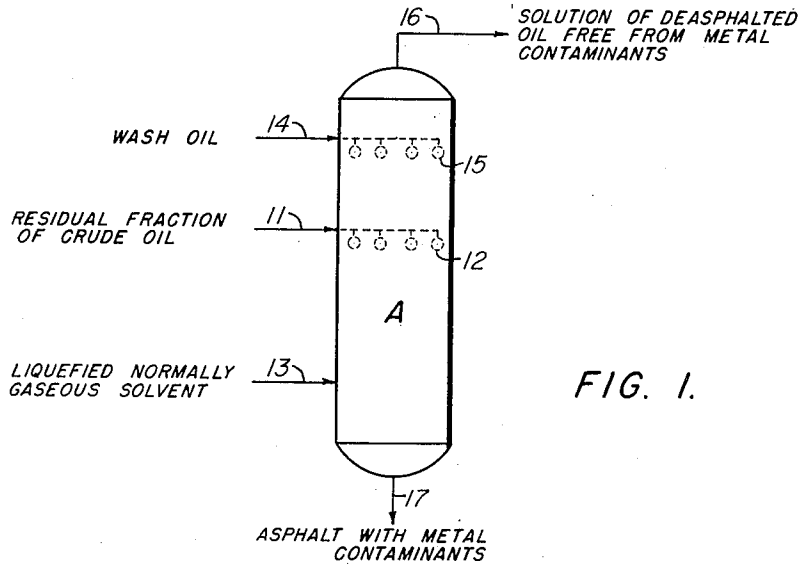


FIG. 1.

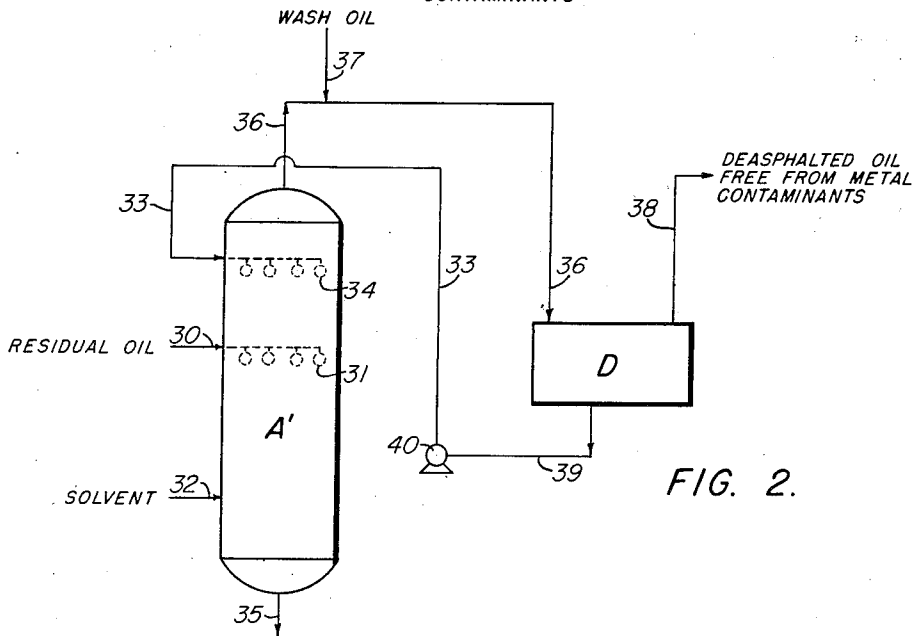


FIG. 2.

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

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7 Claims. (Cl. 196—14.46)

The present invention is directed to a method of removing metal contaminants from residual petroleum fractions.

Substantially all of the crude petroleum oils commercially processed contain substantial amounts of metallic contaminants of the type of nickel, vanadium and iron. The residual oils resulting from the distillation of such crude oils contain such an amount of metal contaminants as to be undesirable feed stock for catalytic cracking operations.

