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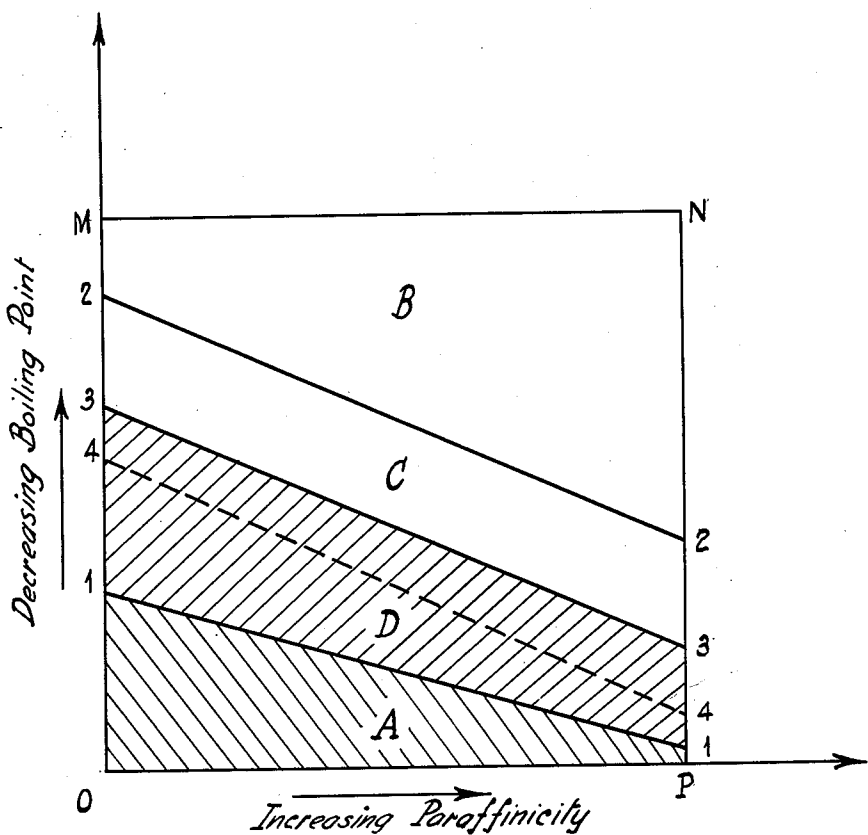
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PETROLEUM TREATING PROCESS INVOLVING SOLVENT
DEASPHALTING AND PROPANE FRACTIONATION

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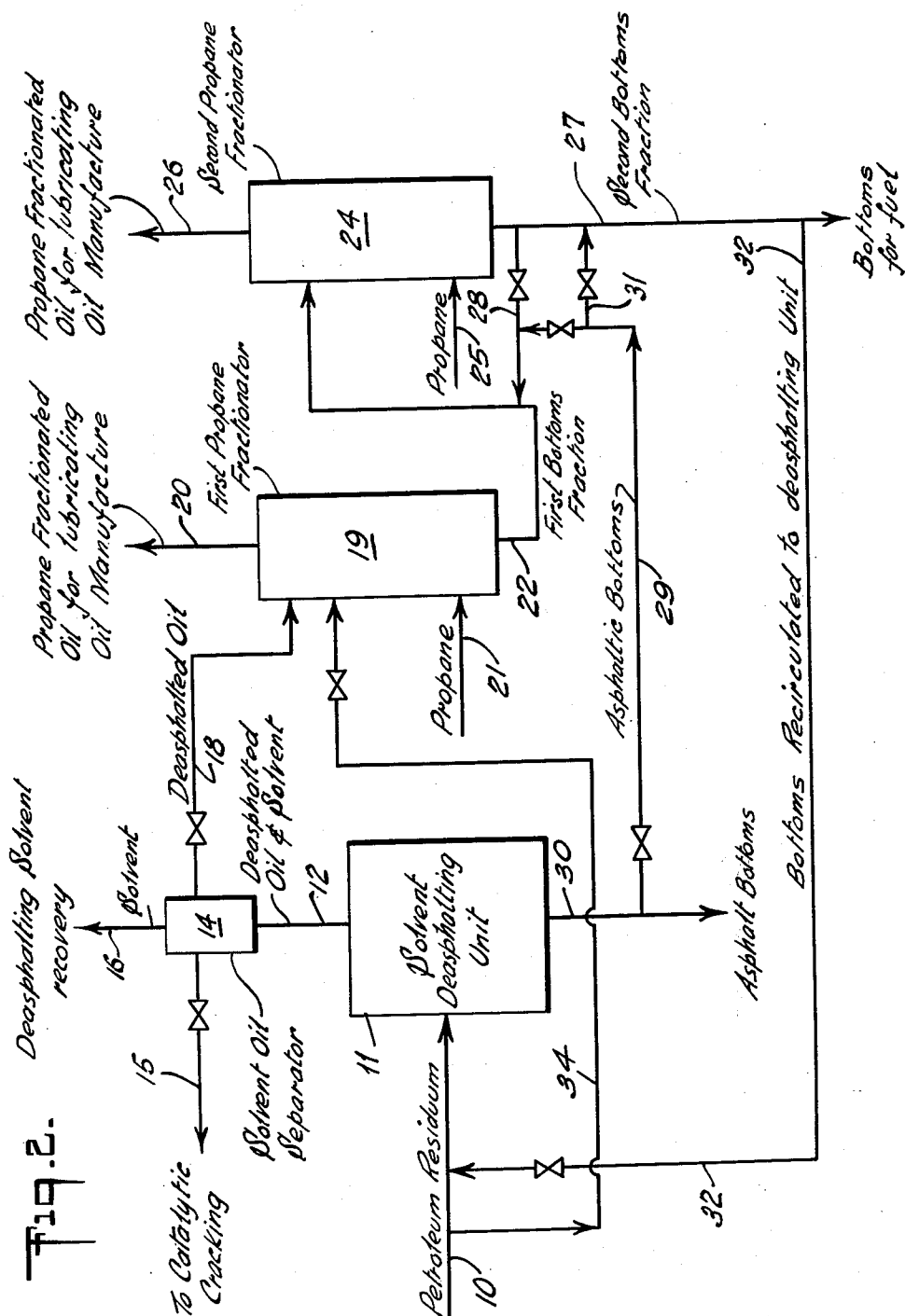
Fig. 1.



