June 7, 1960 R. L. MURPHEY 2,939,838

PETROLEUM TREATING PROCESS

Filed June 24, 1957

United States Patent Office 2,939,838 Patented June 7, 1960

2,939,838

PETROLEUM TREATING PROCESS

Robert L. Murphey, Groves, Tex., assignor to Texaco Inc., a corporation of Delaware

Filed June 24, 1957, Ser. No. 667,647
4 Claims. (Cl. 208—312)

This invention relates to the treatment of residual oils for the separation therefrom of a relatively high quality lubricating oil. More particularly, this invention is concerned with the treatment of a heavy petroleum fraction, such as a residual asphaltic fraction, for the recovery therefrom of a high VI lubricating oil, such as a lubricating oil suitable for use as an aircraft engine oil. In accordance with one embodiment this invention relates to a process for fractionating a heavy residual oil, such as a long asphaltic residuum, into a heavy distillate fraction and a heavy bottoms fraction or short residuum, together with the subsequent separate treatment of said heavy distillate fraction and said short residuum with the ultimate production of a solvent refined dewaxed finished heavy lubricating oil.

It is an object of this invention to provide an improved process for the treatment of residual petroleum oils and the like.

It is another object of this invention to provide a process for the production of a high VI lubricating oil from a residual petroleum fraction, such as an asphaltic petroleum fraction.

Still another object of this invention is to provide a process for the treatment of a residual petroleum fraction, such as a long residuum, wherein there is recovered a finished oil fraction particularly suitable as an aircraft engine oil and the like.

How these and other objects of this invention are accomplished will become apparent with reference to the accompanying disclosure and drawing wherein there is schematically illustrated an embodiment of a practice of this invention directed to the recovery of a heavy lubricating oil fraction from a petroleum residuum.

Referring now in detail to the drawing a crude oil, such as an asphaltic crude oil or the like, is introduced via line 11 into crude still or fractionation unit 12 wherein it is subjected to fractional distillation. From crude still 12 there is recovered overhead via line 14 a gas fraction usually comprising propane and butane and the like, a naphtha fraction via line 15 comprising the gasoline constituents originally present in the crude oil charged to the crude still, a kerosene fraction via line 16, a gas oil fraction via line 18 and a distillate lube oil or lubricating oil fraction via line 19. There is recovered as a bottoms fraction from crude still 12 via line 20 a long residuum, usually having an initial boiling point greater than about 650° F., more frequently having an initial boiling point higher than 700° F., and usually amounting to about 5–35%, more or less, by volume of the original crude.

The long residuum in line 20 is supplied to vacuum still 21 wherein it is fractionated into approximately equal parts by volume into a heavy distillate fraction which is recovered overhead from vacuum still 21 via line 22 and a bottoms fraction or short residuum which is recovered from vacuum still 21 via line 24. The heavy distillate fraction removed overhead from vacuum still 21 via line 22 may comprise 2–15% by volume of the original crude or 20–75% by volume of the long residuum charged to the vacuum still.

The heavy distillate fraction recovered from vacuum still 21 via line 22 is directed via line 22 into solvent fractionation zone 25 where it is subjected to contact with a liquefied normally gaseous hydrocarbon, such as propane and the like. Generally it is preferred to employ liquid propane or a mixture comprised predominantly of liquid propane as the solvent. Within solvent fractionation zone 25 the more paraffinic constituents in the heavy distillate fraction introduced thereinto via line 22 are preferentially dissolved in the liquid propane whereas the more asphaltic, more dense and heavier portions of said heavy distillate fraction are rejected as a separate phase.

Solvent fractionation zone 25 may comprise any suitable means for effecting liquid-liquid contact. For example, the solvent fractionation zone may comprise a combination of mixer-settlers, a RDC (rotating disc contactor) tower, a packed tower and the like. As indicated in the accompanying drawing, solvent fractionation zone 25 is shown as a tower suitable for effecting countercurrent liquid-liquid contact, the heavy distillate fraction being introduced into the upper portion of solvent fractionation zone 25 via line 22 and the liquid solvent (propane) being introduced into the lower portion of solvent fractionation zone 25 via line 26.