The present invention may be briefly described as involving the use of a residual oil or fraction thereof derived from Hawkins crude oil as a wash oil in deasphalting a residual feed stock to serve as a selective solvent removing metallic contaminants from said feed stock.

More specifically, the present invention is directed to a procedure whereby a residual petroleum fraction, that is a fraction containing a major portion of components boiling above 900° F. and contaminated with a substantial amount of metal contaminants which have as their origin metallic contaminants present in the crude oil as produced from the earth, is treated to secure a fraction substantially free from metallic contaminants. The treating step is carried out by continuously introducing a stream of feed stock into a deasphalting zone, continuously introducing a stream of residual oil derived from crude oil produced from the Hawkins field as a wash oil into the tower at a point above the point of introduction of the feed stock, continuously introducing a stream of liquefied normally gaseous hydrocarbon into the tower at a point below the point of introduction of the feed stock, continuously withdrawing a solution of deasphalted oil free from metallic contaminants from the top of the tower and continuously withdrawing an asphalt phase containing substantially all of the metallic contaminants introduced into the tower from the bottom of the tower. The resultant deasphalted oil substantially free from metallic contaminants is a desirable feed stock for a catalytic cracking process whereas the residual oil containing the metallic contaminants which is charged to the deasphalting zone is undesirable for use as a feed stock for a catalytic cracking process.

The residual oil derived from a crude petroleum from the Hawkins field in Texas may be described generally as an oil derived from Hawkins field crude free from components boiling below about 650° F. Characteristics of Hawkins residual oils suitable for use as the wash oil in a process of the present invention, are set out hereafter in Table I:

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TABLE I

Typical wash oil inspections

	1	2
Percent on Crude.....	29.0	4.9
Gravity, °API.....	4.7	645
Viscosity, SSF @ 275° F.....	19.8	24.7
Conradson Carbon, Wt. percent.....	10.2	9.5
Contaminants, #/1,000 bbls.....	15.0	18.5
Ni.....	7.0	7.4
V.....		
Fe.....		

The present invention will be described in greater detail in conjunction with the drawing in which

Fig. 1 is in the form of a diagrammatic flow sheet illustrating one procedure for carrying out the deasphalting step for removing metallic contaminants from the residual oil; and,

Fig. 2 is in the form of a diagrammatic flow sheet illustrating another procedure for treating a residual fraction derived from crude oil to remove metal contaminants therefrom.

Turning now specifically to the drawing and first to Fig. 1, a deasphalting step is carried out in vessel A. A residual fraction derived from a crude oil is charged through inlet line 11 and passes from a distributor 12 into a central part of the tower with liquefied normally gaseous solvent introduced into the bottom of the tower through inlet line 13 to flow upwardly in the tower countercurrent to the residual fraction. A Hawkins residual oil is introduced as the wash oil through line 14 and discharged through distributor 15 in an upper portion of the tower so that it passes downwardly countercurrently to the up-flowing solvent. A solution of deasphalted oil substantially free from metallic contaminants is withdrawn from the top of the tower through outlet line 16 and an asphalt fraction containing substantially all of the metal contaminants introduced into the tower A with the charge stock as well as those metal components introduced into tower A with the wash oil is withdrawn through outlet line 17.

Another procedure for removing the metal contaminants from a residual oil is shown in Fig. 2. In this figure, tower A' is similar to tower A of Fig. 1. In Fig. 2 a residual oil derived from a crude and contaminated with a substantial amount of metal contaminants is introduced through inlet line 30, and discharged through distributor 31 into the central part of the tower. Liquefied normally gaseous hydrocarbon is introduced as solvent through line 32 into the lower portion of the vessel A' so that it passes upwardly countercurrent to the residual oil charged. A Hawkins residual oil is introduced as the wash oil into tower A' by line 33 and distributor 34 which is above distributor 31 so that the wash oil contacts the solution of residual oil as it flows upwardly in the tower. An asphalt fraction consisting of a large part of the introduced wash oil and of asphalt separated from the residual oil charge stock and containing substantially all of the metal contaminants introduced into tower A' both with the residual oil and with the wash oil is withdrawn from the bottom of the tower through outlet line 35. A solution of components of residual oil dissolved in solvent is withdrawn through the top of the tower by line 36 and is admixed there with fresh wash oil introduced through inlet line 37, the components be-

