June 8, 1937. M. H. TUTTLE 2,083,511

REFINING MINERAL OIL

Filed Nov. 20, 1933 4 Sheets-Sheet 1

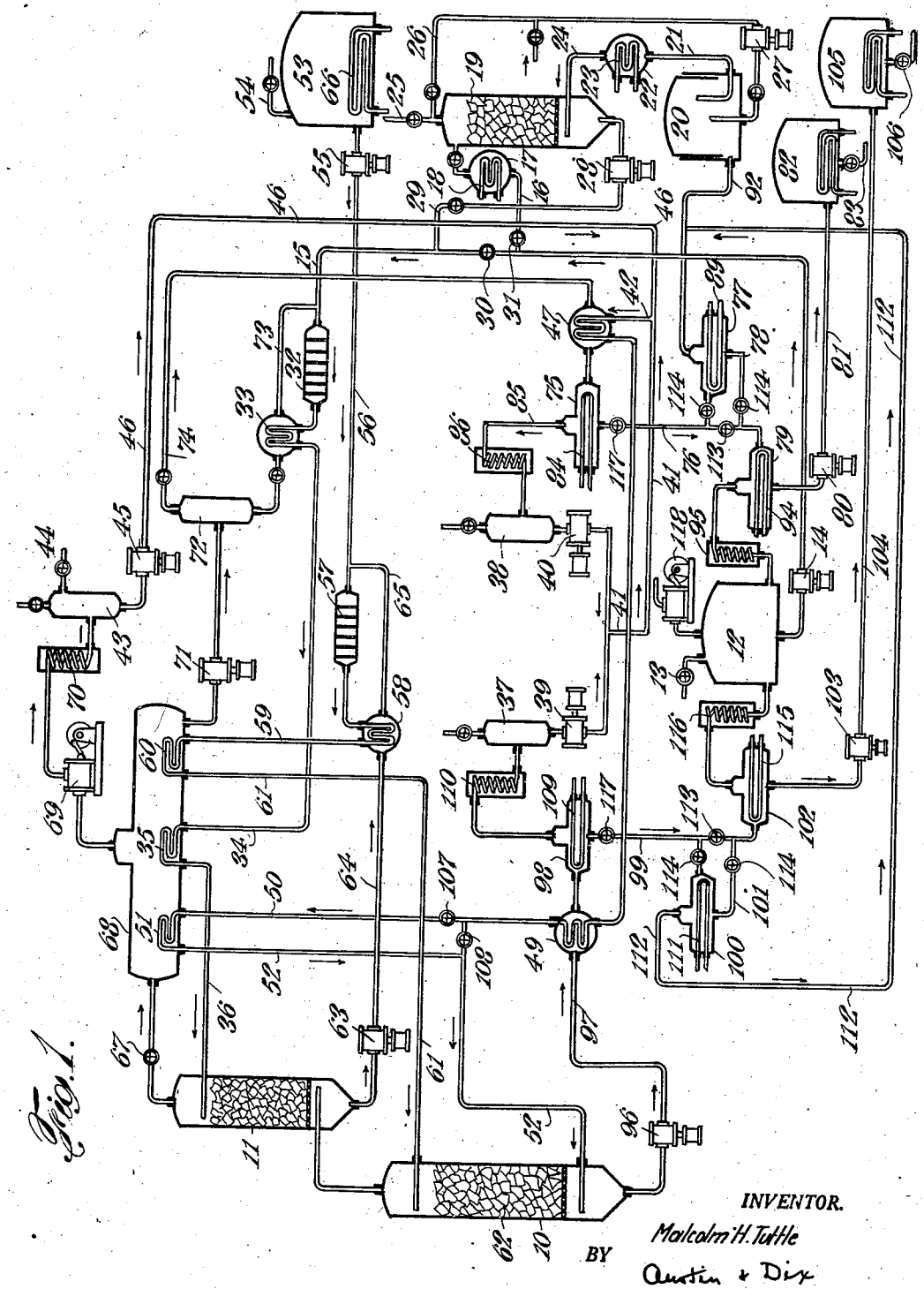


Fig. 1.

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REFINING MINERAL OIL

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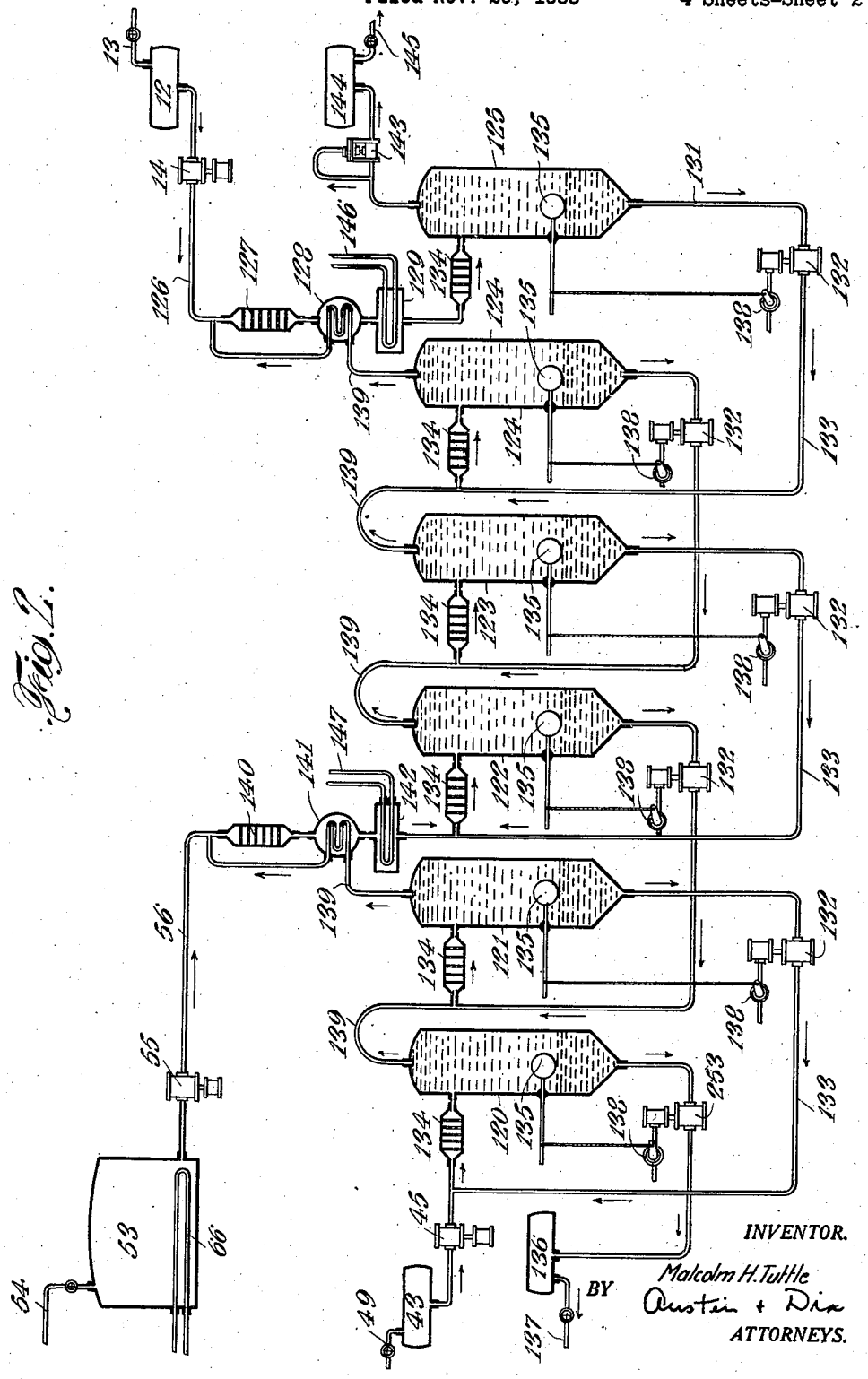


Fig. 2.

