

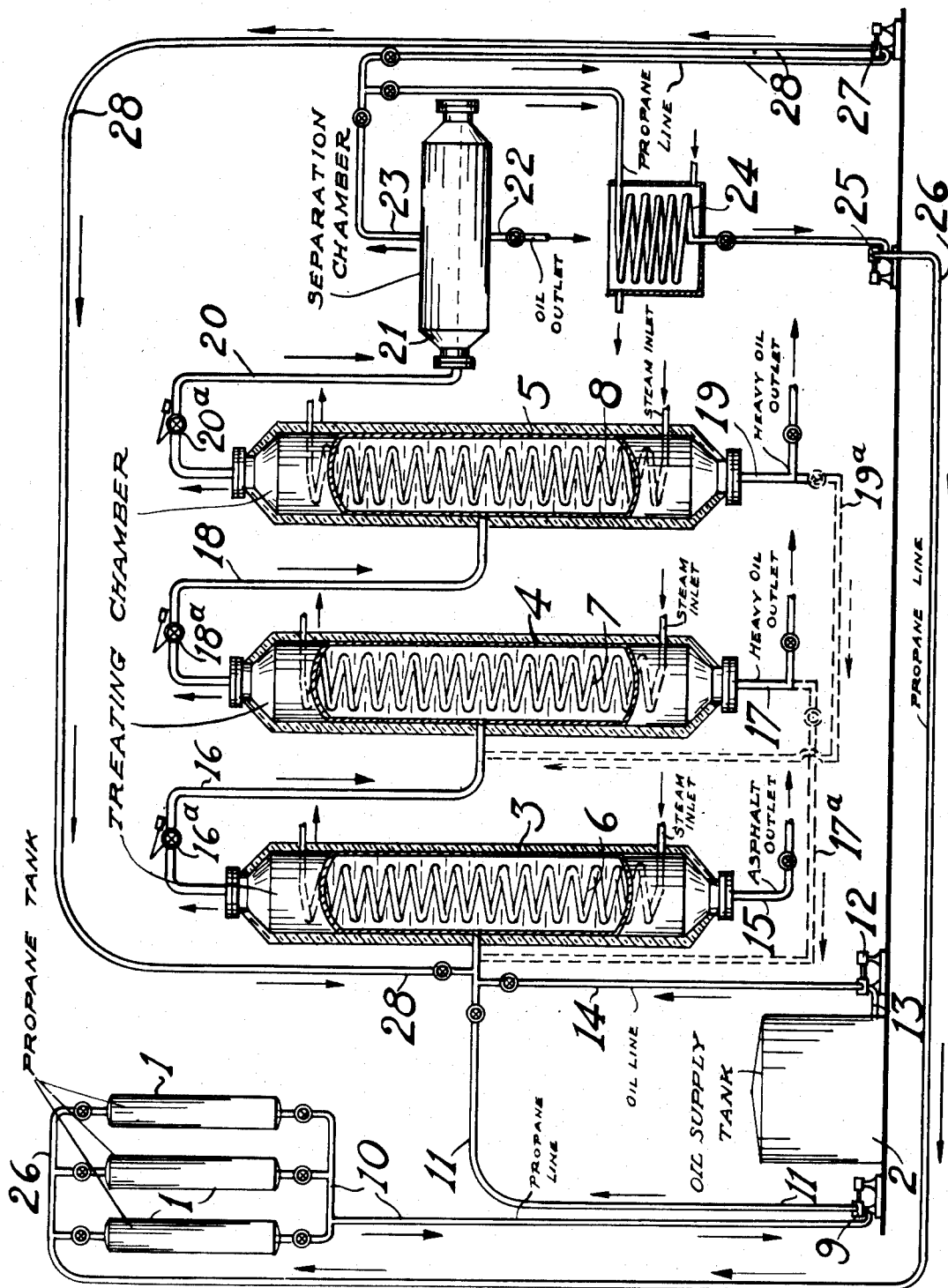
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W. K. LEWIS

