Feb. 24, 1942. A. L. LYMAN 2,274,373

PROCESS OF REFINING MINERAL OILS

Filed Dec. 11, 1939 2 Sheets-Sheet 1

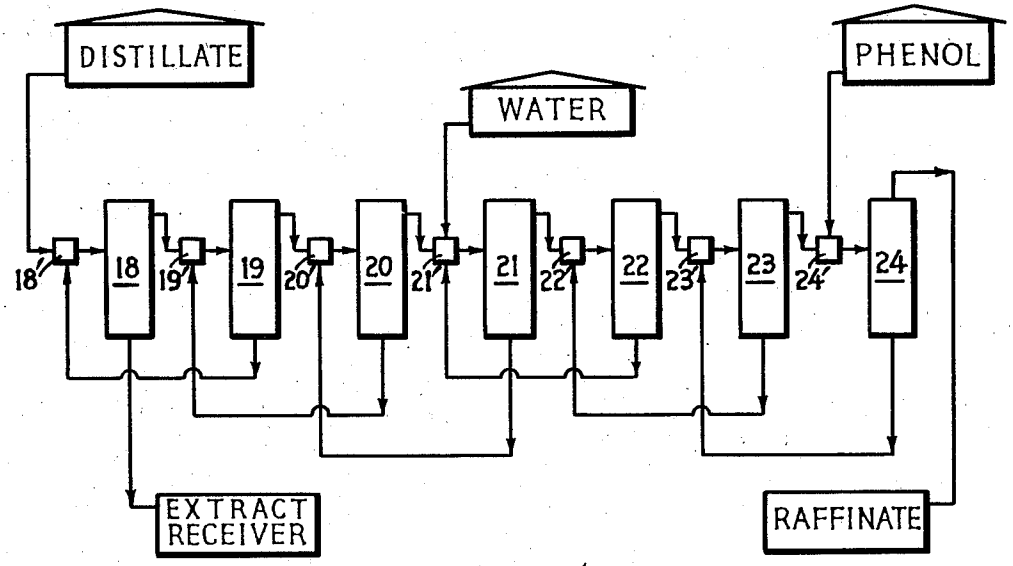


Fig. 1

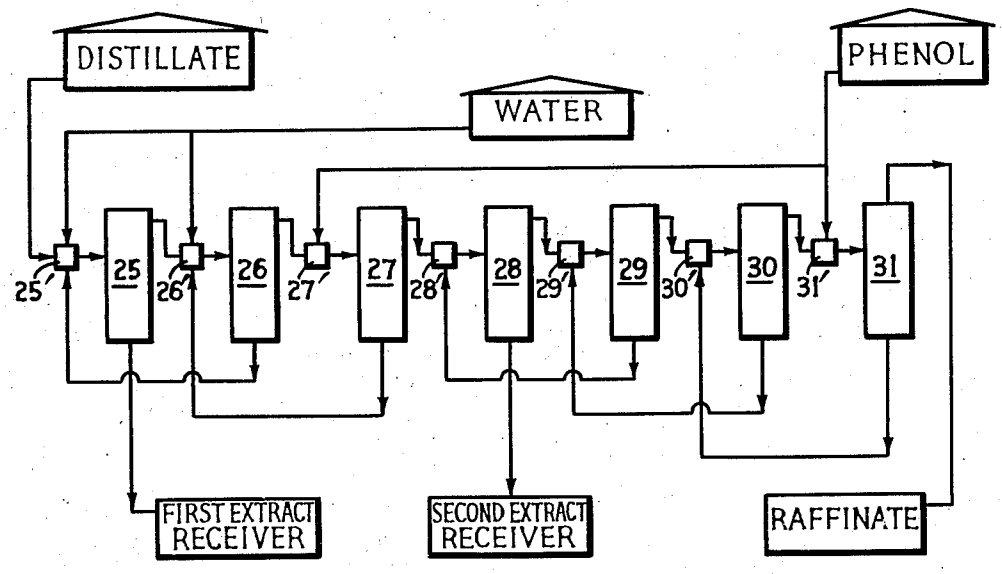


Fig. 2

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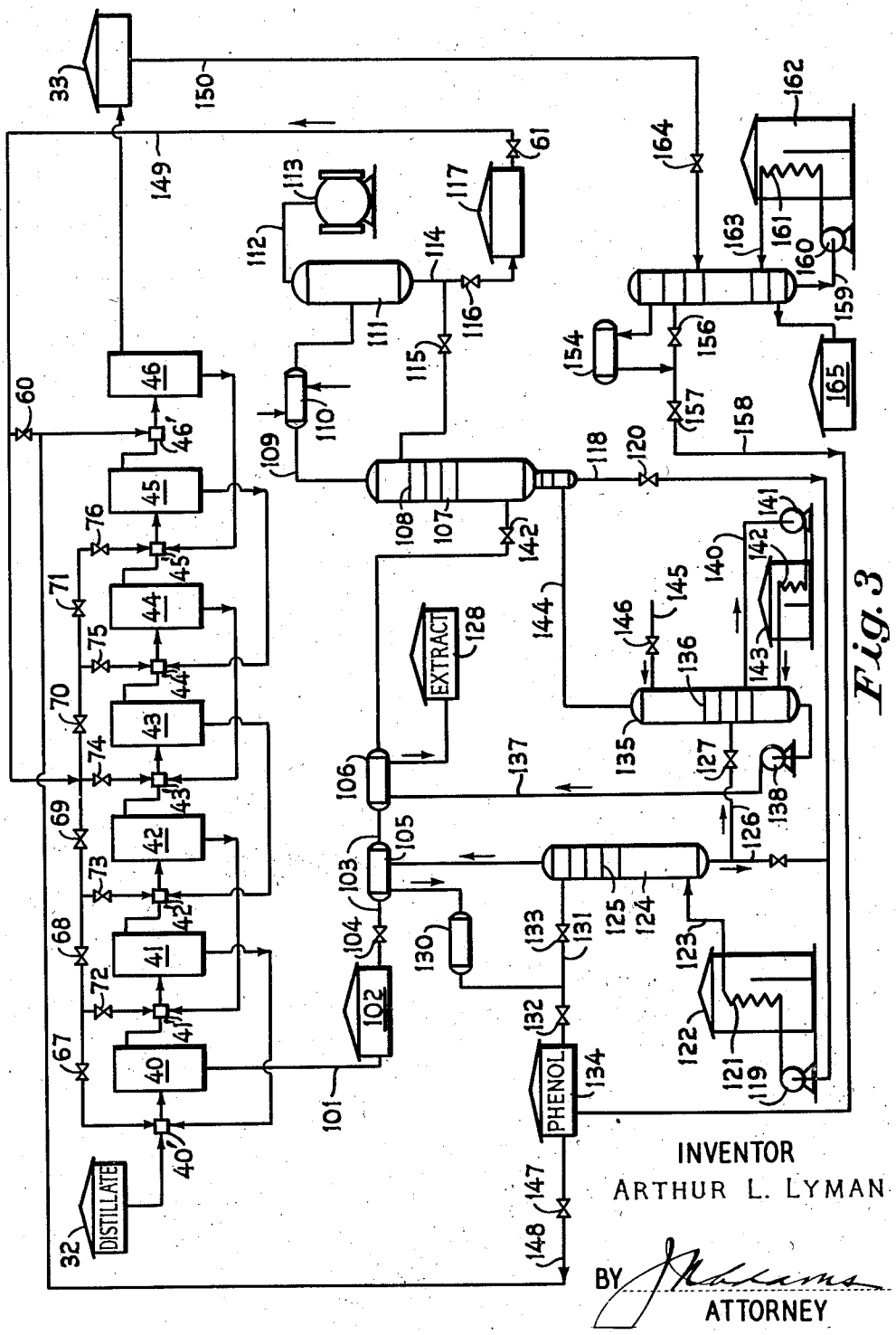


Fig. 3

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2,274,373

PROCESS OF REFINING MINERAL OILS

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Application December 11, 1939, Serial No. 308,714

10 Claims. (Cl. 196—13)

This invention relates to improved processes for refining mineral hydrocarbon oils, and has particular reference to methods of separating crude petroleum oils or their distillates into fractions or components of different chemical compositions, whereby oils of high and of low "viscosity index" may separately be obtained from crude oils or their distillates normally characterized by an inferior viscosity temperature relationship or a low "viscosity index."

As is well known, lubricating oils from Pennsylvania crude petroleums have higher viscosity indexes (as the term "viscosity index" is defined by Dean & Davis in "Chemical and Metallurgical Engineering," 1929, volume 36, pages 618–619) than those oils obtained from Mid-Continent, Gulf, Mexico or California crudes. It is a purpose of my invention to provide methods of extracting from such low "viscosity index" oils, by means of selective solvent refining agents, those hydrocarbons responsible for this inferiority (generally understood to be of unsaturated, aromatic and/or naphthenic molecular structure), thus providing oils consisting wholly or largely of those hydrocarbons characterized by high viscosity indexes (generally understood to be of paraffinic molecular structure).