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REFINING MINERAL OIL

Filed Nov. 20, 1933 4 Sheets-Sheet 3

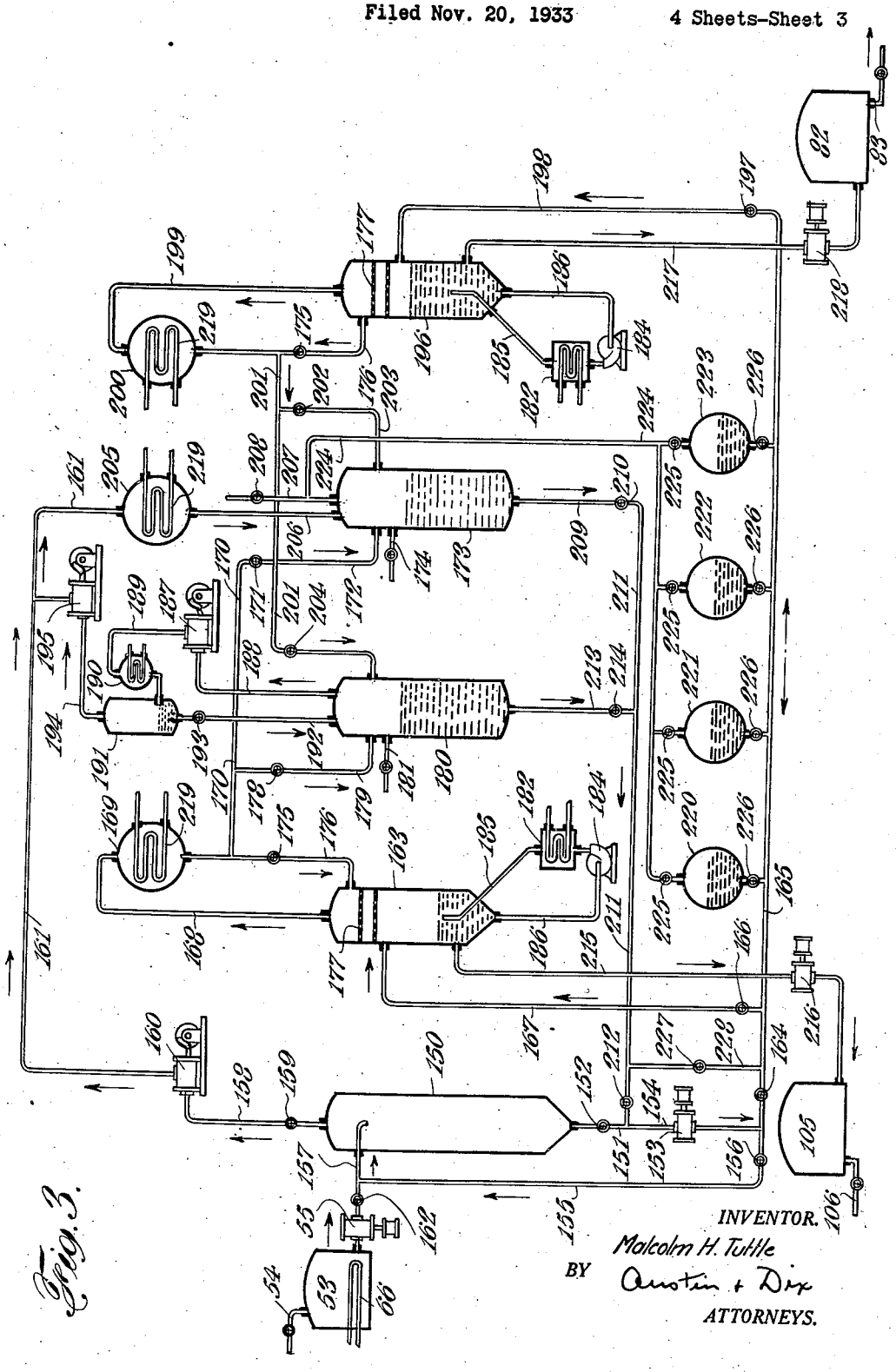


Fig. 3.

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REFINING MINERAL OIL

Filed Nov. 20, 1933 4 Sheets-Sheet 4

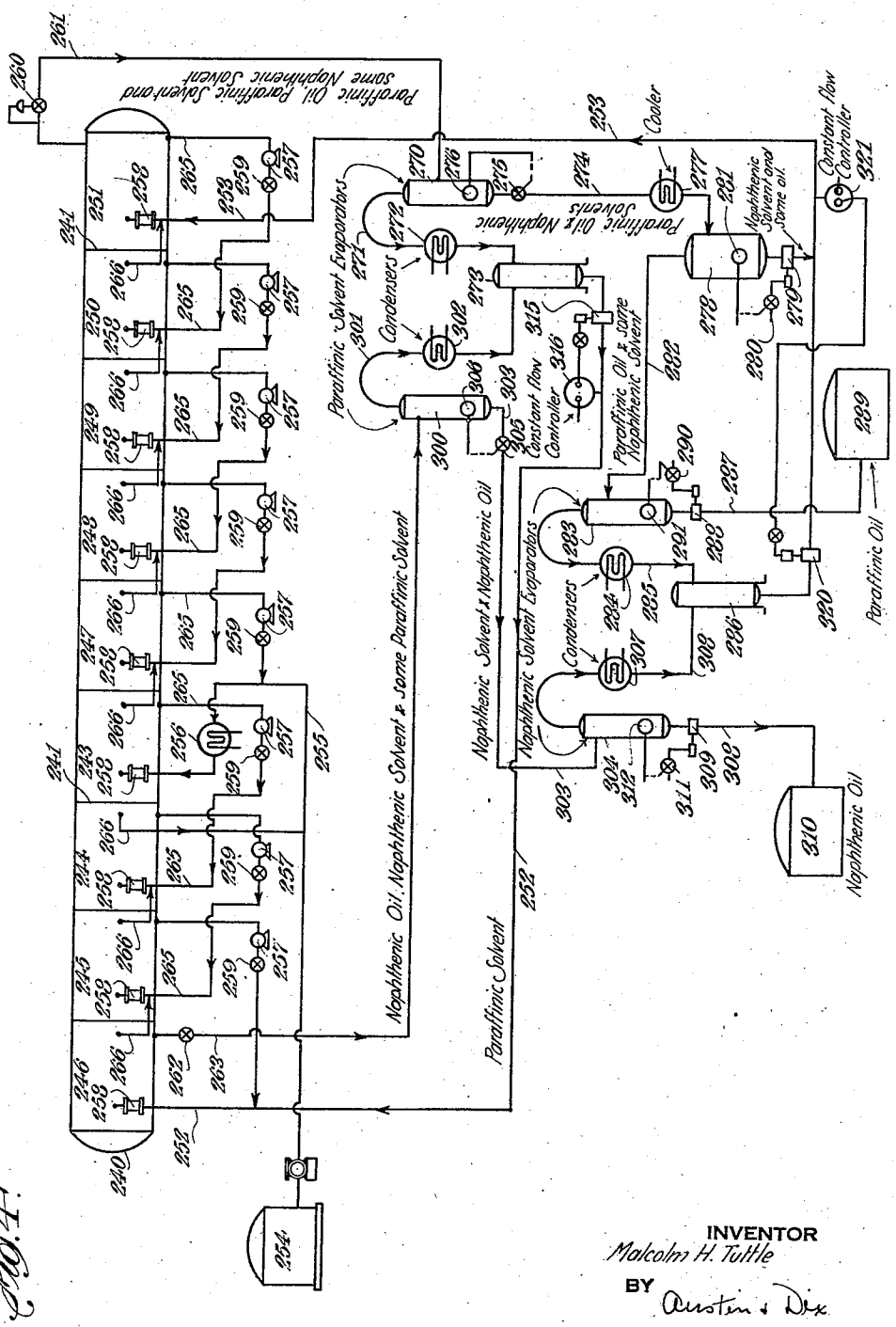


Fig. 4.

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Patented June 8, 1937 2,083,511

UNITED STATES PATENT OFFICE

2,083,511

REFINING MINERAL OIL

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Application November 20, 1933, Serial No. 698,746

6 Claims. (Cl. 196—13)

The present invention has to do with refining mineral oils by means of solvents.

This application is based upon subject-matter divided out of the present inventor's copending application Serial No. 623,483, filed July 20, 1932, and also relates to certain modifications of the examples disclosed in that prior application.

Mineral oils consist principally of intimate mixtures of compounds of carbon and hydrogen in varying proportions. Certain of these compounds are especially useful and suitable for lubricating oil, for instance for internal combustion engines and will be referred to as paraffinic. The other compounds are useful for other purposes but undesirable in lubricating oils and will be referred to as naphthenic.

The solubility of pure paraffinic oil compounds in certain solvents differs from the solubility of naphthenic oil compounds in those solvents and it has been proposed to utilize this selective action for separating a mixture of paraffinic and naphthenic oils, as exists in a mineral oil, into fractions. However, a solvent for naphthenic oil, such as nitrobenzene, which has a limited solvent power for pure paraffinic compounds, in the presence of naphthenic compounds forms a mixture in which the paraffinic compounds have a relatively high degree of miscibility or solubility. Further addition of solvent to the mineral oil mixture to remove more of the naphthenic compounds carries additional paraffinic material into solution so that an attempt to improve the purity of the paraffinic compounds results in both a loss of paraffinic material and a contamination of the naphthenic compounds. In other words, the improvement in the quality of one type of compounds can only be obtained where a single type of solvent is employed, by a lowering of the quality of the other type and is accompanied by a loss in yield of the high quality compounds of the first type.

In accordance with the present development the quality of each class of constituents, paraffinic or naphthenic, may be improved up to the point of producing an excellent yield of practically pure compounds of each type desired, without affecting the quality of the other class; that is, additional naphthenic material may be removed from the mineral oil without loss of paraffinic oil. It is preferred to employ two solvents having a limited miscibility in each other, one of which is a solvent for the paraffinic compounds and the other for the naphthenic.

Through the present invention it becomes possible to produce the final extract of each type of oil in equilibrium with the solvent for the opposite type oil: i. e., the final extract of the naphthenic fraction is accomplished with fresh paraffinic solvent and the final extract of the paraffinic fraction is accomplished with fresh naphthenic solvent.

A feature of the present invention resides in providing improved apparatus to continuously counterflow the solvents and feed the oil, which is to be treated, at an intermediate point where it is subjected to the action of the counterflowing solvents. When the initial separation is made in equilibrium with the charged oil, the composition of each layer is governed to some extent by the composition of the charged oil as well as by the ratio of solvents employed so that the paraffinic layer then contains an appreciable quantity of naphthenic material and the naphthenic layer contains some paraffinic material. The present invention provides for separating the oil to be treated and purifying both layers without loss of oil constituents.

It is also possible to adapt the counterflow principle to batch treatment whereby the oil to be treated is brought into contact with both solvents so that a division into naphthenic and paraffinic layers occurs.

In either the continuous or batch treatment, purification of the resulting fractions without loss of oil desired in that fraction may be accomplished by washing the naphthenic layer, including naphthenic solvent and removed from the other layer, with the paraffinic solvent and the paraffinic layer, including paraffinic solvent and removed from the first-mentioned layer, with naphthenic solvent, and separately recovering the solvents from the washed layers to produce the paraffinic and naphthenic fractions. The relatively fresh solvents used for the final washings, together with the materials taken into solution, may be used for washing less pure fractions at points preceding the final washings. The extent of washing and the amounts of solvents employed may vary with the quality of each type of oil desired and oil to be treated.

