

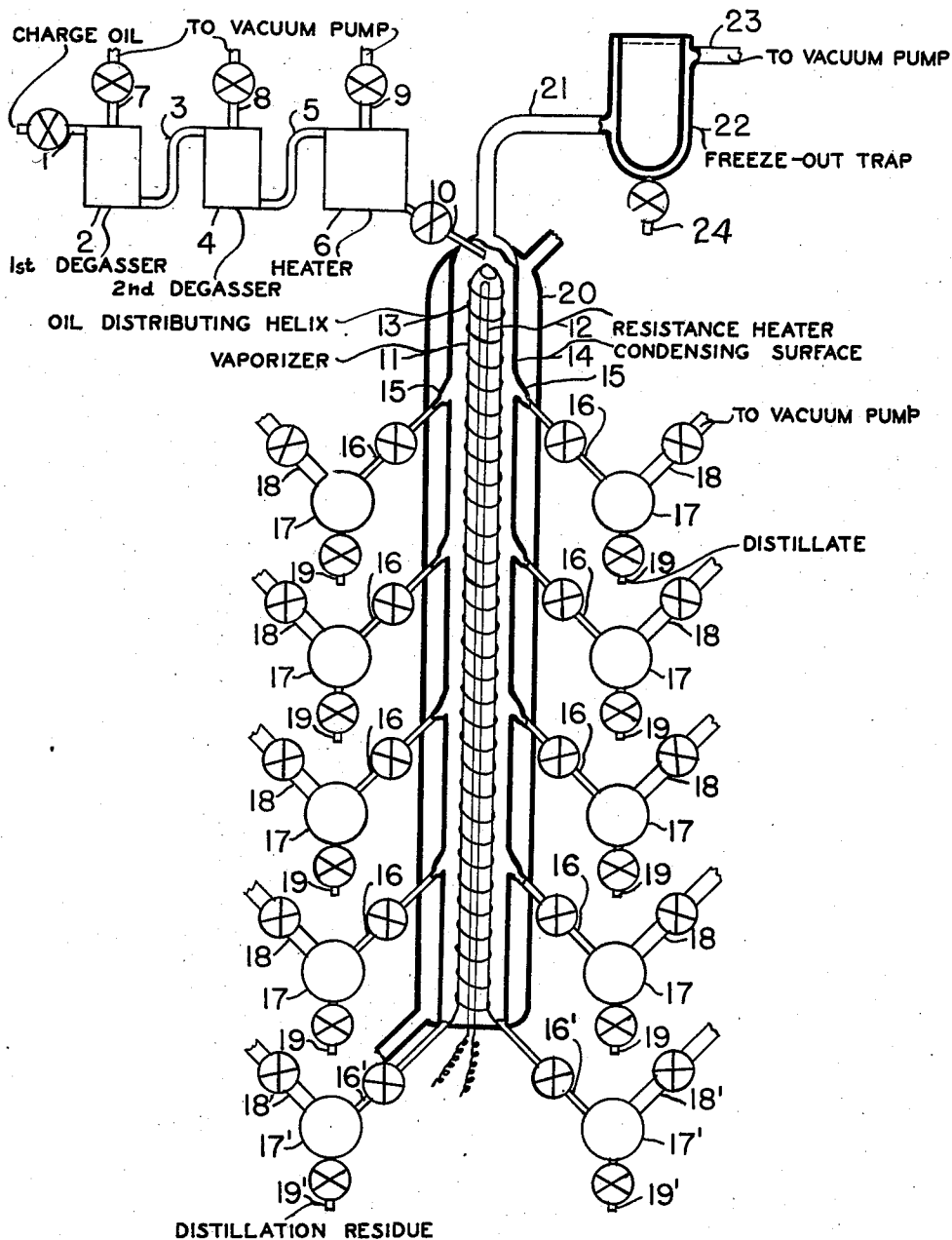
Jan. 21, 1941.