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ing discharged into settling drum D. In settling drum D a phase separation takes place with a lighter phase consisting of a solution of deasphalted oil substantially free from metallic contaminants being withdrawn through outlet line 38, this material after freed from solvent being a desirable charge stock for a catalytic cracking process. The heavier phase is withdrawn from the bottom of drum D through line 39 and pumped by pump 40 into line 33 where it is introduced as the wash oil in tower A' as previously described.

The procedure of Fig. 2 differs from the procedure of Fig. 1 in having an additional stage. By way of example, if a 10% wash used in Fig. 1 causes a removal of 75% of metal components, the additional stage used in Fig. 2 should increase the metal removal from 75% to approximately 92%.

The inspection of residua from the distillation of typical crude oils charged to refinery operations are set out hereafter in Table II. In Table II, columns 1, 2, 3 and 4 show the characteristics respectively of residua derived from a mixture of Gulf Coast and West Texas crudes, a West Texas crude, a Panhandle crude and a Lagunillas crude.

TABLE II
Typical feed stock inspections

	1	2	3	4
Percent on crude	9.8	12.8	15.6	44.0
Gravity, °API	8.7	8.7	20.1	6.5
Viscosity, SSU 210° F	7,250		679	
Conradson Carbon, Wt. percent	18.7	17.3	8.4	24.0
Bomb Sulfur, Wt. percent	3.05	3.67		3.1
Contaminants, #/1,000 Bbls.:				
Ni	13.0	9.0	5.0	24.3
V	14.5	16.0	8.0	199.0
Fe	6.2	8.6	9.4	23.1

The catalytic cracking of fractions of petroleum oils is well known to the art. A description of such a catalytic cracking process may be found in U. S. Patent 2,587,554, issued February 26, 1952, in the name of John Weikart.

In such catalytic cracking operations it has been found that if the charging stock contains as much as three pounds of nickel per thousand barrels of charge stock, the catalytic cracking process is adversely affected. Other metal components such as vanadium and iron are undesirable but are less troublesome than nickel; in general on a weight basis it may be considered that vanadium is perhaps 1/5 as troublesome as nickel and iron is perhaps 1/2 as troublesome as vanadium. Hereafter in the specification and claims where the expression "equivalent to three pounds 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 weight value, vanadium consider at approximately 1/5 its actual weight value and iron considered at approximately 1/10 its actual weight value.

In carrying out the deasphalting step in the present invention where a Hawkins residual oil is used as a wash oil to remove selectively the metal contaminants from the residuum charge, the solvent used in a liquefied normally gaseous hydrocarbon. The use of liquefied normally gaseous hydrocarbon is well known in the deasphalting art. As specific examples of materials which could be used may be mentioned ethane, propane, propylene, butylene, butane and mixtures thereof. Because of pressure limitations in the operating equipment, it is preferred to use butane, propane, propylene and butylenes or mixtures thereof with a desirable commercial mixture consisting of 30% butane and 70% propane.

The preferred amount of solvent employed in the deasphalting step is within the range of 2 to 10 volumes of solvent per volume of residual oil charged to the deasphalting step. As a specific example it has been found that 3.2 volumes of solvent per volume of residual oil charged is a desirable commercial ratio.

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The temperature at which the deasphalting step is conducted may be within the range of 100° to 300° F. 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 100° F. As a specific example a 20° gradient may be used with the top of the tower, at the point where the deasphalted oil is withdrawn being maintained at 180° F. and the bottom of the tower where the asphalt is withdrawn with the residual oil being 160° F.