The present development is especially useful with crude, or asphalt containing oils, or oils which have been "topped" (distilled) to remove low-boiling fractions such as gasoline and kerosene, but which still contain asphalts, although it is also useful in connection with other mineral oils.

A feature of the invention resides in the provision of novel and improved apparatus for the purposes indicated.

A further feature of the invention resides in

the provision of apparatus in which a given layer may be treated repeatedly with solvent for constituents which are impurities in that layer, the solvent being fresher or stronger in each succeeding treatment, so that eventually that layer is treated with substantially pure solvent adapted to remove or strip the remaining small amounts of impurities from that layer.

Another feature resides in apparatus for intimately mixing upper and lower layers from succeeding and preceding chambers in a series and again effecting a separation into layers which are passed in opposite directions through the series of chambers.

A further feature is to provide apparatus which is capable of similarly accomplishing the removal of impurities from the other layer.

A further feature of the invention resides in apparatus in which the solvent for the impurities in each layer flows in counter-current to the impurities in that layer. That is to say, the fresh solvent used to extract the final impurities from the layer is passed to a preceding point and used as the solvent for the preceding extraction.

Another feature of the invention resides in the provision of an improved apparatus in which a plurality of solvents for respective constituents of the oil flow in counter-current relation, or in other words, so that paraffinic solvent is introduced adjacent the end of the apparatus where the naphthenic oil is removed and so that the naphthenic solvent enters the apparatus adjacent the end where the paraffinic oil is removed. Preferably the apparatus is so constructed that the oil is introduced into an extracting chamber intermediate the ends of the system and is separated into fractions which are advanced towards opposite ends of the system, while the solvents flow from the ends of the apparatus in counter-current relation.

In one specific form of apparatus in accordance with the invention the solvents flow through a tower, the paraffinic solvent rising and dissolving paraffinics to form an upper layer and the naphthenic solvent settling and dissolving naphthenics to form a lower layer, the countercurrent flow taking place while the constituents are actually in contact with one another.

In another form of countercurrent method and apparatus in accordance with the invention, a lower layer from a succeeding chamber and an upper layer from a preceding chamber, containing respective solvents, are intimately intermingled and then fed into a generally horizontal settling chamber, near one end, and permitted to gradually settle out toward the other end of the chamber and form therein an upper and a lower layer. Particular advantages are secured with this type of apparatus as will be hereinafter pointed out.

A relatively specific feature of the invention resides in apparatus for carrying out the extraction continuously in a series of separate chambers, although it will be understood either a single chamber of considerable length or discontinuous batch type apparatus may be employed within the broad principles of the invention.

Another feature of the invention resides in apparatus which accomplishes the treatment of both layers simultaneously in a closed system, the solvents being recovered and recirculated.

Other objects, features and advantages of the invention will appear from the detailed description of the several illustrative embodiments described, although it will be understood that the invention in its broader aspects is not limited to such embodiments.

In the drawings in which like reference characters indicate similar parts,

Fig. 1 shows diagrammatically apparatus embodying my invention and whereby my process may be practiced, such apparatus including temperature controlling and solvent recovery features;

Fig. 2 shows diagrammatically a modification of apparatus whereby counterflow of solvents and extraction of paraffinic and naphthenic fractions are effected, the apparatus shown in this figure being adaptable to the solvent recovery and temperature controlling features shown in Fig. 1;

Fig. 3 shows diagrammatically apparatus embodying my invention and whereby my process may be practiced as a batch operation with continuous features;

Fig. 4 is a diagrammatic view of another form of apparatus in accordance with the invention.

In the practice of this invention, oil which is to be divided into fractions which are respectively more paraffinic and more naphthenic than the original oil is treated or extracted with a solvent having greater solvent power for naphthenic constituents than for paraffinic constituents, while the oil is in the presence of a solvent which has greater solvent power for paraffinic than for naphthenic constituents. Usually the latter solvent comprises one or more hydrocarbons of the paraffin series, and it reduces the viscosity of the more paraffinic fraction and facilitates a more rapid and complete separation therefrom by gravity of a solution of naphthenic constituents. Also, it is thought that the advantages of this invention are due in part to a replacement by the paraffinic solvent, which is a paraffin of such paraffinic constituents of the oil as may be dissolved in the naphthenic solvent, the paraffinic solvent being readily recoverable from the more naphthenic fraction, and thus facilitating more complete recovery of the paraffinic constituents of the oil in and as the more paraffinic fraction thereof. In the description herein of apparatus embodying my invention, and whereby my process may be practiced, all of the above-mentioned features of this invention and additional features are present, but it is to be understood that the separate use of the described features falls within the scope of this invention, although such features co-operate when used together to produce the advantages of this invention.

Referring to Fig. 1, a counterflow of paraffinic solvent and naphthenic solvent is maintained through contacting or extracting elements 10 and 11, and the oil to be separated into fractions is introduced to the counterflowing solvents at an intermediate point thereof. The operation will be described in connection with the use of nitro-benzene having sulphur-dioxide absorbed therein as the naphthenic solvent and propane as the paraffinic solvent, although it is to be understood that other suitable solvents may be employed. Nitro-benzene from tank 12, which may be initially filled by make-up inlet 13, is passed by pump 14 through pipe 15, pipe 16, and cooler 17, which contains refrigerant coil 18, into the top of absorber 19, which may be of any construction, causing contact of the liquid with gas therein. Sulphur-dioxide from gas holder 20 is passed by pipe 21 through cooler 22 containing refrigerant coil 23, and pipe 24, to the bottom of absorber 19, from which the residual gas is vented by vent 25 or returned by pipe 26 and pump 27

to gas holder 20. Nitro-benzene charged with sulphur-dioxide is passed from the bottom of absorber 19 by pump 28 through pipe 29 back to pipe 15. By opening valve 30 and closing valve 31, the sulphur-dioxide absorption apparatus and step may be eliminated. Then the naphthenic solvent passes through mixer 32, heat exchanger 33, pipe 34, cooling coil 35, and pipe 36, into the upper portion of extractor 11.

Propane contained in tanks 37 and 38 is passed by pumps 39 and 40 through pipe 41 to pipe 42; and propane in tank 43, which may be initially filled by make-up inlet 44, is passed by pump 45 through pipe 46 to pipe 42. Propane in pipe 42 passes through heat exchanger 47, pipe 48, heat exchanger 49, pipe 50, cooling coil 51, and pipe 52, to the lower portion of extractor 10.

Oil to be separated into fractions is passed from tank 53, which may be supplied by make-up inlet 54, by means of pump 55, pipe 56, mixer 57, heat exchanger 58, pipe 59, cooling coil 60, and pipe 61, to the upper portion of extractor 10.

Contacting and extracting towers 10 and 11 are provided with any type of packing 62, such as coke, bricks, or raschig rings, suitable for permitting contact of the oil and the solvents; and they are maintained completely filled with liquid. Pumps 14, 39, 40, 45, and 55 maintain such pressure within the extracting towers, and cooling coils 35, 51, and 60 maintain liquids flowing to the towers 10 and 11 at such temperature that the liquids in the towers do not vaporize and are at such temperature that separation of a solution of more naphthenic fraction from a solution of more paraffinic fraction occurs. From the bottom of extractor 11 there is drawn by pump 63 a quantity of the heavy fraction separating out in extractor 11, and possibly a part of the lighter layer separating out in extractor 10, depending upon the rate of operation of pump 62. Liquid so withdrawn comprises naphthenic constituents, naphthenic solvent, paraffinic constituents, and paraffinic solvent, and it is passed through pipe 64, heat exchanger 58, and pipe 65, into pipe 56, and mixed in mixer 57 with the incoming oil to be separated. The oil to be separated may contain wax and have a melting point between 85° F. and 90° F. necessitating the use of a steam coil 66 in tank 53 in order that it may be in liquid form; but after admixture with the liquid withdrawn from the extractor by pump 63, the incoming oil may be chilled in cooling coil 60 to a temperature well below that at which the wax therein solidifies, and then the wax solidifies in particles separate from each other and separate from the oil, leaving the oil free to be acted upon by the selective solvents in extractors 10 and 11.

At the temperature maintained within extractors 10 and 11, the solvents have limited mutual solubility, and separation into an upper layer comprising the more paraffinic fraction dissolved in the paraffinic solvent and containing some naphthenic solvent, and a lower layer comprising the more naphthenic fraction dissolved in naphthenic solvent and containing some paraffinic solvent, readily occurs. The resulting upper layer passes from the top of extractor 11 through pressure regulating valve 67 to evaporating tank 68 containing cooling coils 35, 51 and 60. The pressure in tank 68, and therefore the temperature therein, is regulated by withdrawing therefrom vapor of paraffinic solvent by compressor 69, the output of the compressor passing through condenser 70 into tank 43.

The more paraffinic fraction, partly freed of paraffinic solvent, is passed from tank 68 by pump 71 to separator 72. Naphthenic constituents dissolved in naphthenic solvent and collecting in the bottom of separator 72 pass through heat exchanger 33, in which the temperature thereof is raised, and then they pass through pipe 73 into pipe 15 and are mixed with incoming naphthenic solvent in mixer 32. The separation in tank 72 occurs because the temperature and concentration of paraffinic solvent therein are both lower than in the top of tower 11. Thus, naphthenic constituents which are undesirable ingredients of the more paraffinic fraction are eliminated therefrom; and the oil added to the incoming naphthenic solvent in pipe 15 permits the reduction of the temperature thereto in cooling coil 35 to a temperature which may be below the crystallization point of the naphthenic solvent without occurrence of such solidification or crystallization.

