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D. CHURCHILL, JR

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PROCESS OF EXTRACTING HYDROCARBON MATERIAL

Filed March 13, 1934

2 Sheets-Sheet 1

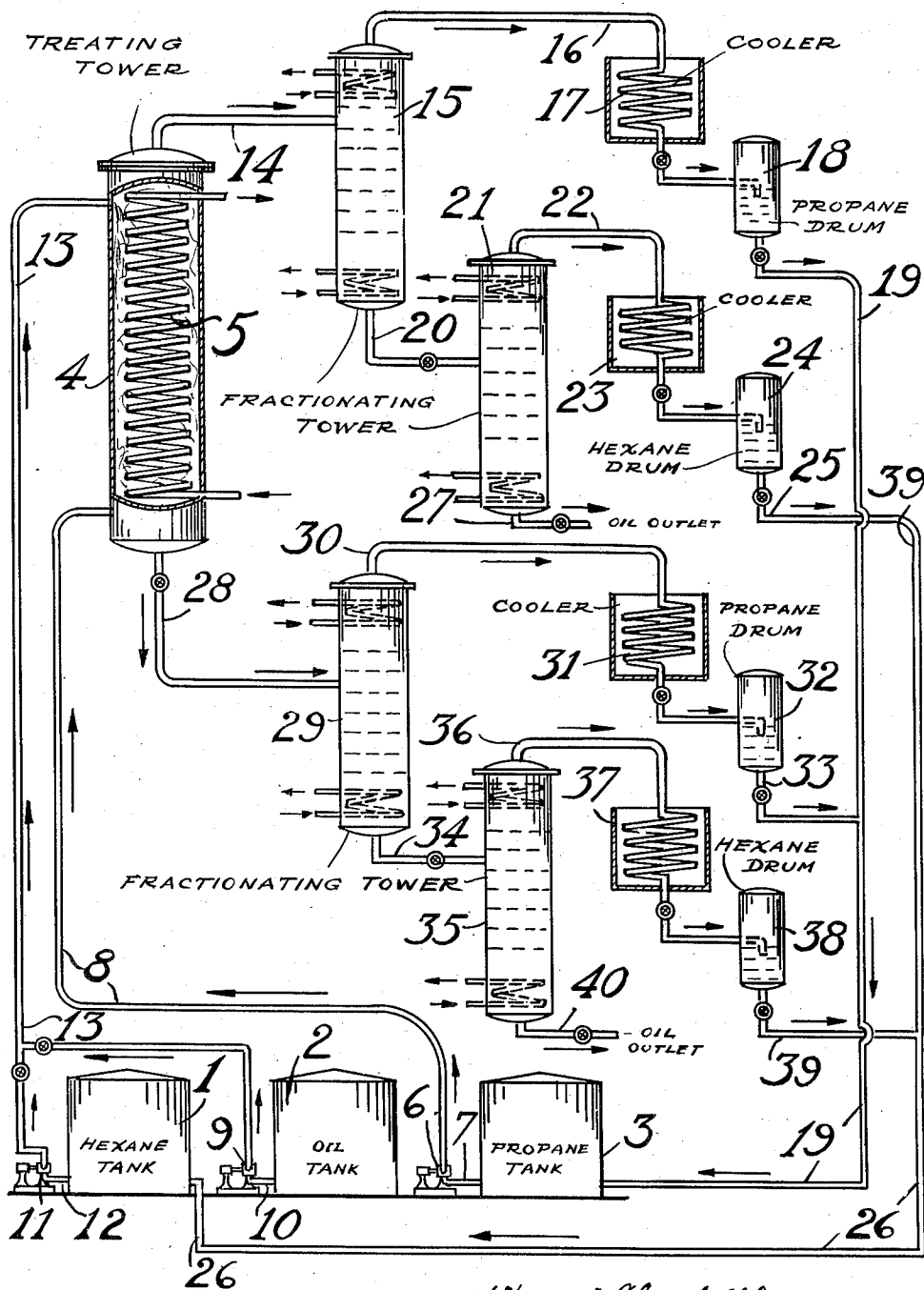


Fig. 1

D. Churchill, Jr. Inventor
P. L. Young Attorney

May 3, 1938.