One of the chief sources of concern to the oil refiner is to prepare oils having a high viscosity index and at the same time obtain satisfactory yields of such highly refined raffinates. These two objectives have heretofore appeared to be in direct conflict. If the refiner selected a solvent refining agent of high selectivity in order to obtain a good yield of raffinate, only a moderate rise in viscosity index, or a moderate degree of refinement was possible. This is due to the fact that a highly selective solvent, as the term "highly selective solvent" is used herein, dissolves from an oil of inferior index, only those hydrocarbons highly unsaturated, aromatic and/or naphthenic in character, and has no material effect in removing from the oil those hydrocarbons intermediate between the highly aromatic and/or naphthenic, on the one hand, and the highly paraffinic, on the other hand. In the use of such a highly selective solvent the refiner obtains an extract small in volume and highly unsaturated or aromatic in composition, and a raffinate large in volume, but of only moderate increase in viscosity index and degree of refinement. If he attempts to prepare an oil of higher viscosity index and higher degree of refinement from a low viscosity index crude or distillate, the refiner is forced to use a solvent agent with much higher solvent power than those which are designated herein as highly selective. Such a solvent is relatively less selective and removes in solution both highly aromatic hydrocarbons and large amounts of those hydrocarbons occupying a position intermediate between the highly aromatic and/or naphthenic, on the one hand, and highly paraffinic, on the other hand, and is therefore relatively non-selective when applied to oils of initially low viscosity index. In the use of such relatively non-selective solvents, the objective of a highly refined raffinate is obtained, but only at a substantial sacrifice in yield. The raffinate is very small in volume and the major proportion of the oil is removed as the extract, which has little utility except as fuel or, as in the case of small volumes of extracts obtained in the use of highly selective solvents, for such purposes as take advantage of the aromatic, unsaturated and/or naphthenic compounds present.

In attempting to overcome these difficulties and to increase the yield of high viscosity index raffinates, various systems have been suggested for more efficiently treating oils with selective solvents. In the conventional methods of solvent extraction used industrially, the solvent chosen has been applied to the oil (whether by single batch, multiple batch, stage counterflow, or countercurrent systems), as a single pure substance or as a constant and uniform mixture with other substances which were added to obtain desired characteristics.

Fractional precipitation has also been proposed in various patents as a method of refining mineral oils. In this type of process the entire mineral oil fraction is dissolved in a solvent which initially has no selectivity by reason of the fact that it dissolves the entire oil fraction. The solvent capacity of this solvent has been decreased in various ways to free portions of the dissolved oil. One such way has been by dilution. So far as known to me, such methods of refining oils do not give yields of high viscosity index raffinates comparable to those obtained by the present invention.

It is therefore an object of this invention to provide a process of refining oils which effects an increased yield of a given high viscosity index raffinate, as compared with prior processes of extraction.

Another object is to provide a process of refining mineral oils which utilizes a novel method and order of steps of combining phenol and a diluent or anti-solvent, such as water, during a selective solvent extraction process.

An additional object of the invention is to provide a process which enables accurate control of the quantity of diluent or anti-solvent added to a selective solvent, and which simultaneously decreases the cost of reclaiming the solvent.

A still further object of the invention is to provide a process of efficiently extracting mineral oils with selective solvents, in which an oil to be extracted, a selective solvent substantially saturated with hydrocarbons dissolved from an oil, and a diluent or anti-solvent are simultaneously mixed, in order to displace the more paraffinic hydrocarbons dissolved in the solvent by the more aromatic, unsaturated, and/or naphthenic hydrocarbons contained in the oil to be extracted.

A still further object of the invention is to provide a closed cyclic system of selective solvent extraction and of solvent recovery which utilizes residual heat from the distillation process in the extraction system.

Another object is to provide a recovery system for a selective solvent containing a diluent which facilitates control of dilution steps in the selective solvent extraction system.

To carry out the process of this invention, I select a solvent refining agent which in its undiluted state is relatively non-selective as measured by its ability to separate aromatic, unsaturated, and/or naphthenic from paraffinic hydrocarbons. My preferred solvent is phenol, although the principle of my invention is not confined to treatment with phenol. It will apply to treatment with aniline, furfural, cresol, or any selective solvent which does not chemically react with the diluent or anti-solvent utilized, but is capable of dilution therewith to produce a solvent having greater selectivity. The use of the general class of known selective solvents in the combination of steps and sequence of operations herein disclosed is contemplated as falling within the broader aspects of the invention. Thus nitrobenzene, cresylic acid and chlorinated ethers, such as BB' dichlorethyl ether, comprise examples of known selective solvents and are operative in my process. Selective solvents in which water is miscible are preferred since water is one of the most efficient diluents or anti-solvents which I have discovered.

It should also be understood that diluents other than water are embraced within the generic scope of this invention. Diluents or anti-solvents which are miscible with the solvent to be used, immiscible with the oil at extraction temperatures and which increase the selectivity of the solvent upon addition in small amounts are operative for my purposes. Phenol and water comprise a preferred combination of solvent and anti-solvent for use in this invention.