The upper layer in separator 72, comprising the more paraffinic fraction and solvents, passes through pipe 74, heat exchanger 47, vaporizer 75, pipe 76, vaporizer 77, pipe 78, pipe 76, vaporizer 79, pump 80, and pipe 81, to paraffinic run-down tank 82, from which it may be withdrawn by pipe 83. In heat exchanger 47, paraffinic solvent is cooled. In vaporizer 75, the heat supplied by coil 84 vaporizes paraffinic solvent, which passes by pipe 85 to liquefying condenser 86, from which liquid paraffinic solvent passes to tank 38. In vaporizer 77, heat supplied by coil 89 drives off sulphur-dioxide gas, which passes by pipe 92 to gas holder 20. In vaporizer 79, heat supplied by coil 94 vaporizes naphthenic solvent, which passes through condenser 95 to tank 12.

Tar collecting in the bottom of extractor 10 and constituting the more naphthenic fraction dissolved in naphthenic solvent and containing some paraffinic solvent, is withdrawn from extractor 10 by pump 96 and passed through pipe 97, heat exchanger 49, vaporizer 98, pipe 99, vaporizer 100, pipe 101, pipe 99, vaporizer 102, pump 103, and pipe 104, to naphthenic run-down tank 105, from which naphthenic oil or tar may be withdrawn through pipe 106. In heat exchanger 49, paraffinic solvent is cooled preparatory to further cooling in coil 51, and the extent of cooling of paraffinic solvent may be regulated by adjustment of valve 107 in pipe 50 and by-pass valve 108. In vaporizer 98, the heat of coil 109 vaporizes paraffinic solvent, which passes to liquefying condenser 110 and then to tank 37. In vaporizer 100, the heat of coil 111 drives off sulphur-dioxide, which passes by pipe 112 to pipe 92.

If sulphur-dioxide or an equivalent ingredient is not employed, vaporizers 77 and 100 are eliminated by opening valves 113 and closing valves 114. In vaporizer 102, the heat of coil 115 vaporizes naphthenic solvent, which passes to condenser 116 and then to tank 12. Pumps 71 and 96 provide the pressure necessary for condensing paraffinic solvent in condensers 86 and 110, and the pressure on the fractions freed of propane is released by valves 117, and vacuum pump 118 insures that naphthenic solvent will be vaporized in vaporizers 79 and 102 at a temperature which will not alter the same or the oil in contact therewith.

In the extraction step in towers 10 and 11, the continuous upward flow of paraffinic solvent and the continuous downward flow of naphthenic solvent, preferably at temperature at which the mutual solubility of those solvents is limited, carries upward paraffinic constituents of the oil and

carries downward naphthenic constituents of the oil. Just prior to flow of paraffinic constituents from the extracting step they are washed with naphthenic solvent, and just prior to flow of naphthenic constituents from the extracting step they are washed with paraffinic solvent, which is a paraffin and replaces paraffinic constituents of the oil which are dissolved in the solution of naphthenic constituents. Apparently paraffinic solvent entering by pipe 52 takes up naphthenic solvent which is released near the top of the extracting towers because of the lower temperature there; and the released naphthenic solvent moves downward and takes up oil constituents, thus giving a circulation within the extracting towers which aids the freshly supplied naphthenic solvent.

In Fig. 2, there is shown a modified form of apparatus whereby the counterflow of solvents and contacting thereof with oil is effected, this apparatus being more suitable in the case of solvents having a smaller difference of specific gravity than nitro-benzene and propane. Through the contacting or extracting tanks 120, 121, 122, 123, 124 and 125, a counterflow of solvents is maintained, and oil to be separated is introduced to such counterflow at an intermediate point thereof. Naphthenic solvent from tank 12 is passed by pump 14, pipe 126, mixer 127, heat exchanger 128, cooler 129, and mixer 134 of tank 125, and then into that tank. From the bottom of tanks 125, 124, 123, 122 and 121, naphthenic solvent passes by pipe 131, pump 132, pipe 133, and mixer 134, into the next preceding tank. The steam supplied each pump 132 is regulated by a valve 138 controlled by a float 135, which floats upon a solution of naphthenic constituents but sinks in a solution of paraffinic constituents. From the bottom of the first tank 120, the more naphthenic fraction dissolved in naphthenic solvent and containing some paraffinic solvent is withdrawn by pump 253 to tank 136, from which it may be withdrawn for recovery of solvents by pipe 137. The steam supply to pump 253 is controlled similarly to the steam supply to pumps 132.

Paraffinic solvent from tank 43 is passed by pump 45 to mixer 134 of the first tank 120. Paraffinic solvent containing paraffinic oil constituents passes from the top of each tank to the mixer 134 of the next succeeding tank by means of pipe 139. In passing from tank 124 to tank 125, the upper layer from tank 124 passes through heat exchanger 128 and then into pipe 126 and is mixed in mixer 127 with naphthenic solvent, and the mixture passes through heat exchanger 128, cooler 129, and mixer 134 of tank 125, and then into tank 125.

Oil to be separated passes from tank 53 through pump 55 and pipe 56 to mixer 140, heat exchanger 141, cooler 142, and mixer 134 into tank 122; and the upper layer of tank 121, in passing to the tank 122, passes through heat exchanger 141 and is mixed in mixer 140 with the oil to be separated, and the oil to be separated enters tank 122 with the upper layer of tank 121 and the lower layer of tank 123.

The more paraffinic fraction in solution in paraffinic solvent and containing some naphthenic solvent passes from the top of tank 125 through pressure-controlled valve 143 to tank 144, from which it may be withdrawn for solvent recovery by means of pipe 145. By adjustment of pressure-controlled valve 143, liquefied solvents may be employed; and the evaporation of solvents in tanks 136 and 144, or either of them, may provide refrigeration for cooling coil 146 in cooler 128 and cooling coil 147 in cooler 142.

In operation, the relative rates of supply of oil and solvents will be so regulated by controlling the rate of the respective supply pumps thereof that the level of the dividing line between the upper and lower layers in contacting and separating tanks 120 to 125 may be properly maintained by pumps 132 and pump 253.

The solvent recovery and temperature regulating features of the apparatus shown in Fig. 2 may be employed in connection with the apparatus shown in Fig. 1 for those purposes.

It will be apparent that from the operation of the construction shown in Fig. 2 the flow of the upper layer in each tank toward the right causes that upper layer to take up more and more paraffinic constituents of the oil, and that it is thoroughly washed with naphthenic solvent before it is passed from the system. It will also be apparent that the lower layer in being passed through the several tanks toward the left in the figure takes up more and more naphthenic constituents of the oil and is thoroughly washed with paraffinic solvent before it is withdrawn from the system. Such thorough washing prior to removal from the system displaces undesirably absorbed constituents; and the presence of added paraffin hydrocarbon increases the proportion of paraffins present and assists the final separation. As a result, proper separation is obtained in the treatment of highly naphthenic oils in connection with which separation could not be obtained by the mere use of nitro-benzene alone, at least without the use of an excessive amount of nitro-benzene.

In the construction shown in Fig. 3, contacting, extracting, and separation are effected in tank 150, which is provided with means for the introduction of oil to be separated, naphthenic solvent, paraffinic solvent, and certain naphthenic layers resulting from intermediate separating steps, as hereinafter described. Tank 150 is provided with means for effecting circulation and agitation of the contents thereof, including pipe 151 containing valve 152, pump 153, pipe 154, pipe 155 containing valve 156, and pipe 157. Tank 150 is also provided with means for controlling the temperature of the contents thereof by solvent evaporation, comprising pipe 158 containing valve 159, and compressor 160, to which leads pipe 158, and from which leads pipe 161, the rate of operation of compressor 160 controlling the evaporation and therefore the temperature in tank 150.

Oil may be supplied to tank 150 from tank 53 by pump 55, which discharges the oil through valve 162 into pipe 157.

A heavier layer comprising more naphthenic constituents, naphthenic solvent, and some paraffinic solvent may be passed from tank 150 to evaporator 163 by closing valve 156, opening valve 152, and operating pump 153 to pass that layer through valve 164, pipe 165, valve 166, and pipe 167. Volatile paraffinic solvent is removed from the contents of tank 163 by passing through pipe 168, cooler 169, pipe 170, valve 171, and pipe 172, to tank 173, in which paraffinic solvent is collected and which may be initially supplied through pipe 174. Valve 171 controls the release of pressure upon the contents of evaporator 163. By opening valve 175, liquid solvent may be passed through pipe 176 on to bubble decks 177 in evaporator 163 to assist in the separation of the solvent vapors

from the liquids. When removal of paraffinic solvent is completed, pressure on the evaporator is reduced to permit vaporization of the naphthenic solvent at a temperature low enough to avoid alteration of either the oil or the solvent. To this end, valve 171 is closed and valve 176 is gradually opened in pipe 179 leading to tank 180, in which naphthenic solvent is accumulated and which may be initially filled by pipe 181. During the evaporation of naphthenic solvent in tank 163, the contents thereof is heated by circulation through heater 182 by means of pump 184, liquid being withdrawn from tank 163 by pipe 185 and returned thereto by pipe 186; and reduced pressure is maintained in tank 163 by means of compressor 187 connected to tank 180 by pipe 188 and discharging by pipe 189 through cooler 190 into separator 191, from which naphthenic solvent flows by pipe 192 containing valve 193 back to tank 180, and non-condensable vapors pass by pipe 194 to compressor 195, which discharges into pipe 161.