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PROCESS FOR TREATING HYDROCARBON OILS WITH LIGHT HYDROCARBONS

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Warren K. Lewis Inventor

By *W. E. Currie* Attorney

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PROCESS FOR TREATING HYDROCARBON
OILS WITH LIGHT HYDROCARBONS

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Warren K. Lewis, Newton, Mass., assignor to
Standard Oil Development Company, a corpo-
ration of Delaware

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This invention relates to the treatment of hydrocarbon oils with light hydrocarbons and is more particularly concerned with the treatment of hydrocarbon oils with light hydrocarbons at or above the critical temperatures of the light hydrocarbons.

It has been found that light hydrocarbons have a selective action on hydrocarbon oils, that is to say, are capable under suitable conditions of separating hydrocarbon oils into fractions of dissimilar molecular weight and/or other characteristics. It has also been found that the selective solvent action of the light hydrocarbons depends to a large extent on the density thereof during the treatment.

It has now been found that particularly advantageous results may be obtained by treating hydrocarbon oils with light hydrocarbons at or above the critical temperatures of the light hydrocarbons and varying the pressure maintained at these temperatures to obtain changes in the density of the liquid phase. Thus, although a light hydrocarbon alone cannot be liquefied at its critical temperature or above, under any pressure, it has been found that if oil is present with the light hydrocarbon, an increase of pressure at temperatures at or above the critical temperature of the light hydrocarbon will cause the latter to dissolve in the oil and thus force it into the liquid phase. As the pressure is increased more and more of the light hydrocarbon will dissolve in the oil with the result that the dissolved light hydrocarbon may then exert a selective solvent action on the oil and cause it to be separated into two phases.

At the critical temperature and the equilibrium vapor pressure of the light hydrocarbon at just below its critical temperature, insufficient light hydrocarbon will be dissolved in the oil and consequently there will be no separation of the oil into two phases. On the other hand, at the critical temperature and some pressure substantially above the critical pressure, a substantial portion of the light hydrocarbon will be dissolved in the oil so that a separation into two liquid phases can occur. It will be understood that the greater the proportion of light hydrocarbon to oil in the liquid phase, the greater will be the amount of oil in the upper liquid layer, so that if sufficient light hydrocarbon is used, substantially all of the oil will be in the one layer (top liquid) under conditions such that all of the liquefied hydrocarbon is dissolved in oil.

The term "hydrocarbon oil" as used herein will be understood to include gas oils, lubricating oils, 55

heavy gear oils, residues, wax-containing distillates or residues and the like whether obtained by the distillation, destructive distillation, hydrogenation, destructive hydrogenation, or cracking of petroleum, shales, coals, mineral oils, tars, pitches, bitumens and the like or by synthetic processes such as polymerization, condensation or volatilization of gaseous, liquid or solid hydrocarbons.

The term "light hydrocarbons" will be understood to include hydrocarbons having 1 to 8 carbon atoms, preferably hydrocarbons having 2 to 6 carbon atoms. As examples of suitable light hydrocarbons may be mentioned methane, ethane, propane, butane, pentane, hexane, ethylene, propylene, butylene, isobutane, isopentane, amylene, isoamylene, hexylene, iso-hexane, cyclohexane or any mixtures of these. Materials containing substantial proportions of these light hydrocarbons may also be used.

The gases derived from a cracking or destructive hydrogenation process, and the gases derived from the stabilization or debutanization of gasoline provide especially convenient and suitable sources of the light hydrocarbons for use in the present process.

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

For convenience in description the light hydrocarbon solvent will be referred to as "propane" but it should be understood that this does not limit the process to propane only. Similarly the initial material to be treated will be referred to as "oil" but this does not limit the process to any particular type of hydrocarbon oil.