Although selection of a proper solvent and a proper diluent is essential to the success of my process, I do not claim as my invention the selective solvents and diluents alone, but rather the particular manner or order in which they are combined during the extraction process.

In practicing this invention it is preferred that the oil be extracted first with a selective solvent in its most dilute and most highly selective state and then with a solvent in a less dilute and a less selective state. By utilizing this particular order of steps, I have found that an increased yield of raffinates is obtained.

In the accompanying drawings, flow diagrams illustrate various processes utilizing the principles of my invention.

Figure 1 illustrates a seven-stage counterflow extraction process in which water is added as a diluent or anti-solvent at the fourth stage.

Figure 2 shows a combination of two extraction processes, the first being a three-stage counterflow process in which water is added to the solvent in the first two stages, and the second being a four-stage anhydrous phenol extraction treatment.

Figure 3 illustrates a seven-stage counterflow phenol extraction process combined with a phenol recovery plant which produces substantially anhydrous phenol to be returned to the extracting system, and water containing phenol to be used as a diluent.

These three specific examples of processes utilizing my invention will now be described in detail.

Figure 1 shows a seven-stage counterflow extraction system in which the distillate flows from left to right through mixer 13', separator 18, mixer 19', separator 19, etc. to mixer 24' and separator 24. The undissolved, refined distillate is removed from the top of separator 24 to storage. The selective solvent, phenol being typical of the type preferred, flows from right to left through mixer 24' to separator 24, then to mixer 23' and separator 23, etc., back to mixer 18' and separator 18. The extract removed from separator 22, which comprises solvent and its dissolved hydrocarbons, is simultaneously diluted with water and mixed with the raffinate from separator 20, in mixer 21'. It has been found that during this step the more paraffinic hydrocarbons dissolved in the extract are freed from solution and replaced by the more unsaturated, aromatic and/or naphthenic hydrocarbons present in the raffinate from prior extraction stages 18, 19 and 20. Some of the freed paraffinic hydrocarbons pass on through the following successive extraction stages to give an ultimate increased yield in raffinate. In the systems herein described, the freed hydrocarbons are not actually separated and separately identified. It is obvious, however, that where a 10% increase in quantity of raffinate is obtained this increase can come only as a result of the hydrocarbons freed by dilution passing on through the extraction system with the raffinate. This result is entirely unexpected and unpredictable since it would seem that hydrocarbons once extracted by the selective solvent would again be dissolved with equal facility. Even more surprising is the fact that such increases in yield of raffinate can be obtained without sacrifice in the viscosity index of the refined oil.

Although I have not found it necessary to separate the hydrocarbons freed from the extract by dilution, such a separation is regarded as within the broader scope of the invention so long as the hydrocarbons freed by dilution are retained in the extraction system for further treatment.

Also, it is to be understood that the extract, raffinate from stage 20 and water need not be simultaneously mixed as shown in Figure 1, although this procedure constitutes an efficient and advantageous mode of operation. The water may be introduced into the extract either before or after it is moved with the raffinate being treated.

A dewaxed distillate from Kettleman Hills, California crude oil was treated by the method of Figure 1. The conditions of treatment and the results obtained as compared with a similar

conventional seven-stage counter-current process are given in the following data:

DISTILLATE TREATED

	Treatment No. 1	Treatment No. 2	Treatment No. 3	Treatment No. 4
Gravity, ° A. P. I.	18.4	18.0	19.7	19.9
Flash, ° F.	460	455	465	445
Viscosity at 210° F.	89	93	81	81

TREATMENT

Phenol selective solvent (volume percent)	215	280	211	312
Water added (percent by wt. based on phenol)	None	2.0	None	4.4
Temp. of extraction, ° F.	120	130	120	130

RAFFINATE (UNDISSOLVED OIL)

Yield (percent of original distillate)	31	34	43	47
Gravity, ° A. P. I.	28.6	29.0	*28.0	*27.6
Flash, ° F.	445	450	465	450
Viscosity at 100° F.	520	530	534	613
Viscosity at 210° F.	63	64	64	68
Viscosity index	90	93	91	90

EXTRACT (OIL REMOVED BY SOLVENT)

Gravity, ° A. P. I.	13.2	12.3	12.1	11.1
Viscosity at 210° F.	150	151	150	170

*Inspections refer to dewaxed raffinates, yields to waxy raffinates.

Attention is directed to the fact that the above data show that a distinct increase in yield of raffinate for the same degree of refinement is obtainable by my process. Comparing treatments 1 and 3 with 2 and 4 respectively, an increase of approximately 10% in the quantity of refined oil is obtained with no material sacrifice in the degree of refinement. In treatment number 2, not only was a 10% more raffinate obtained than in the conventional number 1 treatment but also an actual increase in the viscosity index of the refined oil resulted. The increase in yield of refined oil is of great importance and tremendous advantage in commercial operations.