Upper layers containing the more paraffinic fraction dissolved in paraffinic solvent and containing naphthenic solvent, which are formed and separated in tank 150, may be passed to evaporator 196 by closing valve 166 and passing the layer through pipe 165, valve 197, and pipe 198. Volatile solvent is recovered from the contents of evaporator 196 by passing through pipe 199, cooler 200, and pipe 201, valve 202, and pipe 203, to paraffinic solvent tank 173, the evaporation being controlled by valve 202. As in evaporator 163, separation of liquid from vapors is assisted by reflux liquid passed through valve 175 and pipe 176 to bubble decks 177. After completion of the separation of volatile solvent from the contents of evaporator 196, valve 202 is closed, and the pressure in evaporator 196 is reduced by opening valve 204 in pipe 201, which leads to naphthenic solvent tank 180, in which reduced pressure is maintained as above described. The volatile solvent under high pressure in pipe 161 passes through cooler 205 and pipe 206 to volatile solvent tank 173.

Non-condensable gases in tank 173 may be vented by means of pipe 207 containing valve 208.

Paraffinic solvent may be introduced into tank 150 through pipe 209, valve 210, pipe 211, valve 212, pump 153, and pipes 154, 155, and 157, valve 152 being closed and valve 156 being open. Similarly, naphthenic solvent may be introduced to tank 150 by passing that solvent from tank 180 through pipe 213 and valve 214 to pipe 211.

The more naphthenic fraction, freed of solvents, is withdrawn from evaporator 163 through pipe 215 by pump 216 and passed to tank 105.

The more paraffinic fraction, freed of solvents, is withdrawn from evaporator 196 through pipe 217 by pump 218 and passed to tank 82.

The coolers or condensers, 169, 190, 200, and 205, are cooled by water coils 219.

In order to obtain the beneficial effects of counterflow of solvents during the treatment of successive batches of oil to be separated, in the apparatus shown in Fig. 3, partially treated or extracted heavier layers produced in tank 150 in successive operations are held in a plurality of tanks, which may vary in number, but of which four are shown in Fig. 3, namely, tanks 220, 221, 222, and 223, the contents of these tanks being held at the pressure existing in tank 173 by means of pipe 224 leading from pipe 207 and connected to each of said tanks by a valve 225. Transfer of heavier or naphthenic layers produced in tank 150 to these tanks 220 to 223 is accomplished by closing valves 156 and 212 and opening valve 164, and opening the appropriate one of valves 226, by which said tanks are placed into communication with pipe 165, valve 197 being closed. Transfer of the contents of each of these tanks 220 to 223 is accomplished by closing valve 164, opening the appropriate valve 226, and opening valve 227 in pipe 228, and opening valve 212, and passing the liquid by pump 153 through pipes 155 and 157 to tank 150.

As the result of the treatment of successive batches of oil from tank 53, tank 223 will contain a heavy layer least rich in naphthenic constituents, tank 222 will contain a layer richer in naphthenic constituents, tank 221 will contain a layer still richer in naphthenic constituents, and tank 220 will contain a layer very rich in naphthenic constituents.

Assuming that a lighter or paraffinic layer formed in tank 150 after discontinuance of the circulation of the contents of that tank has been transferred to evaporator 196 for the removal of solvents, as above described, then the contents of tank 220 will be transferred to tank 150, and there will also be transferred to that tank from tank 173 the amount of paraffinic solvent necessary for the treatment of a new batch of oil to be separated. Then the contents of tank 150 is circulated by pump 153, as described, and the necessary cooling of the circulating liquid is accomplished by adjustment of valve 159 and operation of compressor 160, as above described. Circulation is discontinued after sufficient contacting of the ingredients of the mixture has occurred, and there forms in tank 150 a heavy naphthenic layer and a lighter paraffinic layer. The heavier layer is transferred to evaporator 163 for removal of solvents, as above described; and the paraffinic layer is retained in tank 150. Then the naphthenic contents of tank 221 is transferred to tank 150 and circulated by pump 153, and during such circulation there is added to the contents of tank 150 by pump 55 a batch of oil to be separated, drawn from tank 53. Circulation is continued until the added oil is put into solution in the naphthenic and paraffinic solvents in tank 150; and upon cessation of circulation, two layers form and the naphthenic layer is transferred to tank 220 and the paraffinic layer is retained in tank 150. It is to be understood that cooling is maintained during each circulation, in the manner described.

Then the naphthenic contents of tank 222 is transferred to tank 150, and the contents of tank 150 is again circulated and separated into layers, and the naphthenic layer is transferred to tank 221 while the paraffinic layer is retained in tank 150. Then the contents of tank 223 is similarly treated, the resultant naphthenic layer being transferred to tank 222.

Then, the amount of naphthenic solvent necessary for the treatment of a batch of oil to be separated is transferred from tank 180 to tank 150, and the resulting mixture is circulated and the resulting naphthenic layer is transferred to tank 223. During these operations there has been completed in evaporator 196 the removal of solvents from the more paraffinic fraction produced in the preceding cycle of operations, and the solvent-freed more paraffinic fraction so produced is passed to tank 82. Accordingly, the paraffinic layer remaining in tank 150 after the transfer of the naphthenic layer therefrom to

tank 223, is transferred to evaporator 196 for solvent removal.

The cycle being so completed, the system is ready for repetition of the cycle described, and treatment of another batch of oil to be separated.

From the foregoing, it is apparent that in each cycle, each layer from which a final fraction is obtained is subjected to repeated action of both solvents, and is thoroughly washed with the solvent that produces the other layer before it is transferred to its evaporator for solvent removal. Thus, the naphthenic contents of tank 220 is thoroughly washed with paraffinic solvent until equilibrium occurs and the paraffinic solvent has taken up as much as possible of the paraffinic oil constituents present, or has replaced such of those constituents as might have been in solution in the naphthenic contents of tank 220, before the resulting naphthenic layer is transferred to evaporator 193. Each body of naphthenic material is repeatedly contacted with paraffinic material, and the layer from which the desired more paraffinic fraction is to be obtained is thoroughly washed with naphthenic solvent prior to the removal of that layer to evaporator 196. The operation involved in connection with the apparatus shown in Fig. 3 bears resemblance to the operation carried out in the apparatus shown in Fig. 2, it being somewhat as though the upper layers in tanks 120 to 125 of Fig. 2 were retained in a single tank such as tank 150, and the lower layers in tanks 120 to 125 were successively contacted with that single paraffinic layer. The counter-current flow of solvents in Fig. 3 occurs in the advancing of naphthenic solvent successively through tanks 223, 222, 221, and 220, in conjunction with the addition of paraffinic solvent to tank 150 at the beginning of each cycle, when the contents of tank 220 is passed to tank 150, with paraffinic solvent being retained in tank 150 until the contents of tanks 220, 221, 222, and 223 are successively passed through tank 150.

In the operation of the apparatus above described, it is to be understood that the appropriate pumps are to be so operated as to preserve the flow-directions described above and indicated by arrows on the drawings; and that, if desired, check valves or other suitable means may be employed to assist to that end. It is also to be understood that various towers or tanks may be joined together or divided into sections, an example of such modification being the carrying out in a single tower of the operations effected in the separate but joined towers 10 and 11.

The starting up of the various modifications of the apparatus shown in the drawings and described may be effected in any suitable manner, it being helpful in the starting up of the apparatus shown in Fig. 3 to charge tanks 220 to 223 with naphthenic solvent such as nitrobenzene before starting up the apparatus. In such case, the first treatment of the contents of tank 220 will then consist in a charging of the naphthenic solvent with paraffinic solvent.

Referring to Fig. 4, there is shown a modified form of apparatus constructed in accordance with the principles of the invention, and which involves a number of advantages from the standpoints of both structural simplicity and efficient operation. This form of apparatus may include an extractor tank 240 subdivided by partitions 241 into a plurality of similar, generally horizontal extracting and settling chambers or pots 243–251, inclusive. Provision is preferably made for introducing solvents into the end chambers 246 and 251 and for introducing an oil to be treated into a chamber 243 intermediate the end chambers. For instance, a solvent for paraffinic oil, such as propane or other satisfactory solvent, preferably in liquid form, and in the main part, at least, recovered from previous operations, may be introduced through pipe 252 into chamber 246, while a solvent for the naphthenic oil, such as cresylic acid or other satisfactory solvent, which is immiscible with the paraffinic solvent, may be introduced into chamber 251 through pipe 253. The naphthenic solvent may also be recovered in the main from previous operations, as will hereinafter be described.

The oil or stock to be treated may be pumped from a tank 254 through pipe 255 into a cooler 256, into which a portion of the lower layer from near the bottom of chamber 247 is fed by a pump 257 and pipe line 265, and into which a portion of the upper layer from chamber 244 is fed by pipe line 266, the operations being preferably continuous. These layers contain amounts of paraffinic and naphthenic solvents, as well as dissolved constituents, and they are preferably intimately mixed with the raw oil in a suitable mixing device 258, before they are introduced into the chamber 243. The mixed materials may advantageously be admitted near one end of the chamber 243 and allowed to flow together toward the other end of the chamber, while stratifying or settling into layers, the construction being such that with a given rate of flow, the settling into layers has ample opportunity to take place to the desired extent, or, in other words, so that the turbulent condition of the mixture at the point of inlet is sufficiently reduced to permit withdrawal of separate layers at points spaced from the inlet.

The lower layer may be withdrawn from the chamber 243 by a pump 267 and pipe line 268 and introduced to the chamber 244 in mixture with the upper layer from chamber 245, the mixing being accomplished by any suitable mixing device 269 connected with the chamber 244. The upper layer from chamber 243 may be withdrawn from a suitable point above the bottom of the chamber by pipe line 266, and added to a lower layer from chamber 248 and passed into chamber 247 through a mixing device 259 connected with this chamber.

The chambers 244—248 constitute a series of similar chambers which may be termed preceding chambers, and in which the lower or naphthenic layer from the initial separation of the oil is successively treated with paraffinic solvent introduced into chamber 248 and advanced in countercurrent flow to the lower layer from chamber 243. That is to say, the lower layer from chamber 243 is relatively rich in naphthenic constituents, and this layer is treated with solvent for paraffinic oil, the apparatus being constructed so that the paraffinic solvent is richest or freshest in the final stage of the treatment of naphthenic oil, while initially the oil is contacted with solvent which has already taken up considerable paraffinic or lubricating oil constituents.