In carrying out the process of the present invention it will usually be found that metal content of the deasphalted oil is less than 10% of the metal contaminants introduced into the deasphalting zone and also less than the equivalent of one pound of nickel per 1000 barrels of oil.

In order to illustrate further the advantages of the present invention, the following example is given:

EXAMPLE

The feed stock treated was a blend of nonlube residua having the characteristics set out hereafter in Table III:

TABLE III

Sp. gr.	1.0094
O. C. flash, °F.	635
Visc.:	
SSF/210°	725
SSF/275°	108
Conradson Carbon, wt. percent	18.7
Bomb Sulfur, wt. percent	3.05
Agg. Ash #/1000 bbl.	105.9
Ash analysis:	
V—#/1000 bbl.	14.5
Ni	13.0
Fe	6.2
Na	14.8

Two deasphalting runs were made with the operating conditions set out hereafter in Table IV. In Table IV, column 1 shows a procedure in which the feed stock was deasphalted without the use of a wash oil whereas column 2 shows a procedure in accordance with the present invention in which 20 parts of a Hawkins residuum was introduced as wash oil for treating 80 parts of feed stock having the characteristics set out heretofore in Table III. It will be seen that in column 2 where the procedure is carried out in accordance with the present invention, the nickel contaminants of the deasphalted oil are .30 pounds per thousand barrels of oil whereas in column 1 where no wash oil was used, the nickel contaminants of the deasphalted oil are .67 pounds per thousand barrels.

TABLE IV
Operating conditions and inspections

	1	2
Residuum charge	100.0	80
Wash oil	0	20
Operating Conditions:		
Solvent to oil Ratio	3.5	2.95
Solvent Composition, Vol. Percent—		
C ₄	71.3	69.5
C ₃	28.7	30.5
Temperature, °F.—		
Tower top	171	170
Tower middle	161	160
Tower bottoms	151	150
Pressure, p. s. i. g.	400	400
Deasphalted Oil:		
Yield, Vol. Percent	49.0	44.0
Gravity, °API	18.2	19.0
Viscosity, SSU @ 210° F	379	370
Conradson Carbon, Wt. Percent	4.43	3.67
Bomb Sulfur, Wt. Percent	1.58	1.99
Contaminants, #/1,000 bbls.—		
Agg. ash		1.12
Ni	0.67	0.30

It will be noted as shown from the typical analysis of Hawkins residual oils in Table I that the material used as the wash oil in the practice of the present invention

contains substantial amounts of nickel but as shown by the example, the use of Hawkins residuum as a wash oil results in a deasphalted oil containing a very low amount of nickel and particularly useful as a feed stock for a catalytic cracking process. It will thus be seen that Hawkins residual oil has an unexpected characteristic that it has selective action for removing contaminating metallic constituents in a deasphalting process so that the deasphalted oil is substantially free from metallic contaminants. As previously explained in referring to Hawkins residual oils in the specification and claims of the present case, the material referred to is secured by the distillation of crude oil from Hawkins field and is free from components boiling below 650° F.

While specific examples have been given illustrating the practice of the present invention it will be understood that these specific examples are given by way of illustrative purposes only and not by way of limitation.

The invention claimed 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 metallic contaminants including no less than the equivalent of 3 pounds of nickel per thousand barrels of oil consisting of the steps of continuously introducing a stream of said feed stock at a selected point in a deasphalting tower the contents of which are maintained at a temperature within the range of 100° to 300° F., continuously introducing a stream of a residual fraction derived from Hawkins crude free from components boiling below approximately 650° F. into said tower as a wash oil at a point above the point of introduction of said feed stock, continuously introducing a stream of liquefied normally gaseous hydrocarbon into the tower at a point below the point of introduction of the feed stock in an amount within the range of 2 to 10 volumes of liquefied normally gaseous hydrocarbon per volume of feed stock, continuously withdrawing a solution of deasphalted oil in liquefied normally gaseous hydrocarbon from a point in the tower above the point of introduction of said wash oil, said solution of oil containing no more than 10% of the metallic contaminants introduced into said deasphalting tower and no more than the equivalent of one pound of nickel per thousand barrels of oil and continuously withdrawing from a point in the tower below the point of introduction of said stream of liquefied normally gaseous hydrocarbon an asphalt phase containing substantially all of the metallic contaminants introduced into said zone.

