July 21, 1959 N. P. PEET 2,895,902

REMOVAL OF METAL CONTAMINANTS FROM RESIDUAL OILS

Original Filed April 1, 1954

FIG. 1.

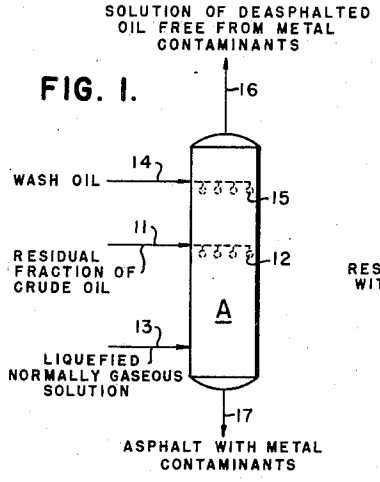
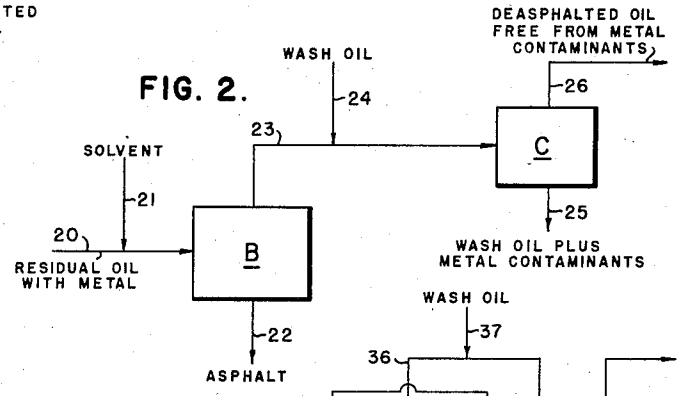


FIG. 2.



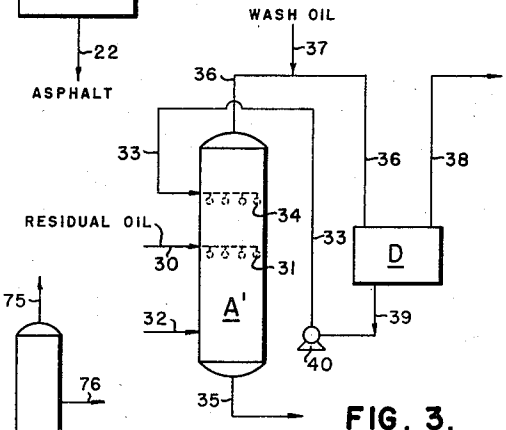


FIG. 3.

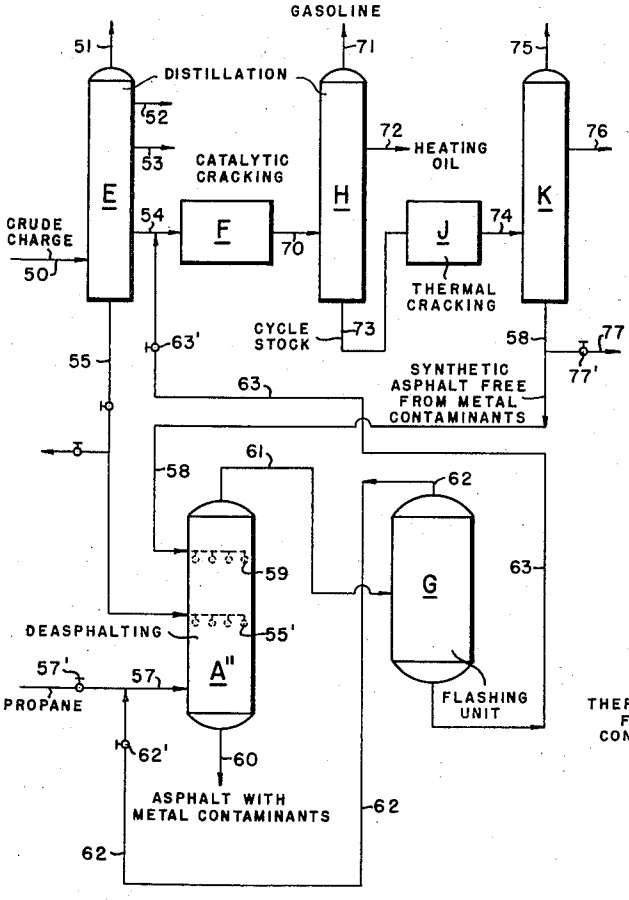


FIG. 4.

