

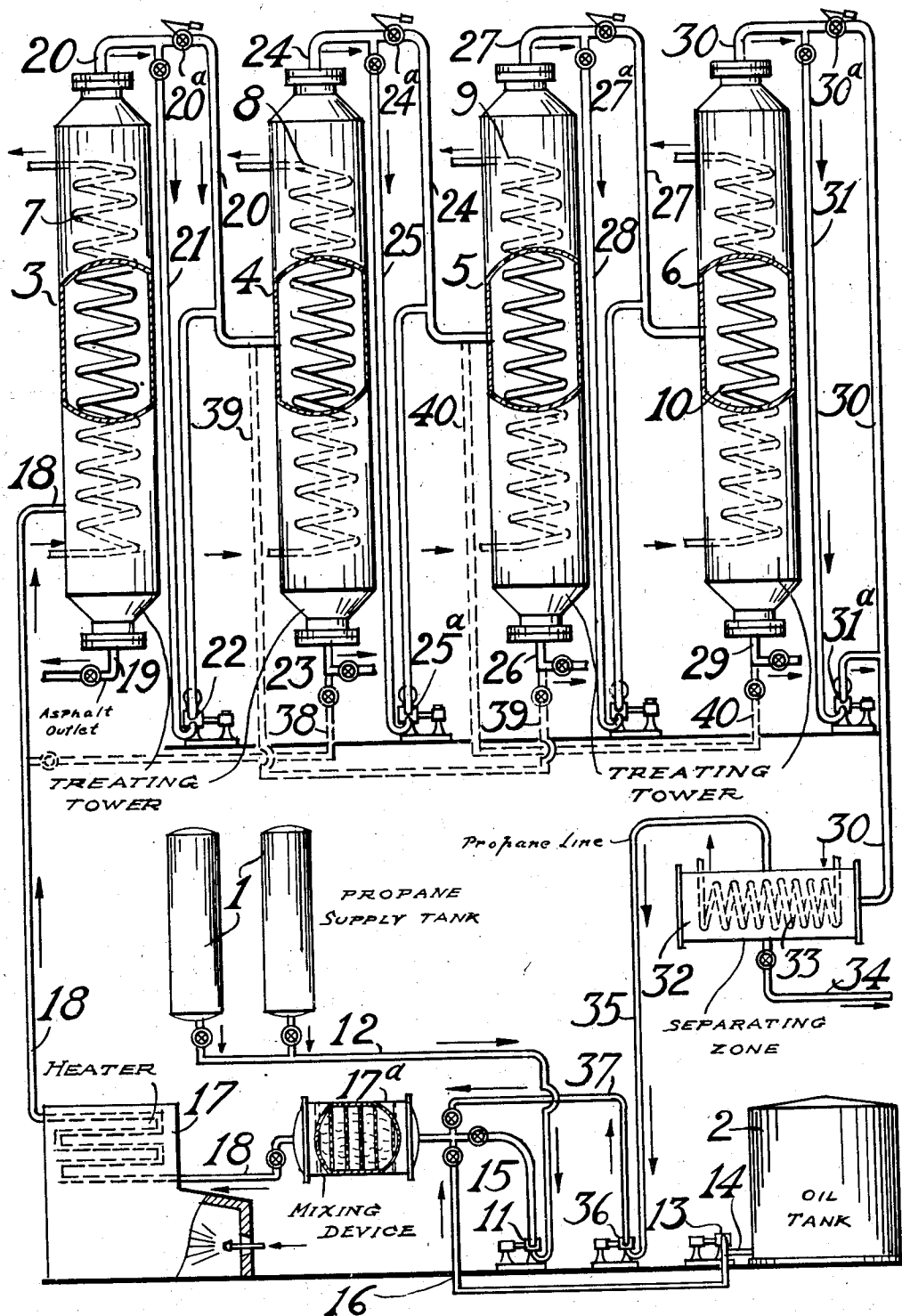
May 28, 1940.