2. A method in accordance with claim 1 in which there is a temperature gradient within the range of 0 to 100° F. between a lower temperature point at which the asphalt phase is removed from the tower and a higher temperature point at which the deasphalted oil is removed from said tower.

3. A method in accordance with claim 1 in which there is a temperature gradient within the range of 0 to 100° F. between a lower temperature point at which the asphalt phase is removed from said tower and a higher temperature point at which the deasphalted oil is removed from said tower and in which approximately one volume of residual oil derived from Hawkins crude oil and free from constituents boiling below approximately 650° F. is introduced into the deasphalting zone for each 4 volumes of feed stock.

4. A method in accordance with claim 1 wherein the said solution of oil withdrawn from the said tower has continuously admixed therewith a Hawkins crude oil residual fraction substantially free from components boiling below about 650° F., wherein the resultant mixture is continuously charged to a settling zone under conditions to obtain phase separation; wherein a lighter phase consisting of a solution of said deasphalted oil containing a still further reduced amount of metallic contaminants is

continuously withdrawn from said settling zone and wherein a heavier asphalt phase is continuously withdrawn from said settling zone.

5. 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 metallic contaminants including no less than the equivalent of 3 pounds of nickel per thousand barrels of oil consisting of the steps of continuously introducing a stream of said feed stock at a selected point in a deasphalting tower, the contents of which are maintained at a temperature within the range of 100° to 300° F., continuously introducing a stream of a wash oil material into said tower at a point above the point of introduction of said feed stock, continuously introducing a stream of liquefied normally gaseous hydrocarbon into said tower at a point below the point of introduction of the feed stock in an amount within the range of 2 to 10 volumes of liquefied hydrocarbon per volume of feed stock, continuously withdrawing a solution of the deasphalted oil in said liquefied hydrocarbon from a point in the tower above the point of introduction of said wash oil, continuously withdrawing an asphalt phase containing substantially all of the metallic contaminants from a point in the tower below the point of introduction of said stream of liquefied hydrocarbon, continuously admixing with said solution of oil about 1 volume of a Hawkins crude oil residual fraction substantially free from components boiling below about 650° F. per 4 volumes of said feed stock, continuously charging said mixture to a settling zone under conditions to obtain phase separation, continuously withdrawing a lighter phase consisting of said solution of oil in said liquefied hydrocarbon in further purified form, continuously withdrawing from said settling zone a heavier asphalt phase, and continuously charging said heavier asphalt phase to said deasphalting tower as said stream of wash oil material.

6. 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 metallic contaminants including no less than the equivalent of 3 pounds of nickel per 1000 barrels of oil, consisting of the steps of continuously introducing a stream of said feed stock at a selected point in a deasphalting tower, continuously introducing a stream of residual fraction derived from Hawkins crude free from constituents boiling below approximately 650° F. into said tower as a wash oil at a point above the point of introduction of said feed stock, continuously introducing a stream of liquefied normally gaseous hydrocarbon into the tower at a point below the point of introduction of the feed stock, continuously withdrawing a solution of deasphalted oil substantially free from metallic contaminants in liquefied normally gaseous hydrocarbon from a point in the tower above the point of introduction of the wash oil and continuously withdrawing an asphalt phase containing substantially all of the metallic contaminants introduced in the feed stock from a point in the tower below the point of introduction of said liquefied normally gaseous hydrocarbon.

7. A method in accordance with claim 6 in which the deasphalted oil contains not more than 10% of the nickel contaminants introduced into the deasphalting tower with the petroleum fraction and no more than 1 pound of the equivalent of nickel per 1000 barrels of oil.

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