Filed Feb. 2, 1959

2 Sheets-Sheet 2

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1

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PETROLEUM TREATING PROCESS INVOLVING SOLVENT DEASPHALTING AND PROPANE FRACTIONATION

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This invention relates to the treatment of petroleum fractions. More particularly, this invention relates to the treatment of high boiling and/or high molecular weight petroleum fractions. Still more particularly, this invention relates to an improved method of fractionating petroleum fractions such as a topped crude or long residuum.

In the manufacture of lubricating oils, asphalt, gasoline and the like from crude oil it is customary to separate a crude oil into various fractions by distillation, such as a gasoline fraction, a kerosene fraction, a diesel oil fraction, and lube oil and gas oil fractions, etc. Following the fractional distillation operation the lubricating oil fraction is usually dewaxed and solvent refined with the eventual recovery of a lubricating oil fraction having improved properties as a lubricating oil. The gas oil fraction is usually catalytically cracked with the resultant production of gasoline.

The residuum from the fractional distillation operation is usually solvent deasphalted for the recovery of asphalt and deasphalted oil which may be catalytically cracked or otherwise treated for the production of valuable petroleum products therefrom.

It is an object of this invention to provide an improved petroleum treating process.

Another object of this invention is to provide an improved method for the recovery of lubricating oil stocks and the like from petroleum residua, such as a long residuum.

Still another object of this invention is to provide a method for the recovery of lubricating oil stocks from a petroleum residuum.

Yet another object of this invention is to provide a method for the production of lubricating oil stocks at an improved yield and which are more responsive to improvement by solvent refining, such as furfural solvent refining.

How these and other objects of this invention are accomplished will become apparent in the light of the accompanying disclosure made with reference to the accompanying drawings wherein FIG. 1 graphically illustrates the compositions of various fractions of a petroleum residuum which are produced in accordance with the practice of this invention and wherein FIG. 2 schematically illustrates various embodiments of the practice of this invention applicable to the treatment of a petroleum residuum and to the recovery of lubricating oil stocks therefrom. In at least one embodiment of the practice of this invention at least one of the foregoing objects will be accomplished.

In accordance with the practice of this invention a petroleum fraction such as a residuum is solvent deasphalted. The resulting deasphalted oil is then subjected to propane fractionation to yield a first propane fractionated oil and a first bottoms fraction. The first bottoms fraction is then subjected to a second propane fractionation operation under conditions relatively less severe than the aforesaid first propane fractionation operation to yield a second propane fractionated oil and a second bottoms fraction. The first propane fractionated oil and the second propane fractionated oil are advantageously

2

separately recovered and treated for the production of lubricating oils therefrom.

In the practice of this invention the solvent deasphalting operation is carried out under conventional conditions of temperature and pressure employing a conventional deasphalting solvent. A suitable deasphalting solvent is a liquefied, normally gaseous hydrocarbon such as a hydrocarbon in the range C_2 – C_5 . Particularly suitable as a deasphalting solvent is a liquefied C_4 hydrocarbon such as isobutane or n-butane or mixtures thereof.