Figure 2 discloses a combination process utilizing successive dilution steps in the first two stages of extraction. The distillate to be treated flows from left to right as in the previous figure and is removed to storage from the last separator designated **31** in the drawings. The hydrocarbons freed from the extract by the dilutions in mixers **25'** and **26'** are retained in the system in the same manner as in Figure 1.

The last four stages of the process involve a stage countercurrent extraction with a substantially less dilute and less selective solvent, preferably phenol. This relatively less selective solvent is introduced in mixers **27'** and **31'** at the third and seventh stages and flows from right to left.

The extract from the first system (stages 25, 26 and 27) is removed from separator **25** and stored as a highly aromatic and/or unsaturated fraction. At such time as is convenient the phenol and dissolved hydrocarbons are separated and recovered therefrom. The extract from the second system (stages 28, 29, 30 and 31) is likewise removed from separator **28** and stored as an extract of a less aromatic and/or unsaturated character.

Figure 3 is an example of a system for extracting a distillate with phenol or a like equivalent solvent combined with a system of recovery which yields substantially anhydrous phenol and also a water fraction which contains phenol and which is suitable for use as a diluent.

In Figure 3 mineral oil distillate to be extracted flows from left to right through mixer **40'**, separator **40**, mixed **41'**, separator **41**, to mixer **46'** and separator **46**. The raffinate as extracted is removed from the top of separator **46** to storage tank **33** and retained for phenol recovery treatment. The extracting solvent flows from right to left entering the system at mixer **46'** and leaving at separator **40** through pipe line **101** to storage tank **102**.

A diluent comprising water which may also contain some phenol, is admitted in desired quantities to the system. Valves **67** to **76** inclusive permit flexibility in the addition of this diluent. The system permits addition of water or other diluent at any single mixer or to any combination of mixers desired. For example, with valve **61** open so that water flows to the system through pipe **149**, water may be admitted to mixers **40'** and **44'** only, by opening valves **67, 68, 69, 70** and **75** and closing valves **71, 72, 73,** and **74**. Likewise, water may be added to all mixers **40'** to **45'** inclusive, and the quantity admitted to each mixer controlled independently of others by adjusting metering valves **67, 72, 73, 74, 75** and **76**, corresponding to mixers **40', 41', 42', 43', 44'** and **45'**, respectively. By utilizing metering valves of suitable well known types at **67, 72, 73, 74, 75** and **76** accurate adjustment and control of the quantity of diluent may be obtained.

Valve **60** connecting the phenol line **148** and the water line **149** enables a proper balance to be maintained between the water and the phenol. For instance, the percent error due to inevitable inaccuracies and variations in the quantity of diluting fluid added, may be decreased by incorporation of phenol in the diluting water.

In the above connection it is pointed out that for any given error in volume of diluent added, the error in the quantity of water incorporated will be reduced one-half if the diluent contains 50% phenol, to one-fourth if the diluent contains 75% phenol, etc. It is apparent that such an expedient enables extremely accurate control of the quantity of water incorporated in the extracting system. Inasmuch as small variations in the amount of water effect profound changes in the selectivity of the extracting solvent, it is also apparent that accurate control of the quantity of water is essential to satisfactory operation of my process. This desired accurate control can be obtained by utilizing as the diluent or anti-solvent, water containing phenol. It is pointed out that water containing up to 80% phenol acts as an anti-solvent and has no selective solvent action on mineral oil. The water used as a diluent should therefore contain no more than 80% phenol.

The system for recovering phenol from the extract and from the raffinate will now be described. In Figure 3, **102** is the storage tank or surge drum which receives the extract from the extracting system. From the storage tank **102**, the extract enters the recovery plant through pipe **103** controlled by valve **104**. Pipe **103** is connected to two heat exchangers **105** and **106** as shown. After passing the heat exchangers which may be either in series as shown or in parallel, the oil flows through an extension of pipe **103** to a control valve **142** and into flash chamber **107**. The chamber **107** may be extended as shown to form a vertical column which

is equipped with suitable means for baffling and contacting liquids and vapors, such as the bubble cap plates 108. A vapor line 109 leads from the top of the column 107 through a suitable condenser 110, thence to a receiver 111. To the top of the receiver 111 there is connected a gas line 112 leading to a pump 113 whereby a reduced pressure may be maintained on column 107 and on the material flowing through line 103. The condensate collected in receiver 111 is withdrawn through a branched pipe 114 equipped with control valves 115 and 116 whereby, when desired, a portion of the condensate may be returned to the column 107 as a reflux for the condensation of oil vapors, and to effect their return to the lower section of the column. The remainder of the condensate from receiver 111 is run to a storage tank 117.

