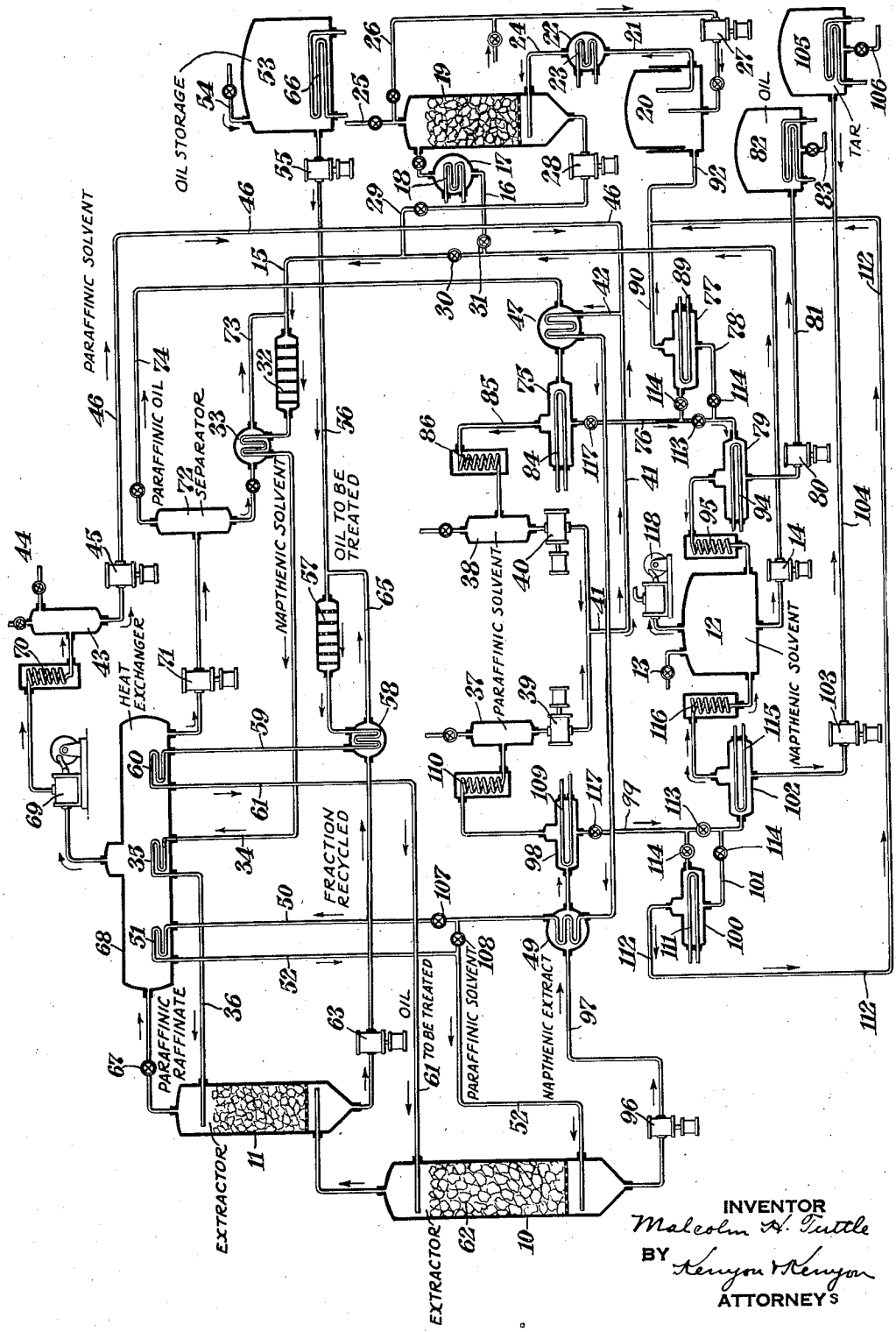
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PROCESS FOR SEPARATION OF MINERAL OIL

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## PROCESS FOR SEPARATION OF MINERAL OIL

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8 Claims. (Cl. 196—13)

This invention relates to an improved process of separating mineral oil stock, by means of solvents, into a paraffinic type fraction, suitable for use as a lubricating oil, and a non-paraffinic or naphthenic type fraction.