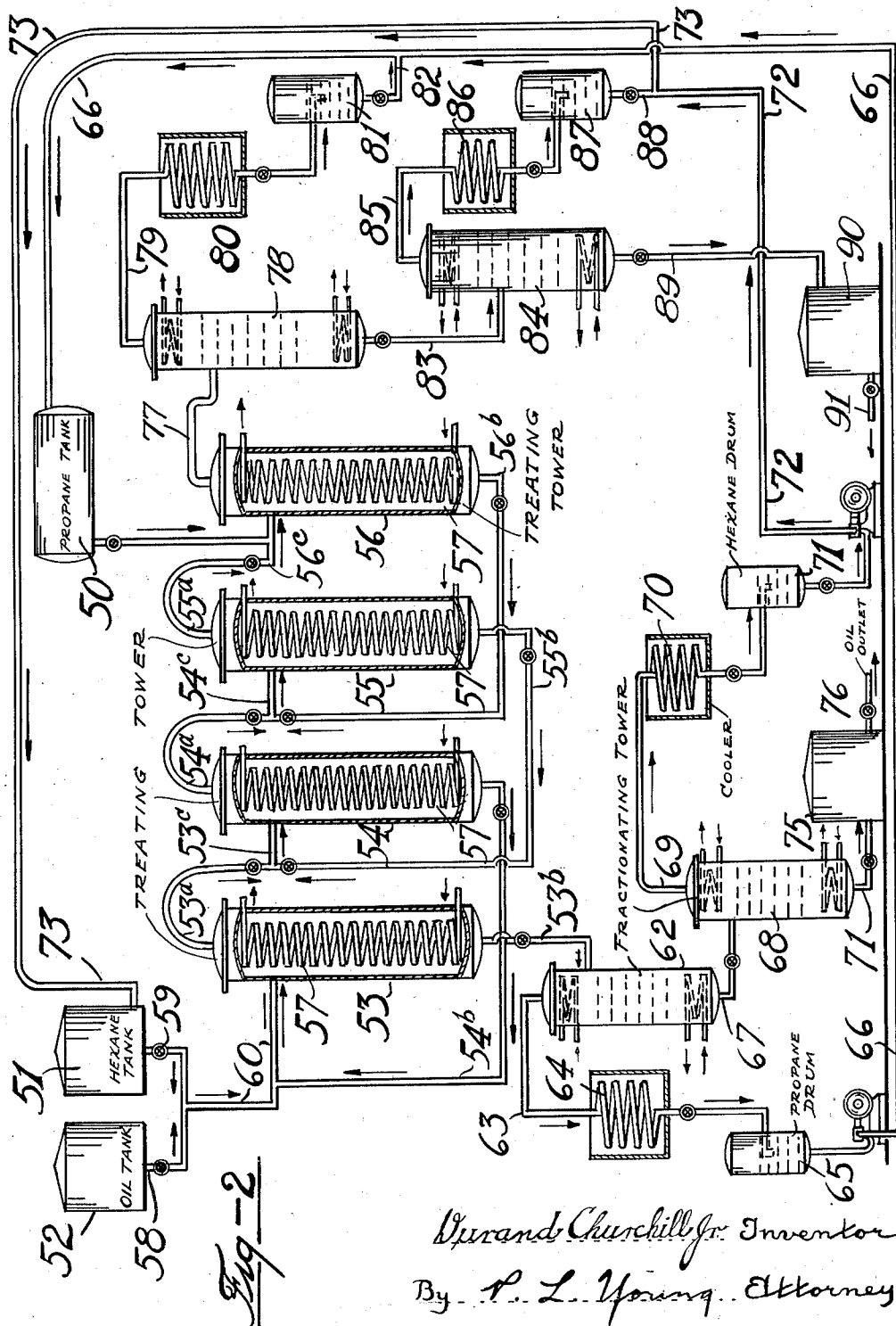
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2 Sheets-Sheet 2



UNITED STATES PATENT OFFICE

2,116,188

PROCESS OF EXTRACTING HYDROCARBON MATERIAL

Durand Churchill, Jr., New York, N. Y., assignor
to Standard Oil Development Company, a corporation of Delaware

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2 Claims. (Cl. 196—13)

This invention relates to a process for extracting hydrocarbon material, with the primary object of separating the hydrocarbon material into its constituent parts.