Referring to the drawing numerals 1 designate supply tanks of propane, numeral 2 designates a supply tank for oil to be treated, and numerals 3, 4 and 5 designate treating chambers adapted to withstand high temperatures and high pressures. Treating chambers 3, 4 and 5 are provided with heating coils 6, 7 and 8 respectively adapted to be supplied with steam or other suitable heating media by means of which the temperature in the towers may be maintained and regulated. Heat may also be supplied by other means as by introducing water or steam directly into the chambers or by supplying heat to the outside thereof.

Pump 9 draws propane from propane tank 1 through line 10 and forces it under pressure

through line 11 into treating chamber 3. Pump 12 draws oil from tank 2 through line 13 and forces it under high pressure through lines 14 and 11 also into treating chamber 3. The temperature in chamber 3 is brought up to the critical temperature of propane or above by means of coil 6 supplied with steam. The pressure maintained in chamber 3 is sufficiently high to cause substantially all of the propane and oil to be completely miscible at the temperature maintained.

Heavy tarry or asphaltic bodies are precipitated and are withdrawn from chamber 3 through line 15.

The liquid in chamber 3 is then withdrawn therefrom through line 16, flows past pressure release valve 16a and is introduced into a second treating chamber 4 maintained under a lower pressure than chamber 3 and at substantially the same or a higher temperature. The decreased pressure in chamber 4 causes an expansion of the mixture therein and the oil-propane solution thereby loses its power to dissolve the heavier fractions of the oil with the result that two oil layers are formed. The further decrease in pressure causes the oil to be distributed between two liquid layers again.

The bottom layer is withdrawn through line 17. The upper layer is withdrawn through line 18, flows past pressure release valve 18a and is introduced into a third treating chamber 5 maintained under a lower pressure than chamber 4 and under substantially the same or a higher temperature than chamber 3.

The bottom layer is removed from chamber 5 through line 19. The upper layer in chamber 5 is withdrawn therefrom through line 20 and, after reduction in pressure at pressure release valve 20a, may be introduced into further treating chambers (not shown), or, if chamber 5 is the final treating chamber, is introduced into separation chamber 21 which is maintained at substantially the critical temperature and pressure of propane.

Under these conditions the propane is substantially completely immiscible with the oil and a separation of the final refined oil and propane occurs. The oil layer contains some dissolved propane which may be recovered by distillation or other means.

The oil layer is withdrawn from separation chamber 21 through line 22. The propane layer is withdrawn from separation chamber 21 through line 23, passed through cooler 24 and then returned by means of pump 25 and line 26 to the propane supply tank 1. Alternatively, and more conveniently, the propane layer from separation chamber 21 may be withdrawn through line 23 and then returned while still at high temperature by means of pump 27 and line 28 directly into the first treating chamber 3.

Various modifications in the method of operating the apparatus may be made as will be understood. For example, the necessary heating may be accomplished in heating coils through which the mixture of oil and propane is passed prior to introducing into the treating chambers. In this event the treating chambers would in effect be settling chambers only.

The bottom layers drawn off from treating chambers 4 and 5 through lines 17 and 19 respectively may be recycled to the next preceding treating chambers through dotted lines 17a and 19a. In this way the process would produce only

two products, asphalt at one end and refined oil at the other.

The heavy asphalt or oil withdrawn through lines 15, 17, 19 and 22 will contain some dissolved propane. This may be substantially completely removed and recovered by reducing pressure to about 140 lbs./sq. in. and the vapors of propane so evolved may be condensed at about 80° F. The last traces of propane may be removed by blowing with steam at about 212° F. It will be understood that if solvents heavier than propane are used, these may be removed by distillation.

In the operation of the process the more important variables are (1) the temperature at which the treatment is carried out; (2) the pressure maintained during the treatment; (3) the proportion of light hydrocarbon solvent to oil; (4) the composition of the light hydrocarbon solvent and (5) the type of initial material selected for treatment.