Mineral oil stocks are physical mixtures of a variety of so-called paraffinic hydrocarbons and a number of types of non-paraffinic hydrocarbons which are generally referred to in the art as naphthenic oils. These naphthenic oils comprise a variety of compounds some of which are aromatic, some asphaltenes, some unsaturated, some naphthenic, and some heterogeneous.

It has been proposed to divide mineral oil into fractions respectively more paraffinic and more naphthenic than the original oil by physically treating or extracting the oil with solvents (e. g. nitro-benzene) having a greater solvent power for naphthenic constituents than for paraffinic constituents, the mixture separating by gravity into an upper layer comprising the more paraffinic fraction and a lower layer comprising the more naphthenic fraction dissolved in the solvent. Complete separation of naphthenic from paraffinic constituents has not been achieved and the lower layer contains a substantial proportion of paraffinic constituents. Treatment of mixed base oils of low asphalt content by such procedure has produced oil having more pronounced paraffinic characteristics than oil produced by acid treating; but separation of residual oils of high asphalt content, by the use of selective solvents heretofore proposed, has proved impracticable or failed. The solvents proposed appear to be miscible in substantially all economical proportions with residual oils of high content of naphthenic constituents or asphalt, and the necessary separation into layers does not occur. It appears that the solvents (e. g. nitro-benzene) form with the asphalt and/or with the naphthenic constituents a mixture having extensive solvent power for paraffinic constituents. Solvents having more limited solubility for naphthenic oils may cause a separation into naphthenic and paraffinic layers, presumably because such solvents do not form with asphalt or naphthenes a mixture having substantial solvent power for paraffins, but no such solvent is known which will produce from residues of Mid-Continent oils of high asphalt content an oil having characteristics comparable to the characteristics of Pennsylvania oils.

To assist in understanding the effects and results of the practice of this invention, reference may be made to certain arbitrary values commonly employed to indicate the nature of oil. For example, paraffinic oil has a lower specific gravity for a given viscosity than does naphthenic oil and the relation of viscosity to specific gravity is indicated by the viscosity-gravity constant determined in accordance with the following equation.

$$a=\frac{G-0.24-0.022 \log (V'-35.5)}{0.775}$$

where

$a$=viscosity-gravity constant.

$V'$=Saybolt viscosity at 210° F.

$G$=specific gravity at 60° F.

Pennsylvania lubricating oils have a viscosity-gravity constant falling between approximately .807 and .827; mixed base Mid-Continent lubricating oils have a viscosity-gravity constant falling approximately between .827 and .867; and naphthenic or asphalt base lubricating oils from the Gulf coast and California have a viscosity-gravity constant falling approximately between .867 and .887. However, specific oils from one field will have a viscosity-gravity constant falling within the range above given for another field. Moreover, the relation of temperature to viscosity is measured by a viscosity index in which Pennsylvania oils have a value of 90 to 100 and oils of lower viscosity index are less paraffinic and the oils of higher viscosity index are more paraffinic.

Herein naphthenic oils of particularly high melting point are referred to as "asphaltic oil" or "asphalt."

Solvents for naphthenic constituents vary in their properties. One class of such solvents, of which nitrobenzene is an example, is made up of solvents which are miscible in all proportions with mixed base mineral oil of high asphalt content, although they are highly selective with respect to naphthenic constituents when paraffinic constituents are present in predominating proportion. For example, while nitrobenzene takes up naphthenic constituents and forms a separate layer with the residual paraffinic constituents when treating a mixed base oil of low asphalt

content, nitrobenzene takes up asphalt and naphthenic constituents and does not form a separate layer with any residual paraffinic constituents when treating a mixed base oil which is high in asphalt content or very high in content of naphthenic constituents. Apparently, the nitrobenzene forms with asphalt or naphthenic constituents a mixture having solvent power for paraffinic constituents. Another class of solvents, of which sulphur-dioxide is an example, having a selective solvent power for naphthenic constituents, has a limited solvent power for constituents of mineral oil, dissolves preferentially asphalts and those constituents of the oil which are of higher molecular weight, and has a definite selectivity for naphthenic constituents. As illustrative of these properties, it has been found that when extracting a 17° A. P. I. residuum of California crude petroleum obtained from Santa Fe springs, nitrobenzene gives a negligible yield of paraffinic oil because of the high solubility of the entire residuum in the nitrobenzene; and extracting of the same residuum with sulphur-dioxide gives a heavy asphalt as one product and a dark oil of naphthenic characteristics as the other product.