It has already been proposed to treat hydrocarbon material with liquefied normal gaseous hydrocarbons such as ethane, propane and butane, and it has been found that the density of the liquefied hydrocarbon extracting agent has an important effect upon the results obtained. For example, it has been found that by regulating the density of the liquefied hydrocarbon solvent the hydrocarbon material may be separated into two fractions having different molecular weight and/or characteristics. Several methods for varying the density of the liquefied hydrocarbon solvent have been suggested. One method is to change the temperature at which the liquefied hydrocarbon solvent is used. Another method is to vary the composition of the liquefied hydrocarbon solvent, that is to say to vary the proportion of lighter and heavier liquefied hydrocarbon components of the solvent. A third method is to vary the pressure under which the treatment is carried out. Each of these three methods effects a change of density of the liquefied hydrocarbon solvent and as the density of the solvent is changed its selective action on the hydrocarbon material is also varied.

The present invention is concerned with a fourth and new method for changing the density of a liquefied hydrocarbon solvent used in the extraction of hydrocarbon material. This method consists essentially in adding to the liquefied hydrocarbon solvent a substance miscible or substantially miscible with the liquid hydrocarbon solvent and capable of increasing its density.

The term "hydrocarbon material" as used herein will be understood to mean liquid hydrocarbons, solid hydrocarbons or mixtures of liquid and solid hydrocarbons. It embraces generally any hydrocarbon material containing fractions of different molecular weight and/or composition or characteristics whether obtained by distillation, destructive distillation, hydrogenation, destructive hydrogenation, or cracking of petroleum oils, shale oils, mineral oils, coals, tars, pitches, bitumens, resins and the like. Also included are hydrocarbons prepared by synthetic processes, by volatilization, or by polymerization, or condensation, in the presence of catalytic materials such as aluminum chloride, sulphuric acid, boron halides, tin tetrachloride and the like. The hydrocarbon material may be a light distillate such as heavy naphtha, kerosene or gas oil, or a heavier

distillate such as lubricating oil, gear oil, or transmission oil, and may also comprise a residue or heavy bottoms. The hydrocarbon material may comprise a crude paraffin wax, heavy paraffin distillates, and solid hydrocarbon carbonaceous materials such as paraffin wax or ozokerite, and the like, or mixtures of these with liquid hydrocarbons. It will be understood that the hydrocarbon material, before being subjected to extraction according to the present process, may be subjected to any of the usual refining treatments such as acid and clay treating, deasphaltizing and dewaxing. If the hydrocarbon material is to be deasphaltized and/or dewaxed prior to extraction according to the present process these operations may be advantageously carried out with liquefied hydrocarbons such as ethane, propane or butane, inasmuch as these materials will be used in the subsequent extraction.

The extracting agent used in the present process may be any hydrocarbon having 1 to 5 carbon atoms or any mixture of these. As examples of suitable light hydrocarbons may be mentioned methane, ethane, propane, butane, pentane, ethylene, propylene, butylene, iso-butane, iso-butylene, iso-pentane, amylene, iso-amylene, or mixtures of any of these, and in general any material relatively rich in hydrocarbons having 1 to 5 carbon atoms. A suitable source of these light hydrocarbons is the gases produced either in a cracking or destructive hydrogenation process, which are relatively rich in propane and butane. Stabilizer bottoms obtained in the stabilization of gasoline also provide a readily available source of the preferred light hydrocarbons.

The density-increasing substance to be added to the liquefied hydrocarbon extracting agent may be any material heavier than the liquefied hydrocarbons which is miscible or substantially miscible therewith. Suitable materials for this purpose are hydrocarbons having 6 carbon atoms or more, preferably hydrocarbons having between 6 and 10 carbon atoms, such as hexane, heptane, octane, nonane, decane, hexylene, heptylene, octylene, nonylene, decylene, heavy naphthas, kerosene, gas oil, or even light lubricating oils. Other materials that are suitable for this purpose are benzol, acetone, pyridine, hydrogenated naphthas or low boiling hydrocarbons prepared by the hydrogenation or destructive hydrogenation of petroleum oils or fractions or extracts thereof, low boiling hydrocarbons prepared by the polymerization or condensation of normally gaseous hydrocarbons, chlorinated hydrocarbons such as chloroform and carbon tetrachloride, and

in general any substance having the characteristics indicated above.