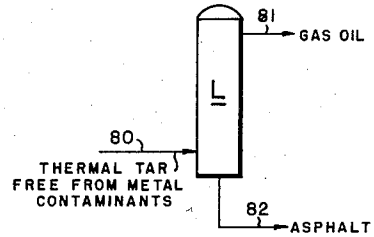


FIG. 5.

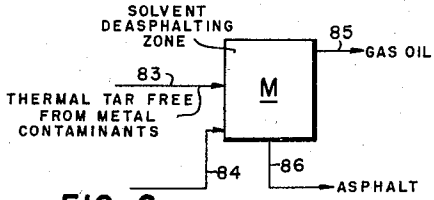


FIG. 6.

INVENTOR.

Nick P. Peet,

BY

Carl G. Ries

ATTORNEY.

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REMOVAL OF METAL CONTAMINANTS FROM RESIDUAL OILS

Nick P. Peet, Baytown, Tex., assignor, by mesne assignments, to Esso Research and Engineering Company, Elizabeth, N.J., a corporation of Delaware

Continuation of application Serial No. 420,373, April 1, 1954. This application November 27, 1956, Serial No. 624,650

12 Claims. (Cl. 208—73)

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

This application is a continuation of Nick P. Peet application Ser. No. 420,373, filed April 1, 1954, now abandoned, entitled "Removal of Metal Contaminants from Residual Oils."

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 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 were introduced as metal contaminants originally present in the crude oil is treated to secure a fraction substantially free from metal contaminants. The treating step is carried out by contacting the residual oil in a contacting zone with liquefied normally gaseous hydrocarbon and a synthetic asphalt substantially free from metal contaminants which serves as a wash oil or material selective for metal contaminants so that in this zone a deasphalted oil phase substantially free from metal contaminants is formed and an asphalt phase containing metal contaminants is formed with said two phases being separately withdrawn. The resultant deasphalted oil phase substantially free from metal contaminants is a desirable feed stock for a catalytic cracking process whereas residual oil with said metallic contaminants which is the charge stock for said zone is an undesirable feed stock for a catalytic cracking process.

In its more specific aspects, the present invention is directed to a procedure for treating gas oil and residual oil fractions derived from crude oil including the treatment of the residual fraction contaminated with metallic contaminants in a deasphalting zone where it is deasphalted in the presence of a liquefied normally gaseous hydrocarbon and synthetic asphalt to separate a deasphalted oil phase and an asphalt phase containing substantially all of the contaminants introduced into the system with said crude, the deasphalted oil then being catalytically cracked along with the gas oil derived from the crude. The products from the catalytic cracking process may be distilled and the resultant residue then thermally cracked and the products from the thermal cracking step distilled, with the resultant bottoms preferably free from gas oil components being used as the synthetic asphalt wash oil in the deasphalting zone of the process.

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;

Fig. 2 is in the form of a diagrammatic flow sheet illustrating another procedure for deasphalting a residual oil to remove metal contaminants therefrom;

Fig. 3 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;

Fig. 4 is in the form of a diagrammatic flow sheet illustrating a system for treating a crude oil charge with combined catalytic cracking, deasphalting, and thermal cracking;

Fig. 5 is in the form of a diagrammatic flow sheet illustrating the removal of gas oil fractions from a thermal tar for preparing a wash oil in the deasphalting step; and

Fig. 6 is in the form of a block diagram illustrating another method for treating thermal tar to remove gas oil therefrom to obtain an asphalt suitable for use as a wash oil.