It has heretofore been proposed to extract residual or asphalt-bearing oils by diluting them with a light hydrocarbon diluent in order to precipitate the asphalt, separating the asphalt, and thereafter extracting the diluted oil with a naphthenic solvent. I have discovered that markedly improved results can be obtained, without preliminary precipitation and removal of asphalt, by counterflowing a paraffinic solvent and a naphthenic solvent which has a broad or general solvent power for all types of naphthenic oils, including naphthenes and asphaltenes, and which has a capacity to dissolve all non-paraffinic constituents of the oil as well as some paraffinic oil, and by introducing the oil to be treated to said counter-flowing solvents at a point above the point where fresh paraffinic solvent is introduced, so that the fresh paraffinic solvent washes the naphthenic extract just before it leaves the system, as distinguished from a process in which the oil to be treated is merely diluted with a light hydrocarbon diluent and the diluent oil is washed with naphthenic solvent.

By employing a naphthenic solvent which is capable of dissolving all the non-paraffinic constituents of the oil, including the asphalt and other naphthenic constituents, and, in addition, some of the paraffinic oil, and by operating in the manner just described, the quality of the oil which is left in the upper or raffinate layer is greatly improved by the removal of all of the undesired constituents, and, on the other hand, a maximum yield of good oil is obtained by the washing of the extract with fresh solvent for paraffinic oil.

More specifically, by using nitrobenzene or the like as the naphthenic solvent, and by introducing the oil to be treated to the presence of this naphthenic solvent, as distinguished from first diluting the oil with a light hydrocarbon diluent, it is possible to separate from the oil all the non-paraffinic constituents, including asphalt, in a unitary operation, and without the precipitation of solid asphalt, and by counter-flowing the paraffinic solvent, particularly liquefied propane, to the naphthenic extract, there is an excellent recovery of the desired paraffinic oil. Other examples of broad solvents which have the capacity to dissolve all types of non-paraffinic constituents, in addition to some paraffinic constituents, are benzaldehyde and nitrotoluene, as distinguished from sulphur dioxide, furfural, pyridine and aniline, which have a limited solvent power for only certain constituents of mineral oil.

A feature of this invention is that treatment of mineral oil with an agent having selective solubility for naphthenic constituents, in the presence of an agent having solvent power for paraffinic constituents may be effected by maintaining counterflow of said agents and introducing the oil to the counterflow agents at a point intermediate the points at which they are introduced, a further feature being that the solution of paraffinic constituents is withdrawn from the resulting mixture at a point on the same side of the point at which the oil is introduced as is the point at which the naphthenic solvent is introduced, and the solution of naphthenic constituents is withdrawn from the resulting mixture at a point on the same side of the point at which oil is introduced as is the point at which the paraffinic solvent is introduced. Further features of this invention are that the counterflow is assisted by the difference in specific gravity between the extracting agents employed, and temperature conditions promoting limitation of the mutual solubility of the counterflowing agents may be maintained by regulation of pressure upon the counterflowing agents; and the operation may be a continuous operation or a batch operation or a batch operation having continuous features.

A further feature of this invention is that solidification of an extracting agent may be avoided when the treating temperatures are below the solidification temperature thereof, by mixing with the extracting agent prior to its introduction to the influence of such temperatures a quantity of oil that will prevent such solidification, a further feature being that the oil so mixed is a fraction separated from one of the final oil products and having characteristics undesirable in constituents of that product.

A further feature of this invention is that solidification of wax-containing oil, as a result of temperatures employed in the extracting operation, is prevented by introducing into the oil prior to its introduction into the extracting operation ingredients withdrawn from the extracting operation which will prevent such solidification. The added ingredients permit wax present to precipitate in particles separate from each other and from the oil, giving a mixture that is fluid and in which the oil is free and ready to be acted upon by the solvents.

Other objects and features and advantages of this invention will appear from the detailed description of the several illustrative embodiments of this invention described herein for the purpose of assisting in the understanding of my invention with the intention that my invention is not limited to such embodiments.

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

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

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 naph-

thenic 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 hydrocarbon 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 63. 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 9, 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 temperatures 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 constitutents, thus giving a circulation within the extracting towers which aids the freshly supplied naphthenic solvent.