W. K. LEWIS ET AL

2,202,389

EXTRACTION OF HYDROCARBON MATERIAL WITH LIGHT HYDROCARBONS

Filed Sept. 7, 1934



Warren K. Lewis Inventors
James M. Whiteley
By W. E. Currie Attorney

UNITED STATES PATENT OFFICE

2,202,389

EXTRACTION OF HYDROCARBON MATERIAL WITH LIGHT HYDROCARBONS

Warren K. Lewis, Newton, Mass., and James M. Whiteley, Roselle, N. J., assignors to Standard Oil Development Company, a corporation of Delaware

Application September 7, 1934, Serial No. 743,046

16 Claims. (Cl. 196—13)

This invention relates to the treatment of hydrocarbon oils with light hydrocarbons, and is more particularly concerned with the extraction of such oils with light hydrocarbons at high temperatures and at varying pressures.

Light hydrocarbons exert under suitable conditions a selective solvent action on heavier hydrocarbon oils whereby the latter may be separated into fractions having different characteristics. The density of the particular light hydrocarbon solvent used has an important effect upon the degree of separation obtained. Thus, in general the lower the density of the light hydrocarbon solvent the greater will be the proportion of the oil thrown out in the bottom or heavier layer. Similarly the higher the density the greater will be the proportion of the oil remaining in the upper or lighter layer.

Several methods of causing a variation in the density of the light hydrocarbon solvent have been proposed. One method is to vary the temperature at which the extraction is carried out. Another method is to vary the proportion of lighter and heavier hydrocarbon components of the light hydrocarbon solvent.

We have now found a new method for varying the density of the light hydrocarbon solvent. This method is to vary the pressure under which the solvent is used. It is particularly useful when the temperature of treatment is within 50 or 150° F. below the critical temperature of the light hydrocarbon solvent.

In a copending application of Warren K. Lewis, Serial No. 739,226, filed August 10, 1934, a method of treating hydrocarbon oils with light hydrocarbons has been described which comprises carrying out the treatment at the critical temperature or above of the light hydrocarbon, and varying the pressure maintained at these temperatures. At the critical temperature or above, the pure undissolved light hydrocarbon exists entirely as a single homogeneous phase. The effect of increasing pressure in the presence of heavier hydrocarbons is to cause the light hydrocarbon vapor to dissolve therein. By a sufficient increase in pressure enough light hydrocarbon may be caused to dissolve in the heavy oil to effect a separation thereof into two layers.

The present method is differentiated from the foregoing method in that the treatment is carried out at high temperatures below the critical temperature of the light hydrocarbon so that it is possible to retain the light hydrocarbon in the liquid phase.

The nature of the present process and the method of carrying it out will be fully understood from the following description read with reference to the accompanying drawing which is a semi-diagrammatical view in sectional elevation of a type of apparatus suitable for the purpose.

For convenience in description the light hydrocarbon solvent will be denoted by the word "propane," but it should be understood that this does not limit the process to the use of propane only. Similarly the initial material to be treated will be denoted by the word "oil."

Referring to the drawing, numerals 1 designate supply tanks of liquid propane, and numeral 2 designates a supply tank of oil to be treated. Numerals 3, 4, 5 and 6 represent treating towers adapted to withstand pressures as high as 100 atmospheres or more and temperatures as high as 500° F. or more. The treating towers 3, 4, 5 and 6 are provided with coils 7, 8, 9 and 10 respectively disposed within them and adapted to be provided either with heating media or cooling media by means of which the temperature within the towers may be adjusted and controlled.

Pump 11 withdraws propane from tanks 1 through line 12. Pump 13 withdraws oil from tank 2 through line 14. Pumps 11 and 13 force liquid propane and oil respectively under pressure through lines 15 and 16 respectively into and through a mixing device 17a such as a series of orifices and thence through a heating means 17 wherein the mixture of oil and propane is brought to a temperature within about 50 or 100° F. below the critical temperature of propane. From the heater the mixture of oil and propane discharges through line 18 into treating tower 3. In tower 3, heavy asphaltic bodies which are precipitated by the propane and remain undissolved settle to the bottom and are removed through line 19.