W. F. HOUGHTON

2,229,209

HYDROCARBON OIL TREATMENT

Filed Aug. 19, 1938



INVENTOR

WILLARD F. HOUGHTON

BY

Wallace J. ...
ATTORNEY

UNITED STATES PATENT OFFICE

2,229,209

HYDROCARBON OIL TREATMENT

Willard F. Houghton, Media, Pa., assignor to The
Atlantic Refining Company, Philadelphia, Pa.,
a corporation of Pennsylvania

Application August 19, 1938, Serial No. 225,673

8 Claims. (Cl. 196—77)

The present invention relates to the separation of hydrocarbon oils of relatively short boiling range and containing paraffinic and naphthenic constituents into fractions respectively richer in such constituents by "short-path" distillation at very low pressures. By "short path" distillation is meant the vaporization of oil molecules from a film of liquid oil at pressures of less than substantially 100 microns and the condensation of the vapors by contact with a condensing surface in close proximity to the vaporizing surface, the distance between the vaporizing and condensing surfaces being relatively short and preferably of the order of the mean free path of the vaporized oil molecules.

A principal object of this invention is the separation of a hydrocarbon oil of relatively short boiling range and containing paraffinic and naphthenic constituents into a plurality of fractions at least one of which is more paraffinic than the original oil and at least one of which is more naphthenic than said oil. The more paraffinic fraction or fractions may comprise one or more distillates or the distillation residue, while the more naphthenic fraction or fractions invariably comprise one or more distillates first vaporized from the oil.

Briefly, my process comprises producing by distillation, for example, by means of a conventional pipe still and fractionating column, a viscous oil fraction having a relatively short boiling range, i. e., of less than substantially 300° F. (assay distillation over point to 90% point at 10 m. m.), and then redistilling said oil fraction at a pressure of less than substantially 100 microns to separate such oil into fractions respectively more paraffinic and more naphthenic than said oil.

It is recognized in the art that mineral oils, such as petroleum, comprise essentially a mixture of hydrocarbons of various groups or homologous series of compounds, such for example, as paraffins of the general formula C_nH_{2n+2} , olefines of the general formula C_nH_{2n} , hydroaromatics and polymethylenes of the same empirical formula, and various other series of compounds of chain and/or ring structures in which the hydrogen to carbon ratio is less than in the foregoing series. A large number of individual compounds of each series and of differing boiling points are present in petroleum.

The various types of crude petroleum, which are generally classified into three groups, namely, paraffinic base, naphthenic or asphaltic base, and mixed base, contain the various series of hydrocarbons mentioned heretofore in different proportions. For example, in the paraffinic base crude oils, such as those obtained from the oil fields of Pennsylvania, there is a relatively high proportion of hydrocarbons having a chain

structure and a high hydrogen to carbon ratio, whereas in the naphthenic or asphaltic base crude oils, there is a relatively large proportion of hydrocarbons having ring structures and a low hydrogen to carbon ratio. Mixed base crude oils, such as are obtained from the Mid-Continent oil fields, contain hydrocarbons in proportions intermediate between these two extremes.

The paraffin base oils and their distillates are said to be more paraffinic than the mixed base oils and their distillates and these in turn are more paraffinic than the naphthene base oils and their distillates. Conversely the naphthene base oils are more naphthenic than the mixed base oils and these in turn more naphthenic than the paraffin base oils. The usual criteria of the degree of paraffinicity or naphthenicity of an oil are the viscosity-gravity constant and the viscosity index. The viscosity-gravity constant is a constant relating viscosity and specific gravity and is described in an article entitled "The viscosity-gravity constant of petroleum lubricating oils" by J. B. Hill and H. B. Coates which will be found in vol. 20, page 641 et seq., of Industrial and Engineering Chemistry. Viscous oils resulting from the conventional distillation of Pennsylvania type crudes have viscosity-gravity constants ranging from about .805 to about .828 and in most instances are below .820. Those resulting from the distillation of Mid-Continent crudes have viscosity-gravity constants ranging from about .835 to about .855, whereas those from naphthenic crudes are generally higher than .860. The viscosity index is a coefficient based on the change of viscosity with temperature and is described by Dean and Davis in vol. 36, page 618 of Chemical and Metallurgical Engineering. The more paraffinic oils are characterized by low viscosity-gravity constants and high viscosity indices, whereas the more naphthenic oils are characterized by higher viscosity-gravity constants and lower viscosity indices.

In the art of distillation of viscous mineral oils as heretofore practiced, the oils were separated into fractions of progressively decreasing volatility, and increasing viscosity and specific gravity. The oil fractions so separated did not differ as between themselves with respect to the types of hydrocarbons present, the paraffin base crudes yielding a series of paraffinic fractions of different viscosities and the naphthenic base crudes yielding a corresponding series of naphthenic fractions of different viscosities. In other words, distillation at atmospheric pressure or at commercially available pressures of the order of 5-10 mm. produced fractions of different molecular weights, boiling ranges, viscosities, and gravities, but such fractions exhibited no substantial change in ratio of the various types

of hydrocarbons comprising said fractions, i. e., the ratio of paraffins to naphthenes did not vary to substantial extent as between the fractions.