From the bottom of column 107 a conduit 118 leads to a valve 120 and pump 119 which discharges through an extension of conduit 118 to the heater 122 and thence through coil 121 and pipe 123 to the side of fractionating column 124, equipped with bubble cap plates 125 or equivalent construction as is well known for such use. The bottoms from column 124 flow through pipe 126 and valve 127 to the side of column 135 equipped with bubble plates and operated at a pressure lower than in column 124. The vapor line 144 from the top of column 135 may be connected to a condenser, but is preferably connected as shown to the lower part of the column 107, thus resulting in a lower pressure in the column 135. The lower part of column 135 is equipped with heating means. Such a means is shown as a fixed external heater 143 and a circulating line including pipe 140, pump 141, heating coil 142 and a return pipe therefrom to the fractionating column. Unvaporized residue from the bottom of the column 135 is drawn through line 137 by pump 138 and flows through the heat exchanger 106. From the exchanger 106 the cooled residue flows to the extracted oil storage tank 128. Provision is made for the introduction of a refluxing material into the upper portion of the tower 135 through line 145, controlled by valve 146.

Pipe line 126 described as connecting the bottom of column 124 with column 135, has a branch containing a valve which connects with line 118 leading to heater 121. By this means part of the bottoms from column 124 may be recirculated through heater 121 to provide additional heat absorbing medium.

The vapors from the top of column 124 flow to heat exchanger 105, thence to receiver 130. The condensate from receiver 130 passes through branch line 131 equipped with valves 132 and 133 whereby a part of the condensate may be returned to the column 124 to serve as a reflux material, and the remainder may be passed to the phenol storage tank 134. This condensate constitutes substantially anhydrous phenol.

The raffinate from the solvent extracting system contains a small amount of phenol which is removed in a distillation column. This raffinate passes from storage 33 through pipe 150 and control valve 164 to an appropriate distillation apparatus. The phenol vapors from the distillation column pass to a condenser 154. The condensed phenol flows through control valve 157 and pipe 158 to phenol storage tank 134. A portion of the condensed phenol, as controlled by valve 156, may be returned to the top of the distillation column as a refluxing material.

The raffinate flows to the bottom of the column as it is freed from phenol. In order to supply heat for the distillation process, a portion of the still bottoms is continuously circulated through pipe 159, pump 160, heating coil 161 and heater 162, and then back through pipe 163 to the column. The purified raffinite is removed to storage tank 165 as it accumulates at the bottom of the still in excess of the amount necessary for circulation as a heating medium.

This recovery system combines with my extraction treatment to give a particularly efficient and flexible process. By controlling pressure, temperature and amount of reflux in column 107 the phenol content of the water is determined. This in turn fixes the accuracy of control in the addition of water to the selective solvent extraction system, as previously pointed out. Furthermore, by utilizing phenolic water as a diluent or anti-solvent, a saving in distillation costs is effected, in that the necessity of completely separating the phenol and water is eliminated.

The entire method and apparatus disclosed in Figure 3 constitute a closed system. After once charging reagents to the system it becomes unnecessary to add more water as diluent or more phenol as a selective solvent, except to replace losses from leakage or evaporation. The system is self-contained and requires only adjustment of operating conditions such as the rate of circulation of the diluent, and the temperature of extraction to obtain the degree of refinement of the mineral oil which may be desired. Also, by insulating storage tanks 117 and 134 against heat losses and by adjusting temperatures of condensers 105 and 110, the temperature of the extraction process can be controlled and residual heat of distillation simultaneously utilized in the extraction process.

From the above discussion it is apparent that the process of Figure 3 in particular is not confined to one which utilizes phenol as a solvent and water as a diluent, but in its broadest aspects includes the use of a selective solvent and a diluent or anti-solvent which renders the selective solvent more highly selective. Other examples of combinations of solvents and diluents are cresylic acid with glycerol, phenol with ethyl alcohol, phenol with ethylene glycol, phenol with BB' dihydroxy ethyl ether, and nitrobenzene with triacetin. The diluents or anti-solvents, glycerol, alcohol, ethylene glycol, BB' dihydroxy ethyl ether and triacetin, were practically completely immiscible with the mineral oils treated and were miscible with the solvents in the amounts used. Each diluent was found to increase the selectivity of the solvent and to be operative in the process of this invention.

The above diluents are representative of several types of organic compounds as follows:

Ethyl alcohol is a low molecular weight aliphatic alcohol; methyl, ethyl and normal propyl alcohol act as diluents or anti-solvents in this process, but isopropyl alcohol and the higher alcohols are miscible with the oil and are therefore undesirable.

Glycerol and ethylene glycol are polyhydroxy aliphatic alcohols. Other members of this class are trimethylene glycol, propylene glycol and pinacole (tetramethyl ethylene glycol).