In general the temperature of treatment should be above the melting point of the oil to be treated but below the cracking temperature thereof. More specifically the temperature maintained should be substantially the same critical temperature of the light hydrocarbon solvent or higher. The temperature is preferably maintained as close to the critical temperature as possible in order to obtain the maximum solubility of the gas in the oil under the pressures used, for it will be understood that as the temperature is increased the solubility of the gaseous propane in the oil decreases. The critical temperatures of some of the preferred light hydrocarbons are as follows:

Hydrocarbon	Critical temperature
	°F.
Ethane.....	93
Propane.....	212
Butane.....	304
Pentane.....	387
Hexane.....	455
Heptane.....	513

It will be seen that the practical temperature range over which the treatment may be carried out will therefore be between about 100° F. and 500° F. Most oils will have melting points that fall well within this range even at the lower end, and cracking temperatures above the upper end of the range. It will be understood that the particular temperature used will depend upon what light hydrocarbon is selected.

The pressure maintained during the treatment will be between the critical pressure of the light hydrocarbon and a pressure at which a substantial amount of the liquefied hydrocarbon will be dissolved in the oil at the temperature of working. This latter pressure will generally be about twice the critical pressure.

The critical pressures of the preferred light hydrocarbons are as follows:

Hydrocarbon	Critical pressure
	Lbs./sq. in.
Ethane.....	750
Propane.....	690
Butane.....	555
Pentane.....	495
Hexane.....	450

It will be seen therefore that the lower pres-

sure limit maintained in vessel 21 may vary from about 400 lbs./sq. in. to substantially above 700 lbs./sq. in. The exact pressure necessary in any particular case will depend upon the particular light hydrocarbon selected and upon the temperature at which it is used.

The volume of light hydrocarbon solvent used determines to a large extent the yield of treated oil, that is to say, since the upper layer will always be saturated with light hydrocarbon, the greater the quantity of light hydrocarbon used, the greater will be the amount of oil found in the upper layer. In general, from 2 to 6 pounds of solvent per pound of oil will give satisfactory results, although from 3 to 4 pounds of solvent per pound of oil are preferred in most cases.

The particular light hydrocarbon selected for use will depend primarily on the nature of the oil to be treated, and more particularly on the melting point and the cracking temperature thereof which represent the minimum and maximum temperatures respectively that should be used. Thus, in the case of very light oils it is preferable to use light hydrocarbons such as ethane, propane and butane. Similarly with the heavier types of oils, light hydrocarbons such as propane and butane are preferable although pentane, hexane and heptane are quite satisfactory.

It has been found that all hydrocarbons having between 1 and 8 carbon atoms have substantially the same density at their respective critical temperatures. Thus, for example, if a particular solvent density is required to accomplish the degree of separation desired, any one of these light hydrocarbons or any mixture thereof may be used, provided other conditions are met, and the required density may be obtained by adjusting the temperature and pressure at which the particular light hydrocarbon or mixture of light hydrocarbons is used. It should also be understood that a suitable light hydrocarbon solvent for use according to this invention may comprise a mixture of hydrocarbons having between 1 and 8 carbon atoms with higher boiling hydrocarbons in which the hydrocarbons having between 1 and 8 carbon atoms constitute the major proportion. Such mixtures would preferably comprise a substantial proportion of hydrocarbons of 1, 2 or 3 carbon atoms. Thus, for example, a mixture of ethane and decane in which ethane constituted the major proportion would provide a suitable solvent because the density of this mixture could be made substantially the same as the density of pure butane or pentane by suitable adjustment of temperature and pressure. Similarly other mixtures of the light hydrocarbons with hydrocarbons having more than 8 carbon atoms could be prepared. The important factor is the density of the light hydrocarbon solvent. Once this density is determined, a wide variety of mixtures can be prepared which will have this density under suitable conditions of temperature and pressure.