The solution of oil and propane free from undissolved asphalt is withdrawn from tower 3 through line 20. If the next tower is to be maintained under a lower pressure than that maintained in tower 3, the mixture will flow past pressure reduction valve 20a whereat the pressure may be reduced to any desired value. If the next tower is to be maintained at a higher pressure then the mixture from tower 3 will flow through by-pass line 20 provided with pressure pump 22.

Assuming that the first tower is maintained at the highest pressure and that the succeeding towers are maintained at progressively lower

pressures, the mixture from tower 3 will flow through line 20 into tower 4 under reduced pressure. In tower 4, the oil will be caused by the reduction in pressure to separate into two layers.

5 The extract or bottom layer comprising the heavier fractions of the oil is withdrawn through line 23.

The upper layer is withdrawn from tower 4 through line 24 provided with pressure reduction valve 24a and by-pass line 25 provided with pump 25a. Thence it discharges under reduced pressure into tower 5 in which another separation into layers is induced by the reduction in pressure. The bottom layer is removed through line 15 26 and the upper layer through line 27, provided with pressure reduction valve 27a and by-pass line 28 provided with pump 28a.

Thence the upper layer from tower 5 discharges into tower 6. Another separation is induced by the reduction in pressure. The bottom layer is withdrawn through line 29, and the top layer through line 30 provided with pressure release valve 30a and by-pass line 31 provided with pressure pump 31a.

25 The upper layer from tower 6 may be forwarded to another tower and as many succeeding towers (not shown) as desired. If tower 6 is to be the last tower then the upper layer withdrawn therefrom is discharged into a separating zone 32 provided with heating means 33. The temperature is raised in the separating zone 32 by means of heating coil 33 to the critical temperature of propane. If the pressure in tower 6 was below the critical pressure of propane then 30 it is increased to that pressure by means of pump 31a prior to discharge into separating zone 32. If the pressure were above the critical pressure then it is reduced to that pressure by means of pressure reduction valve 30a prior to discharge 40 into the separating zone.

In the separating zone which is maintained at the critical conditions of propane, the oil and propane become substantially immiscible in one another, and a layer separation between the oil 45 and propane occurs.

The oil layer which will contain a small amount of propane, say 0.5 pound per pound of oil, may be removed from the separating zone 32 through line 34 and the last traces of propane may then 50 be removed from the oil by distillation or other suitable means.

The propane layer is withdrawn from separating zone 32 through line 35 by pump 36 and may then be returned through line 37 to the propane supply line 15 under the required pressure.

55 The foregoing method of separating the propane and oil has been described in a co-pending application of Gustav A. Beiswenger, Serial No. 626,333, filed July 30, 1932, now Patent No. 2,115,003, dated April 26, 1938, and is especially convenient in the present process, but it will be understood that other methods of accomplishing the separation, such as by distillation under 65 super-atmospheric pressure followed by condensation of the propane or by reduction of pressure to atmospheric followed by recompression of propane vapors, are not precluded.

70 The bottom layers removed from towers 4, 5 and 6 through lines 23, 26 and 29 respectively may be subjected to the same treatment as the upper layers either under progressively decreasing or progressively increasing pressures. The several bottom layers may also be recycled to the next preceding towers as indicated by dotted lines

38, 39, and 40, or the several bottom layers may be mixed in any suitable proportions and all or a portion thereof may be recycled to any one or more of the towers. If desired, the oil may be recovered separately from each bottom layer.

It will be understood that the treatment may if desired be carried out in a single tower with removal of either the top or bottom layer following each change in pressure.

10 In the operation of the process the important variables are the initial material, the light hydrocarbon used as the solvent, the temperature of treatment, the pressure maintained and the proportions of oil and light hydrocarbon.