I have found, however, that by means of short-path distillation conducted at pressures of less than substantially 100 microns, and preferably at pressures of less than 50 microns, I am able to separate a hydrocarbon oil having a relatively short boiling range and containing paraffinic and naphthenic constituents into fractions respectively richer in paraffinic and naphthenic constituents. The hydrocarbon oils to be distilled in accordance with my invention are characterized in having a boiling or distillation range of less than substantially 300° F. at 10 m. m. pressure, and preferably of the order of 200° F. or less. While pressures of from about 50 to about 100 microns will permit a satisfactory distillation separation of many hydrocarbon oils, I prefer to employ pressures of less than 50 microns, for example, of the order of 1 to 20 microns, particularly in the distillation of the very high boiling oils.

It is well-known that viscous hydrocarbon oils, such as those within the lubricating oil range, comprise a complex mixture of hydrocarbons including hydrocarbons of the paraffinic type and hydrocarbons of the naphthenic type, many of which have substantially the same boiling point at atmospheric pressure. Separation of such hydrocarbon oils into fractions differing in chemical composition, i. e., fractions more paraffinic and more naphthenic than the initial oil, cannot be effected by conventional distillation at atmospheric pressure or at reduced pressures of the order of 5-10 m. m. which are now commercially available, since the values of the temperature coefficient of the vapor pressure of the paraffinic and naphthenic constituents are not significantly different at atmospheric pressure or reduced pressures of the order of 5-10 m. m. Heretofore the only practical method of separating oils into paraffinic and naphthenic oil fractions has been selective solvent extraction with solvents having preferential solvent power for naphthenic oil constituents.

However, I have found that even complex, viscous hydrocarbon oils, and particularly those having a relatively short boiling range, may be separated into fractions respectively more paraffinic and more naphthenic by distillation at pressures such that the values of the temperature coefficient of the vapor pressure of the paraffinic and naphthenic hydrocarbons are substantially different. By reason of this change in the relative partial pressures of the paraffinic and naphthenic constituents at very low pressures, i. e., less than about 100 microns, I am able to effectively separate a relatively close-boiling oil into fractions of different chemical types, e. g., fractions respectively richer in paraffinic and naphthenic constituents. By operating at pressures of less than substantially 100 microns, and preferably at pressures of less than 50 microns, the partial pressure of the naphthenic constituents is much greater than that of the paraffinic constituents and separation by distillation may be effected, although the partial pressures of both may be substantially the same at atmospheric pressure.

Short-path or high vacuum distillation apparatus suitable for carrying out my distillation separation of a viscous mineral oil into at least one fraction more paraffinic than the initial oil and at least one fraction more naphthenic than

said initial oil is shown in the accompanying drawing.

Referring to the drawing, hydrocarbon oil having a relatively short boiling range, i. e., less than substantially 300° F., is introduced through valve-controlled line 1 into a conventional electrically-heated degassing unit 2 wherein the oil is heated to a temperature, for example, 175° F. to 300° F. under a pressure of the order of 2 m. m. to 15 m. m. in order to remove the major portion of the dissolved gases and moisture contained in the oil. The partially degassed and dehydrated oil is then passed from the first degassing unit by means of line 3 into a second unit 4 operating within substantially the same temperature range as unit 1 but at a reduced pressure of, for example, 50 to 150 microns. In the unit 4 traces of dissolved gas, as well as a small amount, i. e., usually less than 1%, of the lowest boiling components of the charge oil is removed. The degassed oil is then introduced by means of line 5 into an electrically heated heating unit 6 operating at substantially the same reduced pressure and at the same or slightly higher temperature than that employed in the degassing unit 4. The heating unit 6 is utilized primarily for maintaining the oil at the desired temperature prior to its introduction into the short-path distillation apparatus. Reduced pressure is maintained in the degassing units 2 and 4, and the heating unit 6, by means of valve-controlled lines 7, 8 and 9, respectively, which are connected to a conventional evacuating system (not shown).