In the propane fractionation operations liquefied propane is employed. In the first propane fractionation operation relatively severe conditions are employed, i.e., the first propane fractionation operation is carried out at a relatively high temperature such as a temperature at or about the critical temperature of propane (206° F.). Generally a temperature in the range 2–40 degrees Fahrenheit below the critical temperature of propane is employed in the first propane fractionation operation. Sufficient pressure is employed so as to maintain the propane in the liquid state. In the first propane fractionation the solvent to feed (deasphalted oil) dosage is in the range 4–12 parts by vol. liquid propane to a part by vol. of feed.

The second propane fractionation operation is carried out under conditions relatively less severe than those employed in the first propane fractionation. In the second propane fractionation operation the bottoms fraction rejected or precipitated from the deasphalted oil in the first propane fractionation operation is subjected to propane fractionation usually at a temperature in the range 5–60 degrees Fahrenheit below the temperature employed in the first propane fractionation operation. Like the first propane fractionation operation the pressure employed is at least sufficient to maintain the propane in the liquid state and the solvent to charge oil ratio is in the range 2–12:1 by volume.

As a result of these propane fractionation operations there is recovered from the first propane fractionation step a deasphalted, propane fractionated oil having a relatively low molecular weight. This oil is responsive to treatment in a solvent refining operation, such as in a furfural solvent refining operation, including a solvent dewaxing operation, for production of a lubricating oil. From the second propane fractionation operation there is recovered a deasphalted, propane fractionated oil having a relatively high molecular weight, as compared with the aforesaid solvent deasphalted, propane fractionated oil recovered from the first propane fractionation operation. The solvent deasphalted, propane fractionated oil recovered from the second propane fractionation is also particularly useful and suitable as feed stock for the production of relatively heavy lubricating oils.

Referring now to the drawings, particularly FIG. 1 thereof, there is schematically illustrated therein the composition and properties of a petroleum fraction, such as a long residuum, suitable for treatment in accordance with the practice of this invention. As illustrated in FIG. 1 points OMNP define the composition and properties of a long residuum. When a petroleum fraction having a composition defined within the area MNOP is subjected to solvent deasphalting by contact with liquid isobutane there is recovered therefrom a deasphalted oil having a composition represented by the combined areas D, C and B and an asphaltic bottoms fraction having a composition represented by the area A, the charge to the solvent deasphalting operation being separated along line 1–1.

The resulting deasphalted oil represented by the composition $B+C+D$ is then subjected to propane fractionation under relatively severe conditions, e.g., at a temperature in the range 190 – 205° F., an 8:1 solvent to charge

ratio. From this first propane fractionation operation there is recovered a resulting propane fractionated oil having a composition represented by the area B, the charge to the propane fractionation operation being separated along line 2—2. The resulting bottoms fraction recovered from the aforesaid first propane fractionation will have a composition represented by the areas C+D.

This bottoms fraction having a composition C+D is then charged to a second propane fractionation carried out under relatively less severe conditions than said first propane fractionation, such as a temperature in the range 5–30 degrees Fahrenheit below the temperature employed in the first propane fractionation operation. As a result of the second propane fractionation operation there is recovered overhead a second propane fractionated oil having a composition represented by the area C and a second propane bottoms fraction having a composition represented by the area D, the separation of the charge to the second propane fractionation operation being carried out along the line 3—3.

In view of the foregoing separations a long residuum treated in accordance with the practice of this invention will yield a deasphalted, propane fractionated oil in an amount and having a composition indicated by the areas B+C and asphaltic bottoms fractions in an amount and having a composition represented by the areas D+A. When the second propane fractionation bottoms fraction represented by the area D is returned to the solvent deasphalting operation the separation effected in the solvent deasphalting operation will be modified to the extent that the separation will be carried out along the line 4—4.

Referring now to FIG. 2 of the drawings which schematically illustrates various embodiments in accordance with the practice of this invention a topped crude or long residuum having an initial boiling point at atmospheric pressure in the range 450–900° F. is introduced via line 10 into solvent deasphalting unit 11 wherein it is subjected to liquid-liquid contact with a liquefied, normally gaseous hydrocarbon such as n-butane or isobutane or a mixture thereof. As a result of this contacting which is carried out at a temperature approaching the critical temperature of the liquefied normally gaseous hydrocarbon employed as the deasphalting solvent, such as a temperature in the range 5–60 degrees Fahrenheit below the critical temperature of the deasphalting solvent employed, the solvent to charge ratio being in the range 4–12:1, there is recovered from solvent deasphalting unit 11 via line 12 a mixture of deasphalted oil and deasphalting solvent. The deasphalted oil-solvent mixture is introduced via line 12 into solvent-oil separator 14 for the recovery and separation of deasphalting solvent and deasphalted oil. From solvent-oil separator 14 there may be recovered via line 15 deasphalted oil in a suitable amount for charging to a catalytic cracking unit. Deasphalting solvent such as isobutane or n-butane or mixtures thereof is recovered from separator 14 via line 16. Deasphalted oil is recovered from solvent-oil separator 14 via line 18. The deasphalted oil recovered from line 18 from solvent-oil separator 14 may advantageously still have admixed therewith some of the deasphalting solvent in a minor amount, such as an amount in the range 5–35% by vol.