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 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 wash oil fraction containing as its essential component synthetic asphalt substantially free from metallic contaminants is introduced through line **14** and discharged through distributor **15** into 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 with the charge stock is withdrawn through outlet line **17**.

Another procedure for removing metal contaminants from the residual fraction of crude oil is shown in Fig. 2. In Fig. 2 the residual oil is introduced through inlet line **20** with liquefied normally gaseous solvent added thereto through line **21**, the two components discharging together into drum B where phase separation takes place with an asphalt fraction withdrawn from the bottom of the drum through outlet line **22** and a solution of oil withdrawn from the top of the drum by means of line **23**. A wash oil having as its essential components synthetic asphalt and substantially free from metallic contaminants is introduced by inlet line **24** into the solution flowing through line **23**, the resultant mixture discharging into settling drum C where phase separation takes place. Minor portions of the metal components originally present in the residual oil are removed with the

asphalt by line 22 but the major portion of the metal constituents introduced in the system are withdrawn with the wash oil from vessel C through outlet line 25 and a solution of deasphalted oil substantially free from metal contaminants is withdrawn through outlet line 26.

Another procedure for removing the metal contaminants from a residual oil is shown in Fig. 3. In this figure, tower A' is similar to tower A of Fig. 1. In Fig. 3 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 wash oil having as its essential component synthetic asphalt and substantially free from metallic contaminants is introduced 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' with the residual 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 has admixed therewith fresh wash oil introduced through inlet line 37, the components being 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 being 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. 3 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. 3 should increase the metal removal from 75% to approximately 92%.

A system for treating a crude oil is shown in Fig. 4. In this figure, a crude oil feed stock is charged through inlet line 50 to a distillation unit E' where it is separated into a number of components which may be withdrawn through a number of outlets. For illustrative purposes, outlets 51, 52, 53, 54, and 55 are shown in the drawing although it will be understood that if desired a larger or smaller number of fractions may be obtained from the distillation unit E. As is well known in the art, the distillation step may be carried out by using a single vessel or by using a battery of distillation towers. The fraction withdrawn through line 54 is a gas oil fraction suitable for use as charge stock in a catalytic cracking process and as shown in the drawing is charged to catalytic cracking step F. From distillation step E the residual fraction contaminated with the metallic components introduced with the crude charge is passed by line 55 into deasphalting tower A'' and discharged therein from distributor 55'. Liquefied normally gaseous solvent, for example propane, is introduced into the lower end of the tower through inlet line 57 and wash oil containing as its essential ingredient synthetic asphalt and substantially free from metallic constituents is introduced into tower A by means of line 58 and is discharged into the upper end of the column from distributor 59. Asphalt consisting of the asphaltic components in the wash oil and those in the residual charge and containing substantially all of the metal contaminants introduced with the residual charge is withdrawn through outlet line 60 from the bottom of tower A''. A solution of deasphalted oil and solvent is withdrawn from tower A' through line 61 and passes to flash drum G where the solvent is removed as overhead through line 62 and the solvent may be returned to tower A' by means of inlet line 57. It will be understood that when the system is in equilibrium, valve 57' may be closed and valve 62' opened since no propane from an outside source need be added and when starting up the unit, valve 57' is open and valve 62' is closed.

From the bottom of flash drum G a deasphalted oil suitable for use as a charging stock to a catalytic cracking unit is withdrawn through line 63 and with valve 63' open it is admixed with the gas oil fraction withdrawn from distillation unit E by line 54, the admixed fractions being used as charge stock for catalytic cracking unit F.

The products from catalytic cracking unit F are withdrawn through line 70 and passed to distillation unit H where they may be separated into a number of products. By way of illustration in the drawing, a gasoline fraction is removed from unit H through outlet line 71, a heating oil fraction is removed through line 72 and a bottoms cycle stock fraction is removed through line 73. The cycle stock fraction is sent through line 73 to thermal cracking unit J with the products from thermal cracking unit J passed through line 74 to distillation unit K and there separated into distillate fractions removed through outlet lines 75 and 76 and a bottoms fraction removed through line 58. This entire bottoms fraction may be used as the wash oil in deasphalting step carried out in vessel A'', or alternatively, if desired, only a portion may be used in tower A'' and the remainder withdrawn through outlet line 77 controlled by valve 77'.