The heated charge oil from the heating unit 6 is introduced, by means of valve-controlled line 10, upon the upper closed end of a tubular member 11 constituting the vaporizer of the distillation apparatus. The tubular member 11 is heated internally by suitable means, for example, electrically heated resistance wire 12, and such member is provided externally with a spiral member 13 for effecting a uniform distribution of the oil over the surface of the tubular member 11 and to increase the surface of such vaporizing member. Since the spiral member 13 is preferably snugly wound about the tubular member 11, a portion of the oil introduced at the upper end of member 11 flows downwardly along the spiral while the remainder flows downwardly over the surface of the tubular member 11 between the turns of the spiral member 13. Surrounding the tubular member 11 is a jacket 14 provided with a plurality of gutters 15, each connected by means of a valve-controlled line 16 to a receiver 17. Each of the receivers 17 is provided with a valve-controlled line 18 connected to a suitable evacuating means (not shown), and with a valve-controlled drawoff line 19. Surrounding the jacket 14 is a second jacket 20 through which may be circulated a cooling medium such as air, gas, water or other cooling agent. Jacket 14 is spaced from the tubular vaporizing member 11 only a relatively short distance, i. e., of the order of 2 inches or less, and constitutes the condensing surface upon which the vaporized oil or distillate is condensed. The jacket 14 is provided at its upper end with a line 21 connected with a freeze-out trap 22, which, in turn, is connected to an evacuating means (not shown) by line 23. The freeze-out trap 22 comprises simply a double-walled vessel, the inner chamber of which is filled with a refrigerant such as liquefied nitrogen or a mixture of acetone and solidified car-

bon dioxide, the upper surface of the refrigerant in the chamber being shown by the dotted line. Any volatile materials passing from the top of the distillation column through line 21 are condensed upon the outer surface of the inner chamber and may be withdrawn, when necessary, from the bottom of the trap by means of valve 24. Similarly, if a mercury vapor pump is employed as the evacuating means, such trap functions to condense mercury vapors which may diffuse through line 23 and prevents same from entering the distillation column. During operation of the distillation apparatus, a reduced pressure of less than substantially 100 microns, and preferably less than 50 microns, is maintained within the jacket 14 and the receivers 17.

The oil, in passing downwardly over the heated tubular member 11 is brought to a vaporizing temperature, the more volatile components thereof being vaporized in the upper section of the distillation apparatus, and the progressively less volatile components in the successively lower sections. The vapors, upon condensation upon the walls of jacket 14, form distillate fractions which are collected by the gutters 15 and withdrawn therefrom by means of valve-controlled

line 16 into the evacuated receivers 17. While, in the accompanying drawing, only four sets of gutters and receivers are provided for collecting and removing distillate fractions, a greater or lesser number may be employed. Each gutter is connected with two receivers in order that one may be emptied while the other is being filled, thus providing a continuous distillation process. The unvaporized portion of the oil, upon reaching the lower end of the tubular member 11, is withdrawn from the bottom of the jacket 14 by means of valve-controlled lines 16' into receivers 17' evacuated by suitable evacuating means connected to valve-controlled lines 18', and may be removed therefrom, when necessary, through valve-controlled lines 19'.

My invention may be further illustrated by the following examples, which, however, are not to be construed as limiting the scope thereof. A variety of viscous hydrocarbon oils having boiling ranges of less than substantially 300° F. at 10 m. m. pressure were distilled in a short-path distillation apparatus similar to that above described, and the properties of the initial oils and the products of distillation thereof are given in the following tables.

Stock	Distillation conditions	Properties	Charge	Distillates					Btms.
				Cut 1	Cut 2	Cut 3	Cut 4	Cut 5	
Vacuum distillate from East Texas residuum. Boiling range (10 mm.) 500-700° F.	Pressure 4.1 microns. Max. dist. temp. 392° F.	Vol. percent yield..... API grav.....degrees..... SU vis./130° F.....seconds..... SU vis./210° F.....do..... Vis.-grav. const..... Vis.-index..... O. D. color.....	100.0 20.6 689 100 0.861 31 661	18.3 18.3 403 70 0.885 14 170	17.8 19.9 550 83 0.866 4 195	12.5 21.0 571 89 0.860 25 248	8.9 21.7 590 93 0.854 43 314	8.0 21.7 650 100 0.853 47 387	34.5 21.6 1223 159 0.844 71 1799