Triacetin (glycerol triacetate) is an ester of a trihydroxy aliphatic alcohol and a low molecular weight aliphatic acid. Glycerol monoacetate,

glycerol diacetate, glycol diacetate and glycol diformate are other representatives of this class.

BB' dihydroxy ethyl ether is an aliphatic hydroxy ether in which two hydrogen atoms have been replaced by two hydroxyl groups. The carbitols (diethylene glycol diethyl ether, diethylene glycol monoethyl ether, and diethylene glycol monomethyl ether) are representatives of this class.

These diluents and many others may be utilized in my process and illustrate the applicability to my process of any diluent or anti-solvent which is miscible with the solvent and substantially immiscible with the oil under the conditions of extraction.

In carrying out my process, the quantity of diluent desirable varies with the type of mineral oil to be treated and the degree of refinement desired. With highly aromatic oils, as much as 15% water based on the quantity of phenol has been used. With more paraffinic mineral oils, the quantity of diluent required is considerably less and depends, also, on the ultimate degree of refinement to be effected. As little as 2% water in phenol will be a sufficient quantity of diluent for various of the more paraffinic oils.

The selective solvent used in the final extraction stage need not be anhydrous; the essential features of this invention merely require that the solvent of the final stage should be no more selective than the solvent in the first extraction stages. The amount of water or other diluent permissible in the solvent at the final stage varies with the oil stock being treated, with the refinement desired, and with the solvent utilized.

The temperature of the extraction process consitutes a variable which permits the degree of refinement to be altered at will. For any given solvent, selectivity decreases with increase of temperature. Obviously, temperature variations may be correlated with the amount of dilution of the solvent to obtain any desired selectivity of solvent and refinement of oil.

It is apparent that my process is not limited to use of apparatus of the type illustrated schematically in the drawings. For instance, in Figure 1, mixers 18' to 20' and separators 18 to 20 may be substituted by a single packed tower. The same is true as to mixers 22' to 24' and separators 21 to 24. Two packed towers with an intermediate mixer corresponding to 21' would be fully equivalent to the apparatus shown and within the scope of the present invention. Likewise, the mixers may be in the form of centrifugal pumps and the separators of either the gravity or centrifugal type. It is not necessary that each mixer and its corresponding separator should constitute separate units of apparatus since a single unit which accomplishes first the mixing and then the separation would obviously be satisfactory.

The present application is a continuation-in-part of my copending application Serial No. 87,874, filed June 29, 1936, which in turn may be regarded as in part a division of my copending application Serial No. 708,718, filed January 29, 1934. The generic aspects of the invention involving first treating a mineral oil distillate with a diluted highly selective solvent and then treating the raffinate from such an extraction with a substantially less selective solvent are claimed in my earlier application Serial No. 708,718. The present case is directed to the species wherein the oil freed from solution by dilution of an extract is retained in the extraction system.

I do not claim as my invention, the distillation and recovery system of Figure 3 alone, but claim only the particular combination with a selective solvent extraction treatment of the type herein disclosed.

Although certain specific amounts of solvent and other specific features have been disclosed in my specification, it is to be understood that all such changes and modifications as come within the scope of the appended claims are embraced within the spirit and teaching of my invention.

I claim:

1. In a process of refining liquid mineral hydrocarbons with a selective solvent refining agent which comprises extracting the hydrocarbon with a selective solvent in a diluted and relatively highly selective state, separating the diluted solvent together with its dissolved aromatic hydrocarbons from the remaining undissolved liquid hydrocarbons, extracting said undissolved fraction with a selective solvent in a substantially less dilute and relatively less selective state, and separating the latter solvent together with its dissolved less highly aromatic hydrocarbons from the undissolved oil, the step of diluting at least one of said extracts with an anti-solvent for the oil which is miscible with the selective solvent but immiscible with the oil to free the more paraffinic hydrocarbons dissolved therein, and retaining the freed hydrocarbons in the extracting system.

2. In a process of refining liquid mineral hydrocarbons with a selective solvent refining agent which comprises extracting the hydrocarbon with phenol in a diluted and relatively highly selective state, separating the diluted phenol together with its dissolved aromatic hydrocarbons from the remaining undissolved liquid hydrocarbons, extracting said undissolved fraction with phenol in a substantially less dilute and less selective state, and separating the latter solvent together with its dissolved less highly aromatic hydrocarbons from the dissolved oil, the step of diluting said latter extract with from 2 to 15% water to free the more paraffinic hydrocarbons dissolved therein, and retaining the freed hydrocarbons in the extracting system.