Solvent fractionation zone 25 is operated under rather severe conditions, the solvent to charge oil (liquid propane to heavy distillate fraction) dosage ratio in the range 4–12, usually in the range 8–10, and at a relatively elevated temperature, approaching the critical temperature of the liquefied normally gaseous hydrocarbon solvent (propane) employed. As indicated hereinabove, propane is preferred as the solvent. In some instances it is preferred to operate solvent fractionation zone 25, either isothermally in the range 180–205° F. or with a temperature gradient extending over the range 5–20 degrees Fahrenheit within the solvent fractionation zone 25.

As indicated, there is recovered overhead from solvent fractionation zone 25 via line 28 a so-called propane distillate phase comprising the more paraffinic oil originally present in the heavy distillate fraction now substantially free of asphalt, bitumens, resins and the like. This propane fractionated paraffinic oil after separation of the liquid solvent (propane) therefrom by suitable means (not shown) is introduced via line 28 into solvent refining zone 29. In solvent refining zone 29 the solvent (propane) fractionated oil is subjected to liquid-liquid contact with a liquid selective solvent which selectively extracts the more aromatic hydrocarbons from the less aromatic hydrocarbons. The solvent refining zone 29 may comprise a combination of mixers-settlers, a rotating disc contactor, a packed tower and the like, suitable for effecting liquid-liquid contact between two countercurrently flowing liquid streams. As indicated in the drawing, the solvent fractionated deasphalted oil is introduced into the lower portion of solvent refining tower or zone 29 via line 28 and the selective solvent for aromatic hydrocarbons, preferably furfural, is introduced into the upper portion of solvent refining zone 29 via line 30. Although liquid furfural is the preferred selective solvent, other selective solvents such as nitrobenzene, Chlorex, phenol are useful. There is recovered overhead from solvent refining zone 29 via line 31 a solvent refined oil or raffinate. This solvent refined oil, after removal of the selective solvent therefrom by suitable means, not shown, is introduced via line 31 into solvent dewaxing zone 32 wherein the waxy hydrocarbons are removed therefrom. Dewaxing is preferably effected by contacting the oil charge to dewaxing zone 32 with a liquid dewaxing solvent, preferably a mixture of an aliphatic ketone such as methyl ethyl ketone and an oil solvent such as an aromatic hydrocarbon, e.g., toluene. The wax separated from the refined oil is recovered from solvent dewaxing zone 32 via line 34. The resulting solvent refined dewaxed oil is recovered from solvent dewaxing zone 32 via line 35.

Returning to solvent refining zone 29 there is recovered as a bottoms or extract fraction therefrom via line 36 an aromatic extract phase which is suitable per se as cutter stock or fuel oil or after suitable treatment in clay contacting or finishing zone 39 as a red oil recovered from clay contacting or finishing zone 39 via line 40.

The short residuum recovered as a bottoms fraction from vacuum still 21 is introduced via line 24 into solvent deasphalting zone 41 where it is solvent deasphalted. The solvent deasphalting operation may be a batch operation, a multiple vessel operation or a substantially continuous liquid-liquid countercurrent treating operation as indicated in the drawing and as described hereinabove with respect to the operation of solvent fractionation zone 25, wherein the vacuum bottoms or short residuum is introduced into the upper portion of deasphalting zone or tower 41 and flowed therein in countercurrent liquid-liquid contact with a suitable liquid deasphalting solvent, such as liquefied normally gaseous hydrocarbon, e.g., propane, n-butane, isobutane or mixtures thereof, introduced into the lower portion of deasphalting tower 41 via line 42. If desired, the asphaltic bitumen or resinous fraction rejected from the heavy distillate fraction introduced via line 22 into the solvent fractionating zone 25, with or without the separation of the liquid propane solvent therefrom, and recovered via line 44 may be combined with the short residuum in line 24 via line 45. On the other hand, if desired, this asphaltic or resinous portion so rejected from the heavy distillate in solvent fractionation zone 25 may be separately recovered as product via line 44. There is recovered from solvent deasphalting zone or tower 41 via line 46 an asphalt product.