Under present refinery procedure, a desirable source of the synthetic asphalt to be used as the wash oil free from metallic contaminants in the deasphalting step is secured from the bottoms from the thermal cracking unit J. The thermal bottoms conventionally secured by distilling the products from a thermal cracking unit such as J may contain an appreciable amount of aromatic materials which will dissolve in the solvent in the deasphalting step and form a part of the deasphalted oil recovered from said step. Since these aromatic constituents are not desirable components for a catalytic cracking process, it will often be found desirable to separate them from the thermal bottoms described supra before this material is used as the wash oil in the deasphalted step. Procedures for removing the lighter gas oil fraction from the thermal bottoms are shown in Figs. 5 and 6.

In Fig. 5 a distillation unit L has thermal tar derived from a thermal cracking operation charged by inlet line 80 and a gas oil distillate fraction is removed through outlet line 81 while an asphaltic fraction is removed as bottoms through line 82, said asphalt fraction being free from gas oil components and being particularly desirable wash oil for use in the deasphalting of a residual oil in the procedures as shown in Figs. 1, 2, and 3 and as carried out in tower A'' in Fig. 4.

Another procedure for treating a thermal tar to make it more desirable as the wash oil used in the procedures shown in Figs. 1, 2, and 3 and in tower A'' of Fig. 4 is shown in Fig. 6. In Fig. 6 a solvent deasphalting zone M has a thermal tar charged thereto through inlet line 83, a liquefied normally gaseous hydrocarbon introduced as solvent through inlet line 84 with a solution of gas oil removed through line 85 and an asphalt fraction removed through line 86. The asphalt fraction removed through line 85 is particularly suitable for use as the wash oil in the processes shown in Figs. 1, 2, and 3 and in tower A'' of Fig. 4.

The inspections of residua from the distillation of typical crude oils charged to refinery operations are set out hereafter in Table I. In Table I, columns 1, 2, 3, 4, and 5 show the characteristics respectively of residua derived from a mixture of Gulf Coast and West Texas crudes, a West Texas crude, a Panhandle crude, a Hawkins crude and a Lagunillas crude.

TABLE I

Typical feed stock inspections

	1	2	3	4	5
Percent on Crude	9.8	12.8	15.6	29.0	44.0
Gravity, ° API	8.7	8.7	20.1	4.7	6.5
Viscosity, SSU at 210° F	7,250	------	679	------	------
Conradson Carbon, Wt. percent	18.7	17.3	8.40	19.8	24.0
Bomb Sulfur, Wt. percent	3.05	3.67	------	4.6	3.1
Contaminants, #/1,000 Bbls.:					
Ni	13.0	9.0	5.0	10.2	24.3
V	14.5	16.0	8.0	15.0	199.0
Fe	6.2	8.6	9.4	7.0	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. 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 ⅕ as troublesome as nickel and iron is perhaps ½ as troublesome as nickel. 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 value, vanadium considered at ⅕ its actual weight value and iron considered at ½ its actual weight value.

In carrying out the deasphalting step in the present invention where the wash oil having a synthetic asphalt as its principal component is used to remove selectively the metal contaminants from the residuum charge, the solvent used is 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 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° 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 introduced with the residual oil being 160° F.

In order to illustrate further the advantages of the present invention, operating conditions are set out hereafter in Table II. In this table, column 1 represents a procedure in which residuum is deasphalted without the use of a wash oil whereas column 2 represents a procedure in accordance with the present invention in which 20 parts of wash oil are introduced with 80 parts of residuum. It will be seen that in column 2 where the procedure is carried out in accordance with the present nivention, the nickel contaminants of the deasphalted oil are 0.20 pound per thousand barrels of oil whereas in

column 1 where the procedure was not carried out in accordance with the present invention, in that no wash oil was used, the nickel contaminants in the deasphalted oil are 0.67 per thousand barrels. The residuum oil used as the feed stock for columns 1 and 2 of Table II is the oil whose characteristics are set out in column 1 of Table I.