3. In a process of refining liquid mineral oils with a selective solvent refining agent which comprises extracting the oil with phenol in a diluted and relatively highly selective state, separating the diluted solvent together with its dissolved aromatic hydrocarbons from the remaining undissolved liquid hydrocarbons, extracting said undissolved fraction with phenol in a substantially less dilute and relatively less selective state, and separating the latter solvent together with its dissolved less highly aromatic hydrocarbons from the undissolved oil, the step of diluting at least one of said extracts with phenolic water to free the more paraffinic hydrocarbons dissolved therein, and retaining the freed hydrocarbons in the extracting system.

4. In a countercurrent process of extracting mineral oils with a selective solvent which comprises extracting the oil first with a diluted solvent in a highly selective state and then with a less dilute solvent in a relatively less selective state, the step of diluting said less selective solvent together with its dissolved hydrocarbons with an anti-solvent for the oil which is miscible with the selective solvent but immiscible with the oil while in intimate contact with an undissolved oil containing relatively nonparaffinic hydrocarbons, whereby the more paraffinic hydrocarbon constituents dissolved in the solvent will be re-

placed by the less paraffinic hydrocarbon constituents in the undissolved oil.

5. A process of treating mineral oils which comprises treating the oil in countercurrent extraction with a selective solvent diluted with successively decreasing proportions of water, the oil being treated first with the most dilute and most highly selective solvent, whereby fractions of decreasingly aromatic character are successively removed from the oil, distilling the water from said solvent and its dissolved hydrocarbons, varying the proportion of solvent distilled over with said water inversely with the volume of diluent to be added in said extraction process, separately distilling the remaining anhydrous solvent from the extracted oil, returning the solvent to the extracting system, and adding the aqueous distillate containing solvent as a diluent for increasing the selectivity of the solvent.

6. A process of refining liquid mineral hydrocarbons with a selective solvent which comprises extracting the hydrocarbons with phenol in a diluted and relatively highly selective state, separating the diluted solvent together with its dissolved aromatic hydrocarbons from the remaining undissolved liquid hydrocarbons, extracting said undissolved fraction with phenol in a substantially less dilute and relatively less selective state, separating the latter solvent together with its dissolved less highly aromatic hydrocarbons from the undissolved oil, diluting at least one of said extracts with water to free the more paraffinic hydrocarbons dissolved therein and retaining the freed hydrocarbons in the extracting system.

7. A process of refining liquid mineral hydrocarbons with a selective solvent which comprises extracting the hydrocarbons with furfural in a diluted and relatively highly selective state, separating the diluted solvent together with its dissolved aromatic hydrocarbons from the remaining undissolved liquid hydrocarbons, extracting said undissolved fraction with furfural in a substantially less dilute and relatively less selective state, separating the latter solvent together with its dissolved less highly aromatic hydrocarbons from the undissolved oil, diluting at least one of said extracts with water to free the more paraffinic hydrocarbons dissolved therein and retaining the freed hydrocarbons in the extracting system.

8. A process of refining liquid mineral hydrocarbons with a selective solvent which comprises extracting the hydrocarbons with a cresol in a diluted and relatively highly selective state, separating the diluted solvent together with its dissolved aromatic hydrocarbons from the remaining undissolved liquid hydrocarbons, extracting said undissolved fraction with a cresol in a substantially less dilute and relatively less selective state, separating the latter solvent together with its dissolved less highly aromatic hydrocarbons from the undissolved oil, diluting at least one of said extracts with water to free the more paraffinic hydrocarbons dissolved therein and retaining the freed hydrocarbons in the extracting system.

9. A process for the separtion of mineral oil into fractions relatively more paraffinic in character and relatively less paraffinic in character than the original oil, which comprises extracting said oil in a plurality of stages with a selective solvent for the non-paraffinic fractions of the oil and with an anti-solvent which is adapted to lower the solvent power of the selective solvent for the more paraffinic oil fractions and which is more soluble in the extract phase than in the raffinate phase, removing a raffinate phase and an extract phase from each extraction stage, controlling the quantity of anti-solvent so that the proportion of anti-solvent is increased as the extraction proceeds from the stage at which the final raffinate is withdrawn to the initial oil feed stage to free more paraffinic hydrocarbons dissolved in the selective solvent, and retaining the freed hydrocarbons in the extracting system.

10. A process for the separation of paraffinic and non-paraffinic oil fractions from a mineral oil containing the same which comprises commingling said oil with a selective solvent for the non-paraffinic fractions and an anti-solvent adapted to lower the solubility of the paraffinic fractions in the selective solvent which is more soluble in the extract phase than in the raffiniate phase, separating said phases, re-extracting the raffinate with a selective solvent containing less anti-solvent than in said first extraction and thereby forming a second raffinate phase and a second extract phase, precipitating paraffinic hydrocarbons dissolved in said second extract phase, and retaining said precipitated hydrocarbons in the system for additional extraction.

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