The deasphalted oil recovered overhead from solvent deasphalting zone 41 via line 48, after separation of the deasphalting solvent therefrom by suitable means, not shown, is introduced into solvent refining zone 49. Within solvent refining zone 49 the solvent deasphalted oil is contacted with a liquid solvent which is a selective solvent for the more aromatic hydrocarbons over the less aromatic hydrocarbons. A suitable selective solvent is liquid furfural although other previously disclosed solvents which are selective for aromatic hydrocarbons are suitable. As indicated in the drawing, liquid furfural is introduced via line 50 into the upper portion of solvent refining zone 45 wherein it flows in liquid-liquid countercurrent contact with the deasphalted oil introduced thereinto via line 48. There is recovered from the lower portion of the solvent refining zone 49 via line 51 liquid extract phase comprised predominantly of the more aromatic hydrocarbons. This liquid extract, after separation of the selective solvent therefrom, is suitable as a cutter stock, fuel oil and the like.

The resulting solvent refined oil is recovered overhead from solvent refining zone 49 via line 52 and then introduced into solvent dewaxing zone 54 where it is contacted with a liquid dewaxing solvent such as an aliphatic ketone, e.g., methyl isobutyl ketone, preferably a liquid mixture of an aliphatic ketone such as methyl ethyl ketone, and an oil solvent, such as an aromatic hydrocarbon, e.g., toluene, benzene and the like. There is recovered from solvent dewaxing zone 54 a wax product fraction via line 55 and a solvent refined dewaxed oil via line 56.

The solvent refined dewaxed oil streams recovered via lines 35 and 56 from solvent dewaxing zones 32 and 35, respectively, are preferably combined and the resulting combined oil stream passed via line 58 into clay contacting and/or finishing zone 59 wherein the oil is contacted with a suitable clay treating agent for the removal of any objectionable color bodies and residual resinous materials therefrom in the usual manner. There is recovered from clay contacting or finishing zone 59 via line 60 a product oil fraction comprising solvent refined solvent dewaxed oil of good color, of relatively low carbon residue and exhibiting a relatively high viscosity index (VI) and particularly suitable as an aircraft engine oil.

The following is illustrative of a practice of this invention. An amount of a heavy petroleum fraction was subjected to rather severe propane fractionation at a temperature of about 200° F. by contact with liquid propane at a propane dosage of about 8.2 volumes of liquid propane per volume of heavy petroleum fraction. There was recovered as a raffinate from the above-described operation a propane fractionated oil having a relatively high viscosity index. Another amount of the same heavy fraction was subjected to propane fractionation employing the same propane dosage but under relatively less severe conditions at a temperature of about 150° F. There was obtained from this operation a propane fractionated oil having a viscosity index definitely less than the oil recovered from the propane fractionation which is carried out under the more severe conditions. The test data and the results obtained which indicate the influence of the degree of severity of propane fractionation upon the quality, particularly the viscosity index of the resulting propane fractionated oil, are set forth in accompanying Table I.

TABLE I

Propane fractionation—long residuum

Test No.	1	2
Propane Dosage, Percent	820	850
Temperature, °F.:		
Top Tower	199	163
Bottom Tower	176	148
Propane Fractionated Oil Yield, Percent Basis Operation	34.1	50.5
Propane Fractionated Oil:		
Viscosity, SUS/210°F	93.8	266
Viscosity Index	95.5	80.7

It was observed that it was desirable to maintain a relatively precise temperature control during the relatively high temperature propane fractionation in order to obtain a relatively high VI propane fractionated oil.

Further illustrative of a practice of this invention for the preparation of a relatively high viscosity index aircraft engine oil, a heavy petroleum fraction was subjected to propane fractionation under relatively severe conditions and the resulting propane fractionated oil subjected to furfural refining, dewaxing and conventional finishing treatment such as clay contacting to yield a finished oil. There was recovered as a result of the foregoing operations a relatively high viscosity index oil suitable as an aircraft engine oil. The test data observed in the foregoing operations are set forth in accompanying Table II.

TABLE II

Product	Heavy Petroleum Fraction Long Residuum	Refined Oil	Dewaxed Oil	Acid Treated Oil	Clay Contacted Oil	Typical Aircraft Engine Oil
Processing Conditions (Countercurrent tower, liquid-liquid contacting for propane fractionation).	820% Propane 199° F. Top 189° F. Middle 176° F. Bottom	300% Furfural 190° F. Extract Out (Podbielniak Extractor).	Diln. Ratio 4:1 Wash Ratio 2.5:1 Filt. Temp., 0° F.	1½#/bbl 85% Alky Acid 170° F	3.3#/bbl Dry Millwhite 525° F	
Yield: Operation, Percent	34.1	89.3	79.5 [2]	98.0 Est.	98.0 Est.	