TABLE II

Operating conditions and inspections

	1	2
Residum charge	100.0	80
Wash oil	0	20
Operating Conditions:		
Solvent to oil Ratio	3.5	3.60
Solvent Composition, Vol. Percent:		
C_3	71.3	68.5
C_4	28.7	31.5
Temperature, ° F.:		
Tower top	171	161
Tower middle	161	161
Tower bottom	151	151
Pressure, p.s.i.g.	400	400
Deasphalted Oil:		
Yield, Vol. Percent	49.0	54.0
Gravity, °API	18.2	12.2
Viscosity, SSU at 210° F	379	155
Conradson Carbon, Wt. Percent	4.43	4.06
Bomb Sulfur, Wt. Percent	1.58	1.90
Contaminants, #/1,000 Bbls Ni	0.67	0.20

Typical examples of wash oils suitable for use as the wash oil in the deasphalting step as carried out in Figs. 1, 2, and 3 and in vessel A″ of Fig. 4 are set out in Table III. In column 1, the characteristics of a thermal tar produced by thermal cracking of catalytic cycle stock are shown and in column 2 the characteristics of a reduced thermal tar produced by thermal cracking of catalytic cycle stock are shown.

TABLE III

Wash oil inspection

	1	2
Gravity, °API	9.9	
Viscosity, SSU at 210° F	1,425	
Softening Point, ° F	------	180.
Conradson Carbon, Wt. Percent	19.1	31.0.
Bomb Sulfur, Wt. Percent	2.16	2.06.
Contaminants, #/1,000 Bbls.:		
Ni	0.10	Insufficient Sample.
V	0.10	Do.
Fe	------	Do.

While specific examples have been given in the description of the present invention, it is to be understood that these specific examples are given by way of illustrative purposes only and not by way of limitation.

I claim:

1. A method of 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 deasphalting said feed stock with a liquefied normally gaseous hydrocarbon solvent to separate asphalt from said feed stock and to form a solution of deasphalted oil in said solvent, contacting said solution of deasphalted oil with a wash oil containing as its principal component a synthetic asphalt substantially free from metal contaminants and recovering said thus treated deasphalted oil, said recovered deasphalted oil being substantially completely free from metal contaminants, said synthetic asphalt having been produced by thermal cracking of cycle stock obtained in the catalytic cracking of gas oil.

2. 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 deasphalting said feed stock with about 2 to 10 volumes per volume of feed stock of a liquefied normally gaseous hy-

drocarbon solvent at a temperature within the range of about 100° to 300° F. to separate asphalt from said feed stock and to form a solution of deasphalted oil in said solvent, contacting said solution of deasphalted oil with a wash oil containing as its principal component a synthetic asphalt substantially free from metal contaminants and recovering said thus treated deasphalted oil, said recovered deasphalted oil being substantially completely free from metal contaminants, said synthetic asphalt having been produced by thermal cracking of cycle stock obtained in the catalytic cracking of gas oil.

3. 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 tower, introducing a liquefied normally gaseous hydrocarbon solvent into said tower below the point of introduction of said feed stock and separately introducing a wash oil containing as its principal component a synthetic asphalt substantially free from metal contaminants into said tower above the point of introduction of said feed stock to thereby separate asphalt from said feed stock and to form a solution of deasphalted oil in said solvent, withdrawing said asphalt from the bottom of said deasphalting tower, withdrawing said solution of deasphalted oil from the top of said tower and recovering a deasphalted oil substantially completely free from metal contaminants from said solution, said synthetic asphalt having been produced by thermally cracking cycle stock obtained in the catalytic cracking of gas oil.

4. A method as in claim 3 wherein about 2 to 10 volumes of said liquefied normally gaseous hydrocarbon are introduced into said tower per volume of feed stock and wherein said deasphalting is conducted at a temperature within the range of about 100° to about 300° F.