15 The initial material adapted for treatment according to the present process may comprise any hydrocarbon oil such as gas oil, light lubricating oil, heavy lubricating oil, gear oil, transmission oil, paraffin distillate, residues and the like whether obtained by the distillation, destructive distillation, hydrogenation, destructive hydrogenation, or cracking of coals, tars, pitches, bitumens, resins, lignites, shales, petroleum, mineral oil and other carbonaceous materials. Also included are hydrocarbons prepared by synthetic 25 processes such as polymerization or condensation in the presence or not of catalytic materials such as aluminum, zinc, iron, tin or boron halides; as well as hydrocarbons prepared by voltolization by means of silent electric discharges. The initial material may contain wax or asphaltic bodies or other materials since these can either be removed during the process or will not interfere materially with the operation thereof. The process is particularly adapted to the treatment of 35 viscous lubricating fractions derived from petroleum.

40 The light hydrocarbons suitable for use in the present process comprise hydrocarbons having between 1 and 8 carbon atoms. In general hydrocarbons having between 2 and 6 carbon atoms will be preferred. As examples of suitable light hydrocarbons may be mentioned methane, ethane, propane, butane, pentane, hexane, heptane, octane, ethylene, propylene, butylene, amylene, hexylene, heptylene, octylene, isobutane, isopentane, cyclo-hexane, isoheptane or any mixtures of two or more of these, or hydrocarbon 45 mixtures containing a major proportion of hydrocarbons having between 1 and 8 carbon atoms.

Also suitable for use as the light hydrocarbon solvent are light naphthas whether obtained naturally or by synthetic or hydrogenation processes, casinghead gasoline, natural gasoline and 55 the like.

The gases obtained in the cracking or destructive hydrogenation of heavy hydrocarbon oils and in the stabilization or debutanization of gasolines are generally relatively rich in the preferred light 60 hydrocarbons and provide an especially suitable and convenient source thereof.

65 The temperature of treatment should be above the melting point of the initial material to be treated but preferably below the cracking temperature thereof. The general range of temperature will therefore be between about 50° F. and 550° F. although this is merely illustrative and not limitative. The exact temperature used will depend upon the particular light hydrocarbon or mixture of light hydrocarbons selected as the solvent. In any particular case the temperature maintained is preferably between about 150° F. or less of the critical temperature of the light hydrocarbon and just below the critical temperature. 70

Thus, for propane which has a critical temperature of 212° F., the preferred temperature will be between about 110° F. and just below 212° F. For butane which has a critical temperature of 304° F., the preferred temperature range will be between about 150° F. and just below 304° F. Similarly for other light hydrocarbons or for mixtures thereof.

It will be understood that when a mixture of light hydrocarbons is used as the solvent, under certain conditions of temperature and pressure, both vapor and liquid phases may coexist in which the vapor and liquid will have the same density. The operating temperature in such cases will be below the highest temperature at which vapor and liquid phases can coexist.

The pressure maintained during the treatment is of primary importance in the present process because it is by means of varying the pressure that changes in the density of the solution of oil in solvent which cause changes in the selectivity of the solvent are obtained. In general the pressure should be at least sufficient to retain the light hydrocarbon in liquid phase at the temperature of working. The pressure may vary from this point to pressures several times the equilibrium vapor pressure of the solvent at the temperature of working. It will be understood that the lower the molecular weight of the light hydrocarbon used, the higher will be the pressure necessary to retain the light hydrocarbon in liquid phase at the same temperature of working. It will be found that a relatively small increase in pressure will cause a pronounced change in the density of the light hydrocarbon. Thus with propane the pressure may be varied from say 150 lbs./sq. inch to as high as 1500 lbs. per square inch, although pressures between say 200 and 900 lbs. per square inch will give a wide variation in density at temperatures within about 50° F. of the critical temperature of propane.