TABLE II.—Continued

RAFFINATE

Tests:						
Gravity, °API	27.2	28.4	27.3		27.2	27.4
Flash, COC, °F	560	575	550		550	560
Fire, OC, °F	630	650	625		625	
Viscosity, SUS—						
100° F			1,330		1,313	
150° F	276	240				
210° F	93.8	87.3	99.6		99.1	116.
Viscosity Index	95.5	103.5	89.5		90.0	95.0.
Color, Lovibond, ½"	45 [1]	35	90		20	
Pour, °F	115	115+	+15		+15	+5.
Carbon Residue, Percent	0.24	0.12	0.16		0.11	0.35.

[1] Color darker than stream samples due to handling in compositing stream samples.
[2] Calculated from percent wax assuming 35% oil in wax cake.

Further indicative of the effectiveness of a practice of this invention employing solvent (propane) fractionation in the recovery of a relatively high viscosity index oil from a heavy petroleum fraction, samples of a petroleum residuum were solvent fractionated by contact with liquid propane under varying conditions of severity. It was observed that the severity of propane fractionation and/or deasphalting showed a marked effect on the viscosity index of the solvent fractionated or deasphalted oil. The viscosity index of the fractionated or deasphalted oil on a dewaxed basis increased from 63.6 at 83% solvent fractionation yield (12% basis crude) to 72.9 at 19% deasphalting yield (2.7% basis crude) despite the fact that the latter stock had a pour point 25 degrees Fahrenheit lower than the first stock. These tests indicated that the viscosity index of a propane solvent fractionated or deasphalted oil from a given fraction increases as the severity of the solvent fractionation or deasphalting operation increases. The test results and data observed in the foregoing tests are set forth in accompanying Table III.

TABLE III

800% propane treat, 200% propane wash batch fractionation (deasphalting)

Test No	1	2
Propane Fractionation (Deasphalting), Temp. °F	120	205
Fractionated (Deasphalted) Oil Yield, Wt. Percent, Operation	83	19
Fractionated (Desphalted) Oil Yield, Vol. Percent, Basis Crude	12	2.7
Fractionated (Deasphalted) Oil Viscosity, SUS/210° F	208	85
Dewaxed, Fractionated (Deasphalted) Oil Tests:		
Viscosity:		
SUS/100° F	9,861	1,482
SUS/210° F	262	96.5
Viscosity Index	63.6	72.9
Pour, °F	+30	+5

As will be apparent to those skilled in the art many substitutions, variations and changes are possible in the practice of this invention without departing from the spirit or scope thereof.

I claim:

1. A method of treating a heavy asphaltic petroleum fraction which comprises separating said fraction into a heavy distillate fraction and an asphaltic residuum, subjecting said heavy distillate fraction to contact with liquefied propane under severe conditions at a liquid propane to charge ratio in the range 8–10 and at a temperature in the range 180–205° F. to yield a solvent fractionated oil and a bottoms asphaltic fraction, said solvent fractionated oil being recovered from the aforesaid propane solvent fractionation operation in an amount below about 34% based on said heavy distillate fraction charged thereto, subjecting said solvent fractionated oil to contact with a liquid solvent which is selective for aromatic hydrocarbons to yield a solvent fractionated raffinate, dewaxing said raffinate to yield a dewaxed solvent fractionated raffinate, solvent deasphalting said asphaltic residuum to yield a deasphalted oil, subjecting said deasphalted oil to contact with a liquid solvent which is selective for aromatic hydrocarbons to yield a deasphalted raffinate, dewaxing said deasphalted raffinate to yield a dewaxed deasphalted raffinate, combining the aforesaid dewaxed solvent fractionated raffinate and the aforesaid dewaxed deasphalted raffinate and subjecting the resulting combined raffinate to clay contacting to yield a finished dewaxed refined product oil.