The process has been described as being carried out in a series of treaters, but it will be understood that it may also be carried out in batch operation in a single treater.

The initial material may be preliminarily or subsequently subjected to various treatments. Thus, the oil may first be deasphaltized, dewaxed and filtered or contacted with clay, and if this is to be done it is advantageous to use light hydrocarbons such as propane for the purpose since

the light hydrocarbon is to be used in the subsequent treatment according to the present process, although other methods of deasphaltizing and dewaxing may also be used as will be understood.

The usual finishing and refining treatments may also be applied to the products prepared according to this process.

The initial material may be subjected to hydrogenation, cracking, volatilization or polymerization and condensation treatments either prior to or subsequent to the high temperature treatment.

The several extracts obtained during the extraction may be maintained separate, or may be blended in suitable proportions with each other or with oils derived from other sources.

In many cases it is advantageous and desirable to use selective solvents for naphthenic and aromatic hydrocarbons in addition to and together with the light hydrocarbon solvents. Among such solvents may be mentioned phenols, cresols, xylois, cresylic acid, nitrobenzene, aniline, chloraniline, furfural, liquid sulfur dioxide, dichlorethyl ether, crotonaldehyde, pyridine, benzaldehyde, nitrotoluene, furfuryl alcohol and methyl cellosolve.

One marked advantage of the present method of treating oils with light hydrocarbons at or above the critical temperature of the light hydrocarbons is that by a mere doubling of the pressure at this temperature a great change in the solubility of the light hydrocarbon in the oil may be effected. Thus when using propane, only a small amount of propane will dissolve in the oil at 212° F., the critical temperature of propane, and about 650 lbs./sq. in. the equilibrium vapor pressure of propane at just below its critical temperature. If the temperature is maintained at 212° F. and the pressure increased to say 1300 lbs./sq. in. sufficient propane will dissolve in the oil to cause the latter to be separated into two fractions.

Increasing the pressure in an extremely simple and inexpensive operation, and by means of doing so a tremendous change in the characteristics and effect of the solvent may be obtained. It will be understood that the cost of compression depends upon the change in volume. By doubling the pressure at the critical temperature the volume change is only 2 to 1. Doubling the pressure in the range of 100 lbs./sq.in. would have less effect.

This invention is not limited by any theories of the mechanism of the reactions 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 my intention to claim all novelty inherent in the invention.

I claim:

1. Process for separating a lubricating fraction of petroleum into constituent parts which comprises diluting the lubricating fraction with a light hydrocarbon solvent, bringing the diluted oil to the critical temperature and pressure of the light hydrocarbon solvent, then increasing the pressure to substantially above the critical pressure, removing any material remaining undissolved, reducing the pressure whereby the liquid phase is separated into two layers, removing the bottom layer, reducing the pressure on the upper layer whereby it is again separated into two layers, removing the bottom layer, and finally reducing the pressure on the upper layer to the critical pressure of the light hydrocarbon solvent whereby the oil and light hydrocarbon become substantially insoluble in each other, and recovering the oil layer therefrom.

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

3. Process according to claim 1 in which the light hydrocarbon solvent comprises propane and the pressure is progressively reduced from about 1300 lbs./sq. in. to about 650 lbs./sq. in. while the temperature is maintained at approximately 212° F.

4. Process according to claim 1 in which selective solvents of the class comprising phenols, cresols, xylols, cresylic acid, nitrobenzene, aniline, chloraniline, furfural, liquid sulfur dioxide, dichlorethyl ether, croton aldehyde and pyridine

are used together with the light hydrocarbon solvent.

5. Process according to claim 1 in which selective solvents for naphthenic and aromatic hydrocarbons are used together with the light hydrocarbon solvent.

6. Process according to claim 1 in which the treatment is carried out in a continuous counter-current manner in which the bottom layer from each tower except the first is continuously returned to the next preceding tower.

WARREN K. LEWIS.