On the other hand, chambers 247—251 constitute a series of succeeding chambers, similar in construction and operation, wherein the upper or paraffinic layer from chamber 243 is successively treated with naphthenic solvent introduced into chamber 248 and advanced in countercurrent flow to said paraffinic layer which advances from chamber 247 to 251 in succession.

It will be understood that the number of chambers may be varied, or that a layer may be passed into a chamber further along than the one next to the chamber from which the layer is withdrawn.

The upper or paraffinic layer from end chamber **251** is withdrawn through valve **260** and pipe **261** and treated as hereafter described for removal of solvents, while the lower layer from chamber **246** is withdrawn from near the bottom of this chamber through valve **262** and pipe **263**, and treated for removal of solvents.

The present apparatus is particularly adapted for handling a normally gaseous solvent, such as propane, and maintaining it in a liquid state without the need for refrigeration or for the conduct of operations at temperatures at which wax in the oil would precipitate. The apparatus provides for maintaining the materials in each of the chambers **243**—**251** under adequate pressure, for instance, by pumping the oil and solvents into the system under pressure and limiting the withdrawal of the paraffinic and naphthenic layers to such a rate as to maintain the desired pressure, which may vary considerably depending on the solvent employed: 160 pounds per square inch is satisfactory for propane. In order to prevent vaporization of solvent in chamber **251**, the valve **260** is preferably of any known back pressure type, arranged so that the desired pressure is maintained in chamber **251** regardless of the pressure in line **261**. Extraction chambers **243**—**251** and the connecting pipes for circulating liquid are all maintained full of liquid, so that there will not be air spaces in which a solvent may volatilize to bring about an inefficient operation or the need for unduly large apparatus.

At the same time, it has been found desirable to circulate liquids in the chambers near the center of the apparatus, particularly chambers **243**, **244** and **247**, at a considerably higher rate than the rate at which the final layers are withdrawn from the end chambers. That is to say, where a relatively pure solvent, which is partial to constituents present in relatively small proportions in the liquid in an end chamber, is contacted with such liquid, the constituents are readily stripped from the mixture by the solvent which is "hungry" for them. On the other hand, where the oil is initially treated with solvents already containing substantial amounts of dissolved constituents, the circulation of the liquids is advantageously much greater in order to provide a more intimate contact between all portions of the liquids. Preferably, an equilibrium is established between the solvents and dissolved constituents in each chamber, the recirculation aiding in accomplishing this.

The present apparatus provides for maintaining the desired circulation at various points, by employing a pump **257** for each of the extraction chambers from which a lower layer is withdrawn, and by providing a valve **259** for controlling the rate of flow of each pump. It has been found that advantageous results are secured where the liquid from the bottom of chamber **243** is pumped into the chamber **244** at a rate two to four times as fast as the rate at which layers are withdrawn from the ends of the apparatus, although the invention in its broader aspects is not restricted to any particular rate of recirculation. If desired, it is possible to by-pass a portion of the liquid back into the same chamber from which it was withdrawn in order to aid in maintaining the proper or desired rate of flow. The flow of upper layer from each chamber is thus controlled by the rate at which pumps **257** circulate fluids from the bottom of the chambers, so that by adjusting the flow of the lower layers the flow of upper layers is automatically controlled. The present apparatus is thus capable of establishing conditions of equilibrium in each of the given chambers so that with a given grade of oil the conditions of treatment and quality of the product may be maintained substantially uniform.

The temperature may be around 60° F. in the chamber **243** and possibly slightly higher in the end chambers. Lowering the temperature in the end chambers may increase the recirculation slightly. It has been found advantageous to keep the temperatures throughout at such a degree as to promote the immiscibility of the solvents, and coolers or heaters may be provided if necessary for maintaining the proper, determinable conditions for given solvents.

The present apparatus is particularly simple to construct and efficient to operate where a countercurrent flow of large volumes of liquid is required, and where the solvents are several times the amount of oil under treatment, as is generally desirable. At the same time, the provisions for intimate mixing and subsequent settling in a generally horizontal concurrent flow in the individual chambers appears to produce a superior and more rapid separation of the oil into fractions distributed in the respective solvents. Especial advantages are secured by the construction of the apparatus in such manner that each successive upper layer from the initial layer in chamber **243** to the final layer in chamber **251** grows richer in paraffinic portions of the oil, while the solvent for other constituents of the oil is counterflowing, so that the substantially fresh solvent strips from the paraffinic layer in the final chamber, **251**, the remaining constituents which are not desired in the paraffinic layer. Similarly, the lower layer passing from chamber **243** to the preceding chamber **246** is counterflowed with respect to solvent for the paraffinic or lubricating oil constituents, so that the practically fresh solvent in chamber **246** has to strip but relatively small amounts of paraffinic oil from materials from which most of the paraffinic oil has already been removed.

Excellent results may be secured by separating from the oil a paraffinic layer which may contain some other constituents of the oil, treating the lower with a fluid including a naphthenic solvent, removing the solution thus formed from the paraffinic layer, repeating the solvent treatment and removal to produce successively a more pure layer, and ultimately washing the paraffinic oil with fresh naphthenic solvent. The naphthenic solvent removed from each treatment and containing some non-lubricant constituents is preferably employed as the fluid for the next preceding treatment, where it will dissolve more of said constituents. It will thus be appreciated that as the paraffinic oil contains less impurities the solvent for impurities is stronger in each succeeding step. At the same time, it will be appreciated that the paraffinic oil is dissolved in a paraffinic solvent which in each stage acts to dissolve paraffinic oil carried over by the naphthenic solvent from another stage. There is thus a countercurrent flow in the sense that the less the other constituents mixed with paraffinic oil, the more concentrated is the naphthenic solvent; there is also a countercurrent flow in the sense

that paraffinic solvent and naphthenic solvent flow in opposite directions to one another.

On the other hand, there is separated from the stock a layer relatively rich in non-lubricant constituents and also containing some lubricants, which layer is treated with paraffinic solvent in a system operating upon the principles set forth in connection with the treatment of the paraffinic fraction.

The separation may be promoted by adding water to the crude oil in the apparatus to reduce the solubility of the upper layer in the lower layer.

Apparatus of the following character may advantageously be employed for recovering the solvents from the extracted oil fractions.

The paraffinic oil, paraffinic solvent and some entrapped naphthenic solvent discharged from chamber 251 and passing valve 260 is carried by line 261 to a suitable evaporator 270 in which only the paraffinic solvent is vaporized by heating the mixture to a suitable temperature, say 350° F. where the solvent is propane. The vapor is carried by pipe 271 to condenser 272, where it is liquefied, and the liquefied solvent is passed to storage tank 273. The liquid paraffinic oil and entrapped naphthenic solvent is drawn off from the bottom of evaporator 270 by pipe 274 at a rate controlled by a valve 275 operatively connected to a float 276 in the evaporator, and is cooled in cooler 277 to a suitable temperature, say 140° F., where cresylic acid is employed as naphthenic solvent. Upon passing the cooled mixture into a receiver 278, a substantial portion of the naphthenic solvent forms a lower layer, in which some small amount of oil may be carried, while the paraffinic oil and the balance of the naphthenic solvent form an upper layer. In this manner, a portion of the naphthenic solvent may be separated from the mixture, and may be drawn off from the bottom of the receiver 278 and passed into line 253 by steam pump 279, controlled by valve 280 and float 281, connected in any convenient manner so that the operation of the pump is controlled by the level of naphthenic solvent in the receiver 278.

The upper layer from receiver 278 may be passed through line 282 into an evaporator 283 in which the liquid may be heated by high pressure steam out of direct contact with the liquid, for distilling the balance of the naphthenic solvent from the mixture. If desired a series of evaporators 283 may be employed, and the last traces of solvent may be removed from the non-paraffinics by means of a fractionating tower having a lower flash evaporator portion in which the lighter fractions of the materials are vaporized, and an upper stripping deck portion, in which the non-paraffinic vapors are condensed, the heat of condensation being employed to aid in heating the mixture entering the flash section. Suitable arrangements may be employed for heat exchange between relatively hot and relatively cool materials at desired points in the solvent recovery system. The naphthenic solvent vapors may be liquefied in condenser 284 and passed to storage tank 286 through line 285.

The paraffinic oil from the evaporator or still 283 may be passed through line 287 by steam pump 288, controlled by valve 290 and float 291, and into tank 289.

This oil constitutes a highly superior lubricating oil which may be employed, after dewaxing if it has not previously been dewaxed, for internal combustion engines, without further treatment. In some special cases, however, it may be desirable to subject the oil to other treatment, for instance, for removing specific impurities, which may occur in certain crudes. Such additional treatment, if desirable for any reason, will be minimized where lubricating is produced in accordance with the present invention.

The naphthenic oil, naphthenic solvent, and some paraffinic solvent leaving chamber 246 under the control of valve 262, passes through line 263 into an evaporator 300, in which paraffinic solvent is volatilized. The paraffinic solvent vapors pass through line 301 into a condenser 302, where they are liquefied, and then pass into tank 273. The naphthenic solvent and naphthenic oil from the bottom of evaporator 300 may be passed through line 303 into an evaporator 304. A valve 305 controlled in any convenient manner by a float 306 serves to regulate the flow of naphthenic solvent and oil from the bottom of evaporator 300.

In the evaporator 304, which functions similarly to the evaporator 283, the naphthenic solvent is driven off from the mixture and is condensed in condenser 307 and then passed through line 308 into storage tank 286, where it mingles with the naphthenic solvent removed from the paraffinic oil. The naphthenic oil or tar from the bottom of the evaporator 304 is conveyed by line 308 and pump 309 into storage tank 310. The pump 309 may be a steam pump similar to pump 288 and may be similarly controlled by a valve 311 operatively connected to float 312.