Stock	Distillation conditions	Properties	Charge	Distillates					Btms.
				Cut 1	Cut 2	Cut 3	Cut 4	Cut 5	
Distillate from mixture of East Texas and Venezuela crudes. Boiling range (10 mm.) 445-615° F.	Pressure 2.9 microns. Max. dist. temp. 326° F.	Vol. percent yield..... API grav.....degrees..... SU vis./130° F.....seconds..... SU vis./210° F.....do..... Vis.-grav. const..... Vis.-index..... O. D. color.....	100.0 20.7 365 69 0.863 8 372	30.9 18.4 278 59 0.892 23 29	23.8 20.1 377 69 0.874 -6 42	13.7 21.6 383 72 0.861 20 56	8.7 22.8 378 74 0.851 38 70	6.7 23.6 386 79 0.842 66 84	16.1 23.2 573 95 0.842 58 2640

Stock	Distillation conditions	Properties	Charge	Distillates					Btms.
				Cut 1	Cut 2	Cut 3	Cut 4	Cut 5	
Nitrobenzene raffinate oil from East Texas-Venezuela distillate. Boiling range (10 mm.) 470-662° F.	Pressure 3.0 microns. Max. dist. temp. 327° F.	Vol. percent yield..... API grav.....degrees..... Su vis./130° F.....seconds..... SU vis./210° F.....do..... Vis.-grav. const..... Vis.-index.....	100.0 28.0 199 59 0.818 87	27.6 26.8 156 51 0.822 55	22.5 27.6 191 56 0.822 65	13.8 29.8 194 58 0.805 86	9.6 29.2 206 60 0.808 88	7.2 29.4 220 61 0.806 85	20.2 29.3 305 72 0.803 88

Stock	Distillation conditions	Properties	Charge	Distillates					Btms.
				Cut 1	Cut 2	Cut 3	Cut 4	Cut 5	
Nitrobenzene extract oil from East Texas-Venezuela distillate. Boiling range (10 mm.) 474-700° F.	Pressure 2.3 microns. Max. dist. temp. 320° F.	Vol. percent yield..... API gravity.....degrees..... SU vis./210° F.....seconds..... Vis.-grav. const.....	100.0 14.9 93 0.911	30.6 13.6 67 0.930	22.0 14.3 86 0.918	13.9 14.9 99 0.910	8.3 15.4 106 0.904	7.7 15.9 112 0.898	17.1 15.3 188 0.895

Stock	Distillation conditions	Properties	Charge	Distillates					Btms.
				Cut 1	Cut 2	Cut 3	Cut 4	Cut 5	
White oil from Russian crude. Boiling range (10 mm.) 400-700° F.	Pressure 2.6 microns. Max. dist. temp. 325° F.	Vol. percent yield..... API grav.....degrees..... SU vis./100° F.....seconds..... SU vis./210° F.....do..... Vis.-grav. const..... Vis.-index.....	100.0 27.9 360 53 0.822 78	42.4 28.0 192 45 0.835 69	24.5 26.2 576 59 0.830 53	8.5 27.4 610 63 0.820 67	4.6 28.7 590 64 0.810 78	3.3 29.1 615 66 0.806 82	16.3 29.3 886 82 0.800 95

It will be seen, from the above examples, that in accordance with my invention I am able to separate hydrocarbon oils having a relatively short boiling range into fractions relatively more paraffinic and more naphthenic, respectively, than the initial oil. In the above examples the 1st or the 1st and 2nd distillate fractions are more naphthenic than the initial oil, whereas the succeeding fractions and residue or bottoms are more paraffinic than the initial oil. This is clearly evident from a comparison of the viscosity-gravity constants of the initial oil and the various distillate fractions and residue, the 1st and 2nd distillate fractions having a higher viscosity-gravity constant than the initial oil, and the succeeding fractions and residue having lower viscosity-gravity constants than said initial oil. While, in the above examples, five distillate fractions and a residue were obtained, the distillation may be carried out in such a manner as to yield a greater or lesser number of fractions, and the fractions may be blended with one another as desired. Or the initial oil may be separated by short-path distillation into only one distillate fraction more naphthenic than the initial oil and a residue which is more paraffinic than said initial oil. While I prefer to effect short-path distillation in a continuous distillation system, I may also carry out such distillation in a batch system of suitable design. Furthermore, the initial oil or the distillate fractions or the residue may be subjected to any desired refinery treatment such as solvent extraction, dewaxing, fuller's earth or other adsorbent treatment, acid treatment or other chemical treatment.