The proportion of light hydrocarbon to oil may vary from 2 to 12 volumes per volume of oil although from 3 to 8 volumes per volume of oil will be preferable in most cases. It will be understood that the volume of light hydrocarbon used will determine to a large extent the yield of treated oil obtained since the top layer will always be substantially saturated with lighter fractions of the oil.

One of the important features of the present invention is that any light hydrocarbon having between 1 and 8 carbon atoms may be used with equally satisfactory results. It has been found that the density of all of these light hydrocarbons is substantially the same at their respective critical temperatures and that the same solvent density may be obtained at other temperatures with any of these light hydrocarbons by adjusting the temperature and pressure conditions. Thus if a particular solvent density is found to give the degree of separation desired this solvent density may be obtained with say heptane as well as with propane merely by adjusting the temperature and pressure at which the heptane is used. It will be seen that if heptane is selected as the solvent the temperature will have to be much higher than if propane is used to get the same solvent density but on the other hand the corresponding pressure will be much lower than is necessary with propane. Whether or not heptane is selected instead of propane will depend very largely upon the nature of the initial material and upon practical and economical consideration as to the avail-

ability of heptane and the desirability of operating at higher temperatures. The important thing is that any one of these light hydrocarbons may be made to be satisfactory provided other considerations are equal.

Similarly mixtures of two or more light hydrocarbons will operate as satisfactorily as a single hydrocarbon. Thus, for example a mixture of octane and ethane may be made to approximate say propane or butane so that the temperature and pressure condition required to obtain a particular solvent density for the mixture may be substantially the same as those required for the single hydrocarbon. Also mixtures of say ethane or propane with hydrocarbons higher than octane may be prepared which will have the characteristics necessary for carrying out the present process.

The selectivity of the light hydrocarbon used in the present process may be accentuated by the use of preferential solvents for naphthenic or aromatic hydrocarbons in combination with and together with the light hydrocarbons. Suitable preferential naphthenic solvents for this purpose include phenols, cresols, cresylic acid, xylols, liquid sulfur dioxide, aniline, chloraniline, nitrophenols, nitrobenzene, furfural, dichlorethyl ether, croton aldehyde, cellosolve acetate, glycol diacetate and the like as well as what may be termed "conditioned phenolic substances", that is to say substances such as phenols, cresols, xylols and other alkylated phenols to which have been added small quantities of conditioning agents such as water, caustic soda, caustic potash, methyl, ethyl or propyl alcohol, glycerine, ammonia and the like, the effect of which conditioning agents is primarily to change the miscibility temperatures of the oil and solvent.

In carrying out the process the oil to be treated may be preliminarily deasphaltized, dewaxed or otherwise treated as with acid or clay. If the oil is to be preliminarily deasphaltized and dewaxed it is convenient to do this by means of liquid propane or other liquefied normally gaseous hydrocarbon since the same solvent may be used in the subsequent treatment according to the present process, although it will be understood that the preliminary deasphaltizing and dewaxing may be accomplished by other means and with other solvents.

As indicated above, however, the deasphalting operation may be conveniently included as the first operation of the present process, and in many cases this procedure will be preferable to a separate preliminary deasphaltizing step because the precipitation of asphalt at temperatures close to the critical temperatures of the light hydrocarbons is particularly effective.

Dewaxing, acid and clay treating, and general refining treatments may also follow treatment according to the present process. The oils obtained in the process may also be subjected to cracking, hydrogenation, destructive hydrogenation, polymerization, condensation or voltolization treatments. This last procedure is especially useful and valuable because the products obtained from the high temperature light hydrocarbon treating are free from asphaltic and tarry impurities which are detrimental in cracking, destructive hydrogenation and the like.

The following tables show the effect of variation of pressure and of solvent volume at relatively high temperatures on the selective action of propane. The oil used is a bottoms obtained from Ranger (Texas) crude.