A high yield of naphthenic oil, which may be more or less tarry, depending upon the crude treated, is thus recovered and is useful for many purposes.

In order to return the paraffinic solvent from the receiver 273 into the extraction system, the solvent may be pumped by a steam pump 315 into line 252, and this steam pump may be controlled by a constant flow controller 316, in order to supply the paraffinic solvent to the extraction system at the proper constant rate as is desirable where the extraction is carried out as a continuous operation in the apparatus of Fig. 4. The constant flow controller may be of any known construction. In order to make up for solvent losses, additional solvent may be fed into receiver 273 from any suitable source of supply (not shown).

The naphthenic solvent from the receiver 286 is pumped by steam pump 320 into the line 253 where it mingles with a naphthenic solvent from the receiver 278. The pump 320 is controlled by a constant flow controller 321 connected so that it regulates the total flow of naphthenic solvent into the chamber 251. Additional naphthenic solvent may be supplied to receiver 286 as required, from a source of supply (not shown).

The present apparatus presents a number of advantages, among which is its simplicity of construction. Moreover, the construction is such that an efficient and intimate mixture of the oil constituents and solvents is effective, while at the same time a rapid and efficient separation of the liquids into layers is accomplished. Thus, a sharp separation is achieved between the constituents which are desired in the lubricating oil fraction, and the other constituents, so that not only is a high yield of lubricating oil procured, but substantially all of the oil constituents which are desirable in the lubricants are found in the lubricating oil fraction which, on the other hand, is substantially free of undesirable constituents

where the oil is to be used for lubricating an automobile engine. At the same time, the apparatus is reasonably inexpensive to build.

Where the terms paraffinic solvent and naphthenic solvent are employed herein, they refer to the solvent action rather than to the chemical constitution of the fluids employed as solvents. Moreover, while it is believed that the action of such fluids is really one of dissolving oil constituents, the invention is not to be restricted to this theory of operation, for, it may be that the fluids simply carry along the oil constituents by some action which may not be at present entirely understood. Accordingly, the term solvents is employed with this thought in mind.

Where the term lubricating oil is employed it refers primarily to a fraction suitable for use in internal combustion engines, although the term is not intended to exclude oils with shades of difference in their properties. Moreover, the other constituents removed from certain stock may possess lubricating properties for certain purposes, but these constituents are, nevertheless, referred to herein at certain points as non-lubricant constituents because they are much less desirable for the former purposes.

It will be understood that wax may be removed from the products of the present process, either before commencement of the process, or at some suitable point after the extraction and before or after the removal of solvents from the extracted oil fractions.

In the practice of this invention, the oils treated will preferably be viscous oils, i. e., oils having a Saybolt universal viscosity of upwards of 50 seconds at 100° F., including distillates and residues and mixtures thereof. By treatment in accordance with this invention, oils having characteristics comparable to or better than the characteristics of similar oils produced from Pennsylvania crude petroleum may be readily produced from oils from almost any field, including particularly Mid-Continent and coastal fields, it being an important feature of this invention that oils having such desirable characteristics can be produced from oils having a high content of asphalt, in some cases so high that treatment thereof with a single solvent is impracticable.

In the production of oils in accordance with this invention, preliminary acid treatment is not necessary, although such a step may be performed; and the acid treatment ultimately required is markedly milder and more economical than acid treatment required to attain the same degree of purification without treatment in accordance with this invention. For example, oil treated in accordance with this invention may be brought to desired color by the use of five to ten pounds of 98% sulphuric acid and five per cent of palm clay; whereas the attainment of the same degree of purity without treatment in accordance with this invention requires as much as fifty pounds of such acid, and also a heavy treatment of clay, per barrel of oil.

Oils constituting the more paraffinic fraction obtained by the practice of this invention are dewaxable by known methods to produce oil of any commercially desirable A. S. T. M. pour test, the type of wax-removal employed, i. e., filter pressing or by difference of specific gravity, being so chosen as to be well suited to removal of the wax precipitated by chilling. Moreover, when the solvents employed in the treatment of oil in accordance with this invention include sulphur dioxide, the upper layer of the separation, containing oil, naphthenic solvent, and paraffinic solvent, is well adapted to dewaxing processes, the sulphur dioxide acting to limit the wax remaining in solution after chilling and acting to prevent crystallization of the naphthenic solvent, relatively mild chilling (—10° F.) being required to obtain oil of 0° F. pour test.

The solvents employed are preferably so chosen that their boiling ranges do not overlap each other or overlap the boiling range of the oil treated. Thus, a mixture of oil to be treated and paraffinic solvent is not to be confused with crude oil containing both naphtha and lubricating oil and comprising constituents of gradually increasing boiling point. Preferably, the solvents are separable from one another and from the oil by distillation. In the practice of this invention, it is a feature that the solvent having greater solvent power for naphthenic than for paraffinic constituents of the oil is employed in conjunction with another solvent for the oil which preferably has limited solvent power for the naphthenic solvent. Thus, while preferred paraffinic solvents have been identified heretofore, there may also be used in conjunction with the naphthenic solvent a solvent which has a higher final boiling point than the solvents mentioned or is less paraffinic in composition or is not wholly composed of hydrocarbons or is not possessed of as marked selectively for paraffine hydrocarbons as are the solvents above mentioned.

While the foregoing description makes reference to the liquefying or maintaining liquidity of solvents or the distillation or driving off of solvents, by maintaining temperatures and pressures suitable to such conditions or effects, and such temperature and pressure conditions are readily ascertainable by reference to handbooks or by simple test, it is desirable to maintain in the contacting or extracting steps, and preferably throughout portions of the apparatus in which volatile solvents are transferred or used in liquid form, a pressure much higher than is necessary to maintain liquidity. For example, in the contacting and extracting zones or elements of the apparatus pressures as high as 160 pounds may be maintained in connection with the use of propane. Thus, in the apparatus referred to in the drawings, successful operation has been effected by maintaining the pressure in the neighborhood of 160 pounds in the contacting or extracting elements. In Fig. 1, such pressure may be maintained in towers 10 and 11 while tower 10 is at 75° F. and tower 11 is at about 50° F., while the pressure in receiver 43 is about 135 pounds, all pressures being gauge pressures unless otherwise specified. Wax-containing oil may be maintained at such temperature as will insure complete fluidity thereof, e. g., 135° F. to 145° F., prior to introduction into the system. Subatmospheric pressure may be maintained, with or without simultaneous use of neutral substances acting to increase vapor pressure of the solvents, for the purpose of effecting the driving off or evaporation of solvents without decomposition of the solvents or of the oil; for example, evaporation of nitrobenzene may be effected by maintaining in tank 12 an absolute pressure in the neighborhood of 12 mm. of mercury. Sulphur-dioxide absorbed in naphthenic solvent may be maintained at atmospheric pressure and absorption effected at such pressure, the absorption temperature being in the neighborhood of 45° F.

It is important that the final separation of solution of more paraffinic fraction and solution

of more naphthenic fraction be effected at a temperature conducive to layer formation at which the solvents have mutual limited solubility. In connection with the use of propane with nitrobenzene, an effective separation temperature is between 25° F. and 40° F., for example, a temperature of 30° F. may be maintained in separator 12. When propane is used in conjunction with benzaldehyde, an effective separation temperature is 10° F. When use with nitrobenzene containing absorbed sulphur-dioxide, an effective separation temperature is 0° F.–10° F. When used with nitrotoluene, an effective separation temperature is 15° F. When using aniline with Pennsylvania gasoline having an end point of 300° F., separation may be effected at temperatures as high as 150° F. When using furfural with that gasoline, separation may be effected in the neighborhood of 80° F. When using pyridine with propane, 25° F. will effect separation. When using more volatile solvents than those mentioned, suitable pressures and temperatures may differ from the foregoing temperatures and pressures, but they are readily ascertainable.

Procedure in accordance with this invention produces a fraction more paraffinic than the original oil and which is an oil having more desirable characteristics than the original oil, and a fraction which is more naphthenic than the original oil and which contains the asphalt occurring in the original oil and is an asphalt having valuable commercial properties. The oil obtained represents a substantially greater yield than the yield resulting from the mere use of a naphthenic solvent, and the oil possesses equal or better characteristics than an oil produced by the mere use of a naphthenic solvent.

For the purpose of illustrating the effect and results of procedure in accordance with this invention, various specific examples are herein described, with the understanding that this invention is not in any respect limited thereto but is amplified thereby.

Employing as the oil to be treated a stock compriisng a residue obtained from Santa Fe Springs, California, crude oil and having the characteristics given below, that stock was subjected to treatments as follows:—

A. The stock was subjected to acid treatment in accordance with good refinery practice, using fifty pounds of 98% sulphuric acid per barrel of stock, and the resulting acid sludge (hereinafter referred to as asphaltum loss) was drawn off and the oil was treated with 3% pound of palm clay per gallon by the so-called contact method.

B. The stock, without acid treatment, was treated in accordance with this invention with four pounds of propane per pound of stock and was separated into a more paraffinic fraction hereinafter referred to as the oil fraction and a more naphthenic fraction hereinafter referred to as asphalt and loss. The separation temperature was 75° F. under 120 pounds pressure.

C. The stock was treated with three pounds of nitrobenzene per pound of stock, but no separation was obtained at any temperature down to 30° F., presumably because of the high asphalt content of the stock.

D. The stock was treated with one pound of nitrobenzene and two pounds of propane per pound of stock, the separation of the solution of more naphthenic fraction being effected at 75° F., and the separation of the more paraffinic fraction being effected at 35° F., under 60 pounds pressure.