In another aspect of my invention, the distillate or residue produced by my short-path distillation of a relatively close-cut hydrocarbon oil may be redistilled at low pressure to effect a further separation of paraffinic and naphthenic oil components. For example, a crude petroleum oil may be distilled at atmospheric or reduced pressure to yield an oil fraction having a boiling range of less than substantially 300° F.; such fraction may then be subjected to short-path distillation at a pressure of, for example, 50 microns, to produce one or more distillate fractions and a residue; and finally one or more of the fractions or residue so produced may be redistilled at a pressure of, for example, 5 microns, whereby a further separation of components of the fraction or residue may be obtained.

Or, alternatively, one or more fractions or the residue from the first mentioned short-path distillation operation may be redistilled at a higher pressure, for example, of from about 1 to 10 mm. or higher. In the latter case the first distillates produced at pressures of the order of 1 to 10 mm. will be more paraffinic than the oil charged, and will tend to become less paraffinic as the distillation progresses, the final distillation residue being, in general, more naphthenic than the oil charged.

What I claim is:

1. The method of separating hydrocarbon oil containing paraffinic and naphthenic constituents into a plurality of fractions of progressively increasing paraffinic, which comprises producing by distillation a viscous hydrocarbon oil having a boiling range of less than substantially 300° F. at 10 m. m. pressure, heating said oil at a pressure not substantially in excess of 100 microns to vaporize therefrom oil constituents of progres-

sively increasing paraffinic, and condensing the vaporized constituents to produce liquid oil fractions of progressively increasing paraffinic.

2. The method of separating hydrocarbon oil containing paraffinic and naphthenic constituents into a plurality of fractions of progressively increasing paraffinic, which comprises producing by distillation a viscous hydrocarbon oil having a boiling range of less than substantially 300° F. at 10 m. m. pressure, heating said oil at a pressure not substantially in excess of 100 microns to vaporize therefrom oil constituents of progressively increasing paraffinic, and condensing such constituents substantially immediately upon vaporization to produce liquid oil fractions of progressively increasing paraffinic.

3. The method of claim 2, wherein the pressure during vaporization of the oil is not substantially in excess of 50 microns.

4. The method of separating hydrocarbon oil having a boiling range of less than substantially 300° F. at 10 m. m. pressure and containing paraffinic and naphthenic constituents into distillate fractions at least one of which is more paraffinic and at least one of which is more naphthenic than said hydrocarbon oil, which comprises heating said oil at a pressure not substantially in excess of 100 microns to vaporize therefrom paraffinic and naphthenic oil constituents, and condensing the vaporized constituents into fractions respectively more paraffinic and more naphthenic than said hydrocarbon oil.

5. The method of separating hydrocarbon oil having a boiling range of less than substantially 300° F. at 10 m. m. pressure and containing paraffinic and naphthenic constituents into a distillate fraction more naphthenic than said hydrocarbon oil and a residue more paraffinic than said hydrocarbon oil, which comprises vaporizing from said oil, at a pressure not substantially in excess of 100 microns, the more naphthenic components thereof, and condensing said components out of contact with the unvaporized, more paraffinic residual oil.

6. The method of separating viscous hydrocarbon oil having a boiling range of less than substantially 300° F. at 10 m. m. pressure and containing paraffinic and naphthenic constituents into a distillate fraction more naphthenic than said hydrocarbon oil and a residue more paraffinic than said hydrocarbon oil, which comprises heating said oil at a pressure not substantially in excess of 100 microns whereby the boiling points of the naphthenic constituents are decreased to a substantially greater extent than those of said paraffinic constituents, vaporizing substantially greater quantities of naphthenic constituents than of paraffinic constituents, condensing the vapors substantially immediately upon vaporization and collecting the condensate to produce at least one fraction more naphthenic than the initial hydrocarbon oil and a residue more paraffinic than said initial hydrocarbon oil.

7. The method of separating hydrocarbon oil containing paraffinic and naphthenic constituents into fractions respectively richer in paraffinic and naphthenic constituents which comprises producing by distillation a viscous hydrocarbon oil having a boiling range of less than substantially 300° F. at 10 m. m. pressure and distilling from said oil the more naphthenic constituents thereof at a pressure not substantially in excess of 100 microns.

8. In the method of separating hydrocarbon oil containing paraffinic and naphthenic constituents into fractions respectively richer in paraffinic and naphthenic constituents, the step which comprises subjecting a viscous oil having a boiling

range of less than substantially 300° F. at 10 m. m. pressure and containing paraffinic and naphthenic constituents to distillation at a pressure not substantially in excess of 100 microns.

WILLARD F. HOUGHTON. 5