2. A method of treating a heavy asphaltic petroleum long residuum which comprises subjecting said residuum to vacuum distillation to yield a heavy oil distillate fraction and an asphaltic bottoms fraction, subjecting said heavy distillate fraction to contact with liquid propane under severe conditions at a temperature in the range 180–205° F. and at a liquid propane to charge ratio in the range 8–10 to yield a propane fractionated oil, said propane fractionated oil being recovered from the aforesaid propane fractionation operation in an amount below about 34% based on said heavy distillate fraction charged thereto, subjecting said propane fractionated oil to contact with liquid furfural to selectively solvent extract the more aromatic hydrocarbons from said propane fractionated oil with the production of a propane fractionated raffinate, dewaxing said raffinate to yield a dewaxed propane fractionated raffinate, contacting said asphaltic bottoms fraction with liquid isobutane to yield a deasphalted oil, subjecting said deasphalted oil to contact with liquid furfural to selectively extract the more aromatic hydrocarbons therefrom and to yield a deasphalted raffinate, dewaxing said deasphalted raffinate to yield a dewaxed deasphalted raffinate, combining the aforesaid dewaxed propane fractionated raffinate and the aforesaid deasphalted raffinate and subjecting the resulting combined raffinate to clay contacting to yield a finished dewaxed refined product oil.

3. A method of treating a heavy asphaltic petroleum long residuum which comprises subjecting said residuum to vacuum distillation to yield a heavy oil distillate fraction and an asphaltic short residuum, subjecting said heavy distillate fraction to contact with liquid propane under severe conditions at a temperature in the range 180–205° F. and at a liquid propane to charge ratio in the range 8–10 to yield a propane fractionated oil and an asphaltic bottoms fraction, said propane fractionated oil being recovered from the aforesaid propane fractionation operation in an amount below about 34% based on said heavy distillate fraction charged thereto, subjecting said propane fractionated oil to contact with liquid furfural to selectively solvent extract the more aromatic hydrocarbons from said propane fractionated oil with the production of a propane fractionated raffinate, dewaxing said raffinate to yield a dewaxed propane fractionated raffinate, admixing said asphaltic bottoms fraction with said asphaltic short residuum and subjecting the resulting admixture to deasphalting by contact with a liquefied normally gaseous hydrocarbon to yield a deasphalted oil, subjecting said deasphalted oil to contact with liquid furfural to selectively extract the more aromatic hydrocarbons therefrom and to yield a deasphalted raffinate, dewaxing said deasphalted raffinate to yield a dewaxed de-

asphalted raffinate, combining the aforesaid dewaxed propane fractionated raffinate and the aforesaid deasphalted raffinate and subjecting the resulting combined raffinate to clay contacting to yield a finished dewaxed refined product oil.

4. A method of treating a heavy asphaltic petroleum long residuum which comprises subjecting said residuum to vacuum distillation to yield substantially equal amounts by volume of a heavy oil distillate fraction and an asphaltic short residuum, subjecting said heavy distillate fraction to contact with liquid propane under severe propane fractionation conditions at a solvent to charge dosage ratio of about 8:1 and at a temperature not lower than about 30 degrees Fahrenheit lower than the critical temperature of propane, to yield a propane fractionated oil and an asphaltic bottoms fraction, said propane fractionated oil being recovered from the aforesaid propane solvent fractionation operation in an amount below about 34% based on said heavy distillate fraction charged thereto, subjecting said propane fractionated oil to contact with liquid furfural to selectively solvent extract the more aromatic hydrocarbons from said propane fractionated oil within the production of a propane fractionated raffinate, dewaxing said raffinate to yield a dewaxed propane fractionated raffinate, admixing said asphaltic bottoms fraction with said asphaltic short residuum and subjecting the resulting admixture to deasphalting by contact with a liquefied normally gaseous hydrocarbon to yield a deasphalted oil, subjecting said deasphalted oil to contact with liquid furfural to selectively extract the more aromatic hydrocarbons therefrom and to yield a deasphalted raffinate, dewaxing said deasphalted raffinate to yield a dewaxed deasphalted raffinate, combining the aforesaid dewaxed propane fractionated raffinate and the aforesaid deasphalted raffinate and subjecting the resulting combined raffinate to clay contacting to yield a finished dewaxed refinished product oil.

References Cited in the file of this patent

UNITED STATES PATENTS

1,827,537	Morrell	Oct. 13, 1931
1,881,534	Harding	Oct. 11, 1932
1,983,241	Pier et al.	Dec. 4, 1934
2,115,960	Lindeke	May 3, 1938
2,316,395	Bray et al.	Apr. 13, 1943
2,687,982	Baumann	Aug. 31, 1954
2,692,222	Packie	Oct. 19, 1954
2,853,427	Bentley et al.	Sept. 23, 1958