TABLE I
Treatment at saturation pressures

	Volumes propane per vol. oil @ 80° F.	Temp., °F.	Pressures, lbs./sq. in.	Yield oil (top layer)	Saybolt vis. @ 210° F.	Color Robinson (diluted)
8	-----	149	375	81.4	114	2 1/4
8	-----	162	400	75	100.5	2 1/4
10	8	185	500	55.7	85.5	5 1/4
12	-----	149	375	84	115	3
5	-----	185	490	47.7	90.5	2

TABLE II
Treatment at pressures above saturation pressures

	Volumes propane per vol. oil @ 80° F.	Temp., °F.	Pressures, lbs./sq. in.	Yield oil (top layer)	Saybolt vis. @ 210° F.	Color Robinson (diluted)
8	-----	192	850	52.5	86	-----
12	-----	180	640	67	97	5 1/4
12	-----	192	850	67	96.5	6 1/4
5	-----	180	640	58.5	105	2 1/4
25	5	192	850	51.5	85.4	5 1/4

In the above tables the term "saturation pressure" means the equilibrium vapor pressure of propane at the respective temperatures, that is to say, the pressure exerted by the vapors of propane at those temperatures when the vapors are in equilibrium with liquid propane.

The present process is particularly suitable for preparing valuable hydrocarbon products.

For example, oils of extremely high viscosity of the order of 1000, 2000, 5000 or even 10,000 seconds Saybolt viscosity at 210° F. may be obtained by subjecting a heavy hydrocarbon oil to the above described treatment. The lighter fractions are progressively removed by the successive treatments at varying pressures, and the final bottom layer after removal of any light hydrocarbon solvent contained therein will comprise an extremely viscous oil. Such viscous oils are adapted for various special purposes and may be used as such or may be blended with lighter oils to increase the viscosity of the latter.

Another valuable use of the present process is in the recovery of natural pour inhibiting materials from petrolatum or materials rich in petrolatum. By repeated treatment of the petrolatum under progressively increasing pressures, a concentrated form of the natural pour inhibitors contained in the petrolatum may be obtained.

Similarly the present process is especially useful in preparing concentrated synthetic pour inhibiting agents, and in preparing concentrated products from oils prepared by volatilization and other special treating processes. Long residual oils of low Conradson carbon content may be prepared by the present process, and the present invention contemplates the method of preparing the above products and the products themselves.

This invention is not limited by any theory of the mechanism of the process nor by any details which have been given merely for purposes of illustration, but is limited only in and by the following claims in which it is intended to claim all novelty inherent in the invention.

We claim:

1. The method of treating hydrocarbon oils which comprises diluting the same with a light hydrocarbon solvent, heating the mixture to a high temperature below the critical temperature of the light hydrocarbon solvent, increasing the

pressure to several times the equilibrium vapor pressure of the light hydrocarbon at the temperature of working, separating the two layers formed, reducing pressure on the upper layer whereby a further separation is caused, again separating the two layers, reducing pressure on the upper layer, separating the two layers, reducing pressure on each layer to the critical pressure of the light hydrocarbon solvent and heating the two layers to the critical temperature of the solvent whereby the oil is caused to separate from the light hydrocarbon, and recovering the oil layers.

2. The method of treating hydrocarbon oils which comprises diluting the same with a light hydrocarbon solvent, heating the mixture to a high temperature below the critical temperature of the light hydrocarbon solvent, increasing the pressure to several times the equilibrium vapor pressure of the light hydrocarbon at the temperature of working, separating the two layers formed, reducing pressure on the bottom layer whereby a further separation is caused, again separating the two layers, reducing pressure on the bottom layer, separating the two layers, reducing pressure on each layer to the critical pressure of the light hydrocarbon solvent and heating the two layers to the critical temperature of the solvent whereby the oil is caused to separate from the light hydrocarbon, and recovering the oil layers.

3. Process according to claim 1 in which the recovered light hydrocarbon is returned to the first step of the process.

4. Process according to claim 1 in which the light hydrocarbon solvent comprises propane.

5. Process according to claim 1 in which the oil is first deasphaltized by means of a light hydrocarbon.

6. Process according to claim 1 in which a selective solvent for naphthenic hydrocarbons is used together with the light hydrocarbon solvent.