The nature of the process and the method of carrying it out will be fully understood from the following description read with reference to the accompanying drawings, of which—

Figure 1 is a semi-diagrammatic view in sectional elevation of a type of apparatus adapted for carrying out the process in a countercurrent manner in a single tower, and

Figure 2 is a semi-diagrammatic view in sectional elevation of a suitable type of apparatus for carrying out the process in a countercurrent manner in a series of towers.

In the description the liquefied hydrocarbon extracting agent will be denoted by the word "propane", which is typical of the type of extracting agent used. Similarly, the density-increasing substance which is added to the liquefied hydrocarbon solvent will be denoted by the term "hexane", which may be taken as typical of a suitable density-increasing substance for use according to the present invention. The hydrocarbon material to be extracted will be denoted by the term "oil."

Referring to Figure 1, numeral 1 designates a supply tank for hexane. Numeral 2 designates a supply tank for oil to be treated. Numeral 3 designates a supply tank for propane, and numeral 4 designates a treating tower. Tower 4 is provided with a coil 5, which is adapted to be supplied either with a heating medium or a cooling medium, by means of which the temperature within the tower may be regulated.

Propane is withdrawn from tank 3 by pump 6, through line 7, and is discharged through line 8 into the bottom portion of tower 4. Oil is withdrawn from tank 2 by pump 9, through line 10, hexane is withdrawn from tank 1, by pump 11, through line 12, and a mixture of hexane and oil is discharged through line 13 into the upper portion of tower 4.

In tower 4 the mixture of oil and hexane flows downwardly in countercurrent relationship to the upwardly rising stream of propane. In this way the propane as it rises through the tower becomes richer and richer in hexane and its density is thereby progressively increased. The initial density of the propane is maintained sufficiently low to cause a separation of the oil into constituent parts by maintaining a suitably high temperature in the tower. The oil is thereby separated into two fractions.

The lighter fraction is removed from tower 4, through line 14, and is discharged into a fractionating tower 15, wherein propane is flashed off. The propane vapors leave tower 15, through line 16, pass through cooler 17, and condensed propane is collected in drum 18, from which it may be withdrawn and returned to the main propane supply tank 3, through line 19. The propane free material is removed from tower 15, through line 20, and is discharged into a second fractionating tower 21, wherein hexane is distilled off. The vapors of hexane flow out of tower 21, through line 22, pass through cooler 23, and the condensed hexane is collected in drum 24, from which it may be withdrawn and returned to the main hexane supply tank 1, through lines 25 and 26. The oil is withdrawn from tower 21, through line 27.

The heavier fraction formed in tower 4, is withdrawn therefrom through line 28 and discharged into fractionating tower 29, from which propane vapors are withdrawn through line 30,

passed through cooler 31, and collected in drum 32, from which the propane may be withdrawn and returned to the main propane supply tank 3, through lines 33 and 19.

The propane free extract is withdrawn from tower 29, through line 34, and introduced into fractionating tower 35, from which hexane vapors are withdrawn through line 36 and passed through cooler 37 and collected in drum 38, from which the hexane may be withdrawn and returned to the main hexane supply tank 1, through lines 39 and 26. The oil is withdrawn from tower 35 through line 40.

Referring to Figure 2, numeral 50 designates a supply tank for propane. Numeral 51 designates a supply tank for hexane, and numeral 52 a supply tank for oil to be treated. Numerals 53, 54, 55 and 56 designate four treating towers each of which may be provided with a temperature regulating coil 57, which is adapted to be supplied either with a heating medium or a cooling medium.

Oil is withdrawn from tank 52, through line 58, and hexane is withdrawn from tank 51, through line 59. The mixture of the two flows through line 60, and discharges into the upper portion of tower 53.