5. A method as in claim 4 wherein the temperature at the deasphalted oil outlet of said tower is from about 0° to about 60° F. higher than the temperature of said tower at the asphalt outlet.

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 metal contaminants which comprises continuously introducing feed stock into a deasphalting tower, continuously introducing from about 2 to 10 volumes per volume of feed stock of a liquefied mixture of about 70 volume percent of propane with about 30 volume percent of butane introduced into said tower below the point of introduction of said feed stock and separately continuously introducing a wash oil containing as its principal component a synthetic asphalt substantially free from metal contaminants into said tower above the point of introduction of said feed stock to thereby form an asphalt phase and a deasphalted oil phase comprising a solution of deasphalted oil in said liquefied mixture, continuously withdrawing said asphalt phase from the bottom of said tower, continuously withdrawing the solution of deasphalted oil from the top of the tower and continuously recovering a deasphalted oil substantially completely free from metal contaminants from said solution, said synthetic asphalt having been produced by thermal cracking of cycle stock obtained in the catalytic cracking of gas oil.

7. 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 solvent to form an asphalt phase and a solution of deasphalted oil in said solvent, separately withdrawing said asphalt phase and said solution from said deasphalting zone, contacting said solution with a wash oil containing as its principal component a synthetic asphalt substantially free from metal contaminants, removing said synthetic asphalt from contact with said solution and recovering a deasphalted oil substantially completely free from metal contaminants from said solution, said synthetic asphalt having been produced by thermal cracking of cycle stock obtained in the catalytic cracking of gas oil.

8. A method as in claim 7 wherein said feed stock is deasphalted in said deasphalting zone with about 2 to 10 volumes of liquefied normally gaseous hydrocarbon per volume of feed stock at a temperature within the range of about 100° to about 300° F.

9. 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 tower, introducing a liquefied normally gaseous hydrocarbon solvent into said tower below the point of introduction of said feed stock, introducing a wash oil fraction into said tower above the point of introduction of said feed stock to thereby form an asphalt phase and a solution of deasphalted oil in said solvent, withdrawing said asphalt from the bottom of said tower, withdrawing said solution from the top of said tower, contacting said thus withdrawn solution with a wash material containing as its principal component a synthetic asphalt substantially free from metal contaminants under conditions to form a lighter phase consisting of a solution of deasphalted oil substantially completely free from metal contaminants in said solvent and a heavier phase, charging said heavier phase to said deasphalting tower as said wash oil and separating said deasphalted oil from said solvent, said synthetic asphalt having been produced by thermal cracking of cycle stock obtained in the catalytic cracking of gas oil.

10. A method as in claim 9 wherein about 2 to 10 volumes of said liquefied normally gaseous hydrocarbon are introduced into said tower per volume of feed stock and wherein said deasphalting is conducted at a temperature within the range of about 100° to about 300° F.

11. A method as in claim 10 wherein the temperature at the deasphalted oil outlet of said tower is from about 0° to about 60° F. higher than the temperature of said tower at the asphalt withdrawal point.

12. An improved method for treating a metals contaminated crude petroleum oil including the steps of distilling said crude petroleum oil to obtain a distillate gas oil fraction and a residual fraction contaminated with a substantial amount of said metallic components of said crude oil, deasphalting said residual fraction with a liquefied normally gaseous hydrocarbon solvent to separate asphalt from said residual fraction and to form a solution of deasphalted oil in said solvent, contacting said solution of deasphalted oil with a wash oil containing as its principal component a synthetic asphalt substantially free from metal contaminants, recovering said thus treated deasphalted oil and mixing the same with said distillate gas oil fraction, charging said mixture to a catalytic cracking zone to catalytically crack the same, distilling the products from said catalytic cracking zone to recover distillate products lighter than said feed mixture to said catalytic cracking zone and a cycle stock fraction, thermally cracking said cycle stock fraction, distilling the products from said thermal cracking to recover a bottoms product comprising a synthetic asphalt substantially free from metal contaminants, said thus obtained synthetic asphalt being the synthetic asphalt utilized for the contacting of said solution of deasphalted oil.

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