7. Process for separating hydrocarbon oil into two normally liquid fractions which comprises diluting the oil with a light hydrocarbon solvent, maintaining sufficient pressure to retain the light hydrocarbon solvent in liquid phase, causing a portion of the oil to be thrown out of solution by varying the pressure maintained on the mixture, separating the two liquid layers thereby formed and recovering the oil therefrom.

8. Process for separating a hydrocarbon oil into two normally liquid fractions which comprises dissolving the oil in a light hydrocarbon solvent, heating the mixture to a high temperature below the critical temperature of the light hydrocarbon solvent, maintaining at least sufficient pressure to retain the light hydrocarbon solvent in the liquid phase at the temperature of working, effecting a change in the density of the solvent sufficient to cause a portion of the oil to be thrown out of solution solely by varying the pressure maintained thereon, separating the two layers thereby formed and recovering the oil from each layer.

9. The method of separating a heavy hydrocarbon oil into a series of normally liquid fractions which comprises dissolving the oil in a light hydrocarbon solvent, heating the solution to a temperature within 100° F. of the critical temperature of the light hydrocarbon solvent, maintaining a pressure at least sufficient to retain the light hydrocarbon solvent in liquid phase at the temperature of working, progressively changing the pressure maintained on the solution whereby

a sufficient change in the density of the solvent is effected to cause a portion of the oil to be thrown out of solution, separating the two liquid layers formed after each pressure variation and recovering the oil from the several layers.

10. The method of treating heavy hydrocarbon oil which comprises diluting the same with several volumes of liquefied propane, heating the mixture to a temperature between 110 and 212° F., progressively varying the pressure between about 200 and 900 pounds per square inch whereby the mixture is caused to separate into two layers, separating the two layers formed after each pressure variation, and recovering oil from the several layers.

11. The method of treating a heavy hydrocarbon oil which comprises diluting the same with from 3 to 8 volumes of a liquefied hydrocarbon solvent consisting essentially of butane, heating the mixture to a temperature between 150 and 304° F., progressively varying the pressure maintained from several times the equilibrium vapor pressure to a pressure substantially therebelow, but always sufficient nevertheless to retain the solvent in liquid phase, separating the two layers formed after each pressure variation, and recovering oil from the several layers.

12. The method of treating a lubricating fraction of petroleum which comprises diluting the same with a liquefied normally gaseous hydrocarbon, removing asphaltic material remaining undissolved, chilling the solution to a temperature at which wax is caused to precipitate, removing the wax so precipitated, heating the remaining

oil solution to a temperature within about 50° F. of the critical temperature of the liquefied normally gaseous hydrocarbon solvent, increasing the pressure to several times the equilibrium vapor pressure of the liquefied hydrocarbon at the temperature maintained, separating the two layers into which the solution is thereby caused to separate, progressively decreasing pressure to cause further separation into two layers, separating the two layers after each pressure variation and recovering oil from the several layers.

13. Process according to claim 8 in which the light hydrocarbon solvent comprises hydrocarbons having between 1 and 8 carbon atoms.

14. Process according to claim 8 in which the light hydrocarbon oil is diluted with between 3 and 8 volumes of light hydrocarbon solvent per volume of oil.

15. Process according to claim 8 in which a selective solvent for naphthenic hydrocarbons is used together with the light hydrocarbon solvent.

16. Process for treating a petroleum lubricating oil which comprises diluting the same with several volumes of a liquefied normally gaseous hydrocarbon, subjecting the mixture to a high temperature below the critical temperature of the liquefied normally gaseous hydrocarbon and progressively varying the pressure in the range not below the vapor pressure of the system whereby the solubilities of the respective constituents of the lubricating oil are varied.

WARREN K. LEWIS.
JAMES M. WHITELEY.