Propane is withdrawn from tank 50, through line 61 and discharges into the upper portion of tower 56.

Temperature is maintained in the four towers sufficiently high to cause the propane to effect a separation of the oil into two phases.

The upper layer from tower 53 is withdrawn through line 53a and introduced into the upper portion of tower 54 through line 53c. The upper layer from tower 54 is withdrawn through line 54a and is introduced into the upper portion of tower 55, through line 54c. Similarly the upper layer in tower 55 is withdrawn through line 55a and discharged into the upper portion of tower 56 through line 56c.

The bottom layer in tower 56 is withdrawn through line 56b and is introduced into the upper portion of tower 55 through line 54c. The bottom layer in tower 55 is withdrawn through line 55b and introduced into the upper portion of tower 54 through line 53c. Similarly the bottom layer in tower 54 is withdrawn through line 54b and introduced into the upper portion of tower 53 through line 60, along with the entering oil and hexane.

The bottom layer in tower 53 is withdrawn through line 53b and introduced into fractionating tower 62, wherein propane is distilled off. The propane vapors are removed through line 63, passed through cooler 64 and are collected in drum 65, from which the condensed propane may be withdrawn and returned to the main propane supply tank 50 through line 66. The propane free material in tower 62 is withdrawn therefrom through line 67 and introduced into a second fractionating tower 68, wherein hexane vapors are flashed off and withdrawn through line 69, passed through cooler 70, and collected in drum 71, from which the hexane may be withdrawn and returned to the main hexane supply tank 51, through lines 72 and 73. The oil is withdrawn from tower 68 through line 74, and may be collected in drum 75 from which it is withdrawn through line 76.

The upper layer in tower 56 is withdrawn therefrom through line 77, and introduced into tower 78 wherein propane is flashed off, the vapors removed through line 79, passed through

cooler 80 and collected in drum 81, from which the condensed propane may be withdrawn and returned to the main propane supply tank 50, through lines 82 and 66.

5 The propane-free material in tower 78 is withdrawn through line 83 and introduced into fractionating tower 84, wherein hexane is flashed off and the vapors are removed through line 85, passed through cooler 66, and collected in drum 87, from which hexane may be withdrawn and returned to the main hexane supply tank 51, through lines 88 and 73. The oil is withdrawn from tower 84, through line 89, and collected in drum 90, from which it may be withdrawn through line 91.

15 In the operation of the process the important variables are the temperature at which the treatment is carried out, the pressure maintained during the treatment, the proportions of hydrocarbon material and extracting agent, and the quantity of density increasing substance added to the extracting agent.

20 The temperature of the treatment may be varied widely. In general, the minimum temperature in any particular case will be the melting point of the material to be extracted. Similarly, the maximum temperature would be the temperature at which the hydrocarbon material or a part thereof begins to crack. Temperatures between say -50°F. and 600°F. will ordinarily be suitable. The temperature maintained in the treating tower is preferably regulated so that at the treating temperature the density of the liquefied hydrocarbon extracting agent will be sufficiently low to cause a separation of the hydrocarbon material into constituent parts. It will be understood that the selectivity of the liquefied hydrocarbon solvents changes appreciably with temperature, inasmuch as the change of temperature causes a change in density of the solvent. Therefore, depending upon the particular type of separation desired, the temperature in the treating tower may be regulated accordingly. Having once selected a particular temperature at which the liquefied hydrocarbon solvent will cause the degree of separation desired, the density of the liquefied hydrocarbon solvent is thereafter varied to cause a change in the density, and, therefore, the selectivity of the solvent by the addition of a density-increasing substance. It is also possible to change the density of the liquefied hydrocarbon solvent by progressively changing the temperature simultaneously with a progressive change in the quantity of density-increasing substance added, although the change of density by merely changing temperature per se forms no part of the present invention. A particular advantage of the present method of changing the density, that is to say by adding a density-increasing substance, is that the temperature in the treating tower may be maintained substantially constant during the treatment.