The resulting deasphalted oil recovered from solvent-oil separator 14 via line 18 is then introduced into first propane fractionator 19 wherein it is subjected to liquid-liquid contact with liquefied propane under relatively severe conditions of temperature and solvent dosage, such as a temperature in the range 190–205° F. and a solvent to charge oil volume dosage in the range 6–12:1. From first propane fractionator 19 there is recovered overhead via line 20 a solvent deasphalted, propane fractionated oil having a relatively low molecular weight and particularly suitable as a charge stock for the manufacture of lubricating oil. As indicated in the drawing, liquid pro-

pane employed in first propane fractionator 19 is introduced into the lower portion thereof via line 21.

There is recovered from the lower end of first propane fractionator 19 via line 22 a first bottoms fraction which is then introduced into second propane fractionator 24 wherein it is contacted with liquid propane introduced thereinto via line 25 under propane fractionation conditions relatively less severe than those employed in the aforesaid first propane fractionation operation, such as a temperature in the range 5–40 degrees Fahrenheit below the propane fractionation temperature employed in the first propane fractionation operation and a solvent to charge oil volume dosage in the range 2–12:1.

There is recovered from the second propane fractionator 24 via line 26 a solvent deasphalted propane fractionated oil particularly suitable for the manufacture of high molecular weight, viscous, heavy lubricating oils. A portion of the second bottoms fraction recovered from the lower end of second propane fractionator 24 via line 27 is desirably returned to second propane fractionator 24 via lines 28 and 22. That portion of the second bottoms fraction thus returned to the second propane fractionator serves to improve the separation effected between the propane fractionated oil and the relatively less desirable bottoms within second propane fractionator 24.

To further improve the separation effected within second propane fractionator 24 there is advantageously introduced thereto via lines 29, 28 and 22 asphaltic bottoms recovered from solvent deasphalting unit 11 via line 30. If desired, a portion of the asphaltic bottoms removed from solvent deasphalting unit 11 via line 30 may be returned or recycled thereto via lines 29, 31, 27, 32 and 10 to improve the solvent deasphalting operation carried out within solvent deasphalting unit 11 and to increase the yield of deasphalted oil recovered therefrom via line 12.

Further in accordance with yet another embodiment of the practice of this invention the petroleum fraction or long residuum supplied as charge stock via line 10 to solvent deasphalting unit 11 is also supplied as charge stock to first propane fractionator 19 via line 34. This supply as charge stock of the petroleum residuum via line 30 to first propane fractionator 19 together with the recycle of the second bottoms recovered from second propane fractionator 24 via line 27 back to solvent deasphalting unit 11 via lines 32 and 10 should result in maximum yield of deasphalted oil suitable as charge stock for catalytic cracking and recovered via line 15 from solvent-oil separator 14, as well as a minimum yield of asphalt bottoms recovered from solvent deasphalting unit 11 via line 30 for a given carbon residue specification as a charge stock to a fluid catalytic cracking unit.

As will be apparent to those skilled in the art in the light of the foregoing disclosure many modifications, alterations and changes may be made in the practice of this invention without departing from the spirit or scope thereof.

We claim:

1. A petroleum treating operation which comprises solvent deasphalting a petroleum residuum employing a liquefied C₄ hydrocarbon as the deasphalting solvent, subjecting the resulting deasphalted petroleum residuum to a first propane fractionation operation to separate therefrom a first oil fraction and a first bottoms fraction, subjecting said first bottoms fraction to a second propane fractionation operation to separate therefrom a second oil fraction and a second bottoms fraction, said first propane fractionation operation being carried out under conditions more severe than said second propane fractionation operation including a temperature within the range of 5 to 60° F. above said second propane fractionation operation, and passing said second bottoms fraction to the solvent deasphalting operation.

2. A method in accordance with claim 1 wherein said

5

first stage propane fractionation is carried out in the presence of a deasphalting solvent.

3. A method in accordance with claim 1 wherein said deasphalting solvent is isobutane.

4. A method in accordance with claim 1 wherein said deasphalting solvent is n-butane.

5. A method in accordance with claim 1 wherein an amount of said petroleum residuum is subjected to said first propane fractionation operation together with said deasphalted oil.

5**6****References Cited in the file of this patent****UNITED STATES PATENTS**

1,988,713	Bray	Jan. 22, 1935
2,086,487	Bahlke et al.	July 6, 1937
2,527,404	De Vault	Oct. 24, 1950
2,538,220	Willauer	Jan. 16, 1951

FOREIGN PATENTS

422,471	Great Britain	Jan. 7, 1935
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