Other ways of carrying out my invention, and other types of apparatus, are illustrated in my Patent No. 2,083,511 granted June 8, 1937, which embodies subject matter divided from the present application.

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 percent 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.

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 drawing, 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 72. When propane is used in conjunction with benzaldehyde, an effective separation temperature is 10 F. When used 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.

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 comprising a residue obtained from Sante 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 3/8 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.

In connection with these tests, there are 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 Stanta Fé Springs residuum, and the character-

istic 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 | 1004 | 1004 | 1004 | 1004 |

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 |
|---|---|---|---|---|
| 1 | 100% | 56.6 | 72.0 | 70.3 |
| 2 | 0% | 43.4 | 28.0 | 29.7 |
| 3 | 21 | 25.8 | 26.2 | 25.5 |
| 4 | 505 | 304 | 245 | 301 |
| 5 | 89 | 75 | 72 | 73 |
| 8 | Dark green | 130 | 50 | 78 |
| 10 | .861 | .827 | .825 | .830 |
| 11 | 60 | 92 | 123 | 90 |

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. Process of separating a residual mineral oil stock, without preliminary precipitation of asphalt, which comprises counterflowing a paraffinic solvent and a naphthenic solvent having a general solvent power for all naphthenic type oils including naphthenes and asphaltenes, and having a capacity to dissolve substantially as large an amount per volume of solvent as has nitrobenzene, introducing the oil to be treated, containing its entire asphalt content, to said counterflowing solvents at a point space from the point where fresh paraffinic solvent is introduced, controlling the temperature of the extraction at a point where the paraffinic and naphthenic solvent cause the oil to separate into layers, separating the layers and recovering the solvents from the separated layers.

2. Process as claimed in claim 1 wherein the paraffinic solvent is a liquefied normally gaseous hydrocarbon.

3. In a process for separating mineral oil containing paraffinic and naphthenic constituents into fractions respectively more paraffinic and more naphthenic than the original oil, the steps comprising contacting the oil with liquid propane and nitrobenzene, and separating the resultant solutions by difference of specific gravity, the said propane and nitrobenzene being adapted to form a layer solvent system when contacted with each other.

4. Process of refining mineral oil which comprises introducing the oil to be treated into nitrobenzene, withdrawing the resulting extract layer counterflow to liquid propane, and separating the pronane and oil dissolved therein from the extract.

5. Method of solvent refining mineral oil without the need for preliminary removal of asphalt, which comprises counterflowing liquefied propane and nitrobenzene, introducing the oil to be treated to said counterflowing solvents at a point above the point where fresh propane is introduced, separating a paraffinic raffinate, and separating a naphthenic extract countercurrent to fresh propane.

6. Method of solvent refining mineral oil without the need for preliminary removal of asphalt, which comprises counterflowing substantially immiscible paraffinic solvent and a naphthenic solvent having a selective solvent power for all naphthenic type portions of the oil including asphalt, said naphthenic solvent being capable of dissolving substantially as wide a range and as large a quantity of said portions and asphalt as does nitrobenzene, per unit of solvent, introducing the oil to be treated to said counterflowing solvents at a point above the point where fresh paraffinic solvent is introduced, separating a paraffinic raffinate, and separating a naphthenic extract countercurrent to fresh paraffinic solvent.

7. The method as claimed in claim 6 wherein said paraffinic solvent is liquid propane.

8. Method of solvent refining mineral oil without the need for preliminary removal of asphalt, which comprises counterflowing substantially immiscible paraffinic solvent and a naphthenic

solvent having a selective solvent power for all naphthenic type portions of the oil including asphalt, said naphthenic solvent being capable of dissolving substantially as wide a range and as large a quantity of said portions and asphalt as does nitrobenzene, per unit of solvent, introducing the oil to be treated to said counterflowing solvents at a point above the point where fresh paraffinic solvent is introduced, separating a paraffinic raffinate countercurrent to fresh naphthenic solvent, and separating a naphthenic extract countercurrent to fresh paraffinic solvent.

MALCOLM H. TUTTLE.

CERTIFICATE OF CORRECTION.

Patent No. 2,153,353. April 4, 1939.

MALCOLM H. TUTTLE.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, line 48, for "diluent oil" read diluted oil; page 4, first column, line 20, for "pipe 9" read pipe 99; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 13th day of June, A. D. 1939.

Henry Van Arsdale

(Seal) Acting Commissioner of Patents.