65 The pressure maintained in the treating tower should be at least sufficient to retain the light hydrocarbon solvent in the liquid phase. This pressure, naturally, will depend upon the particular light hydrocarbon selected as a solvent and upon the temperature of working. In general, the required pressure will be between atmospheric and 20 or 50 atmospheres or more. It is also possible to vary the density of the light hydrocarbon solvent by varying the pressure maintained during the treatment simultaneously with a change in density by the addition of a

density-increasing substance. This method of changing the density is particularly useful when operating at temperatures above the critical temperature of the solvent, under which conditions, by a very slight change in pressure, the density of the light hydrocarbon solvent may be substantially changed. The variation of density by changing pressure per se, however, forms no part of the present invention.

10 The quantity of light hydrocarbon solvent used may vary between about 2 and 12 volumes per volume of hydrocarbon material. It is preferred, however, to use from 3 to 8 volumes per volume of hydrocarbon material. The quantity of density-increasing substance added to the light hydrocarbon solvent may be varied over a wide range, say from 10 to 90%, depending upon the particular density-increasing substance selected. It will be understood that although in the description the density of the light hydrocarbon solvent is progressively increased by the addition thereto of a density-increasing substance, the process may be carried out in a reverse manner, that is to say the density may be progressively decreased by starting out with a mixture relatively rich in the density-increasing substance, and gradually adding more and more of the light hydrocarbon solvent.

25 It will be understood, also, that the density of the light hydrocarbon solvent may be varied by the simultaneous addition of a density-increasing substance and the variation of the composition of the liquefied hydrocarbon solvent itself. Thus, for example, if the liquefied hydrocarbon consists of a mixture of propane and ethane, the density of this mixture may be varied by changing the proportions of propane and ethane. The variation of density by this means per se, however, forms no part of the present invention. It will also be understood that the density of the light hydrocarbon solvent may be varied by all four methods simultaneously, although in general the variation of density by the present method alone is preferred.

30 The process has been described as being carried out in a countercurrent manner. It may also be carried out, however, with equally satisfactory results as a batch process or in a series of batch operations.

35 The present process is particularly useful in the extraction of a solid hydrocarbon material, which may be first dissolved in one of the density-increasing substances and thereafter certain portions of the dissolved material may be precipitated by the addition of progressively increasing quantities of a light hydrocarbon solvent. Thus, for example, to cite a specific case, crude paraffin wax may be dissolved in a heavy naphtha or a light gas oil and thereafter progressively increasing quantities of propane may be added to the solution, whereby heavy tarry fractions and colored bodies may be caused to separate from the solution, leaving a substantially pure wax dissolved in the naphtha or light gas oil. It will be seen from this example that, in effect, by means of the present process a solvent having the same density as a light hydrocarbon, such as butane, may be approximated by a mixture of a material having a much greater density than butane with a light hydrocarbon having a density lower than that of butane.

70 Various modifications of the present process may be made, as will be understood. The products obtained according to this process may be subjected either in the presence or absence of

the solvent to any of the usual refining treatments, such as acid and clay treatment, dewaxing, hydrogenation, destructive hydrogenation, polymerization or condensation, selective solvent refining, by any of the known methods. In many cases the oils obtained according to this treatment are better adapted for destructive hydrogenation and cracking processes and selective solvent refining processes than are the initial materials, because during the treatment a substantial portion of the tarry and asphaltic bodies are removed therefrom, with the result that a much wider fraction of oil may be subjected to destructive hydrogenation or cracking without encountering the difficulties incident to the presence in the heavier fractions of tarry and asphaltic bodies.

This invention is not limited by any theories of the mechanism of the reactions nor by the details which may have been given merely for pur-

poses of illustration, but is limited only in and by the following claims in which it is my intention to claim all novelty inherent in the invention.

I claim:

1. Process for separating hydrocarbon material into constituent parts which comprises extracting the hydrocarbon material with a normally liquefiable gaseous hydrocarbon solvent at a temperature above the critical temperature of the liquefiable hydrocarbon solvent and varying the density of the liquefiable hydrocarbon solvent by a progressive change in pressure and by the addition to the liquefiable hydrocarbon solvent of a substance miscible therewith and capable of changing its density.

2. Process according to claim 1 in which the substance added to change the density is a non-hydrocarbon substance.

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