E. The stock was treated with one pound of nitrobenzene and four pounds of propane per pound of stock, the separation conditions being as described in test "D".

F. The stock was treated with two pounds of nitrobenzene and four pounds of propane per pound of stock, the separation conditions being as stated in test "D".

G. The stock was treated with two pounds of nitrobenzene and two pounds of propane per pound of stock, the separation conditions being as in test "D".

In order to compare the effect of treatment in accordance with this invention with other treatment, in connection with a less asphaltic stock, tests were made with a stock of reduced asphaltic content consisting of the oil resulting from test "B", substantially freed of asphalt by propane treatment, as follows:—

H. The stock of reduced asphalt content was treated with one pound of nitrobenzene per pound of such stock, the separation temperature being 50° F.

J. The stock of reduced asphalt content was treated with one pound of nitrobenzene and two pounds of propane per pound of such stock, the separation of the more paraffinic fraction being effected at 35° F. and the separation of the naphthenic fraction being effected at 75° F.

K. The stock of reduced asphalt content was treated with one pound of nitrobenzene and two pounds of petroleum ether per pound of such stock, the separation being effected at 50° F.

L. The stock of reduced asphalt content was treated with one pound of nitrobenzene saturated with sulphur-dioxide at 45° F. and two pounds of petroleum ether per pound of such stock, the separation being effected at 0° F.

M. The stock of reduced asphalt content was treated with two pounds of nitrobenzene and four pounds of propane per pound of such stock, the separation temperature being as stated in test "J".

An example of the treatment of an overhead distillate of Mid-Continent petroleum, said distillate having a specific gravity of 22.5° A. P. I., a flash point of 560° F., a Saybolt universal viscosity of 153 seconds at 210° F. and 1125 seconds at 130° F., a viscosity gravity constant of .838, and a viscosity index of 64, is as follows:

N. The Mid-Continent distillate was treated with one pound of nitrobenzene and two pounds of Pennsylvania gasoline having an end point of 300° F., the separation being effected at 50° F.

In connection with these tests, there is given below values which are the average of a number of values obtained by repetition of the tests, with respect to the stock treated and the oil recovered, as follows:—

1. Percentage, based upon the stock treated, yield of oil, this being the oil obtained by acid treating and clay treating or the more paraffinic fraction freed of solvent.
2. Percentage, based upon the stock treated, of loss of acid-treated oil or more naphthenic fraction freed of solvent.
3. A. P. I. gravity of the resulting oil.
4. Saybolt universal viscosity at 130° F.
5. Saybolt universal viscosity at 210° F.
6. Flash point in degrees F.
7. Fire test in degrees F.
8. Lovibond color, quarter inch cell.
9. Conradson carbon.

10. Viscosity gravity constant.
11. Viscosity index.

With respect to the asphalt or more naphthenic fraction, there are given below:—

12. Specific gravity.
13. Melting point.
14. Ductility.

The average yields and characteristics of products obtained in tests "A" to "G", employing Santa Fe Springs residuum, and the characteristic of the charging stock, as explained above, were as follows:—

Stock	A	B	C	D	E	F	G
1. 100%---	39%	82.1%	No separation	61.5%	70.5%	66.5%	56.8%
2. 0%-----	61%	17.9%	---do----	38.5%	29.5%	33.5%	43.2%
3. 16.8----	25.4	21.0	---do----	26.3	25.1	26.7	28.4
4. 1430----	297	505	---do----	232	257	232	206
5. 168-----	72	89	---do----	65	71	65	62
6. 445°----	450°	450°	---do----	450°	450°	450°	450°
7. 505°----	510°	510°	---do----	510°	510°	510°	510°
8. Black--	Dark green	Dark green	---do----	50	50	45	39
9. --------	0.9	0.7	---do----	0.39	0.40	0.39	0.38
10. .885----	.831	.861	---do----	.827	.834	.824	.813
11. 42------	86	60	---do----	103	110	103	102
12. --------	Not recovered	1.074	---do----	1.048	1.078	1.072	1.046
13. --------	---do---	160	---do----	113	141	137	105
14. --------	---do---	Brittle	---do----	100+	100+	100+	100+

The average yields and characteristics of products having a flash test of 450° F. and a fire test of 510° F. obtained in tests H and J to N, employing oil of lower asphalt content, and the characteristics of the charging stocks, as explained above, were as follows:

Stock	H	J	K	L	M	Stock	N
1. 100%------	56.6	72.0	70.3	78.0	56.8	100%	82%
2. 0%-------	43.4	28.0	29.7	22.0	43.2	0%	18%
3. 21-------	26.8	26.2	25.5	25.2	29.7	22.5	25
4. 505------	304	245	301	300	206	1125	665
5. 89-------	75	72	73	73	64	153	124
8. Dark green	130	50	78	115	38		
10. .861----	.827	.825	.830	.832	.803	.838	.823
11. 60------	92	123	90	90	115	64	100

While the foregoing specific examples of charging stocks and final products relate to Santa Fe residue, to such residue treated with propane for the removal of asphalt, and to a Mid-Continent distillate, it is to be understood that this invention relates to all oils having a viscosity upward of 50 seconds at 100° F. and containing both naphthenic and paraffinic constituents.

From the foregoing, it appears that by the practice of this invention products of highly desirable characteristics are obtainable from oils not separable by the use alone of a practicable proportion of a naphthenic solvent and that this invention yields products having marked superiority over products obtained by use of naphthenic solvent alone. From the foregoing results, the effects of increasing and decreasing the proportion of the solvents to the oil and to each other is indicated sufficiently to enable the operator to achieve the desired results; and it is demonstrated that the use of a paraffinic solvent as herein described results in marked increase of yield and marked improvement of viscosity index. In the practice of this invention, the proportions of solvents may be extensively varied and the above results indicate the effects of such variations and enable the operator to obtain whatever results he may desire, and commercial conditions will impose some limitation upon those proportions. Also, the operator may vary the duration of treatment and may repeat the treatments to improve the results.

I claim:

1. In oil refining apparatus, a chamber adapted to effect a preliminary stratification of a liquid mixture, a series of successive chambers in which the lower layer removed from the first-named chamber is treated, and a series of successive chambers in which the upper layer removed from the first-named chamber is treated, and means to cause an upper layer to flow from a chamber in the first-named series to a chamber in the second-named series.

2. In oil refining apparatus, a chamber adapted to effect a preliminary stratification of a liquid mixture, a series of successive chambers in which the lower layer removed from the first-named chamber is treated, and a series of successive chambers in which the upper layer removed from the first-named chamber is treated, and means to cause an upper layer to flow from a chamber in the first-named series to a chamber in the second-named series and to cause a lower layer to flow from a chamber in the second-named series to a chamber in the first-named series.

3. In oil refining apparatus, means comprising a plurality of chambers adapted to cause contact between counterflowing liquids, means near the bottom of an end chamber for admitting a relatively light solvent thereto, means at a higher point for admitting a relatively heavy solvent to the other end chamber, means at a point intermediate the point of admission of said counterflowing liquids for admitting oil to an intermediate chamber, means for withdrawing the relatively light solvent and materials dissolved therein from near the top of the second-named end chamber, means for withdrawing the relatively heavy solvent and materials dissolved therein near the bottom of the first-named end chamber, and means for pumping the relatively heavy liquid from one chamber to another.

4. In oil refining apparatus, means adapted to cause contact between counterflowing liquids, means near the bottom of said first-named means for admitting a relatively light solvent thereto, means at a higher point for admitting a relatively heavy solvent, means at a point intermediate the point of admission of said counterflowing liquids for admitting oil to first-named means, means for withdrawing the relatively light solvent and materials dissolved therein near the top of said first-named means, means for withdrawing the relatively heavy solvent and materials dissolved therein near the bottom of said first-named means, means for removing lighter solvent from the mixture withdrawn from near the top of the first-named means, means for cooling the remainder and separating heavy solvent therefrom, and means for returning the separated heavy solvent and any oil contained therein to the first-named means.

5. In oil refining apparatus of the character described, a series of chambers, means to introduce a solvent into one end chamber, means to introduce a solvent into the other end chamber, means to introduce oil to be refined into an intermediate chamber, means to introduce material containing solvent withdrawn from each of said end chambers into said intermediate chamber, said intermediate chamber being constructed and arranged to enable the mixture to separate into layers, means to pump the lower layer from

said intermediate chamber into a chamber between said intermediate chamber and an end chamber, means to cause the upper layer from said intermediate chamber to flow into a chamber between said intermediate chamber and the other end chamber by a differential pressure, means whereby a lower layer may be withdrawn from an end chamber and whereby an upper layer may be withdrawn from the other end chamber at a combined rate substantially equal to the rate of feed of oil and solvents into the end chambers and intermediate chamber, whereby all of said chambers may be maintained substantially full of liquid.

6. Method of separating oil into raffinate and extract fractions by means of solvents, which comprises admitting a solvent for raffinate type of constituents present in the oil into one end chamber of a series of extraction chambers, admitting a solvent for extract type of constituents present in the oil into the opposite end chamber, admitting the oil to be refined into an intermediate chamber, passing mixtures containing said solvents into said intermediate chamber to cause the oil to separate into raffinate and extract layers therein, passing the extract layer from said intermediate chamber into an adjacent chamber and toward the first-named end chamber, passing the raffinate layer from said intermediate chamber into an adjacent chamber and toward said second-named end chamber, withdrawing an extract fraction from the first-named end chamber, withdrawing a raffinate fraction from a point adjacent the second-named end chamber, returning portions of oil and solvents from said adjacent chambers to said intermediate chamber, and maintaining a substantially higher rate of flow of oil and solvents between said intermediate chamber and said chambers thereadjacent, than the rate of withdrawal of raffinate and extract fractions from the end chambers.

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