This invention relates to refining mineral oils by means of solvents.

Mineral oils are composed mainly of mixtures of compounds of hydrogen and carbon, certain of which are partially useful as lubricating oils, for instance for internal combustion engines. Others are not desired in lubricating oils but find other uses. For convenience, the first type oil will be referred to as paraffinic and the other type as naphthenic oil.

In my copending application Serial No. 623,483, filed July 20, 1932, there is described a highly advantageous process for separating a mineral oil into a lubricating oil fraction of superior quality, and another fraction containing the balance of the mineral oil. Such process has especial advantages when applied to asphalt base or mixed base residua resulting from the topping of crude oils to remove gasoline and/or kerosene, though it is also useful for treating other oils.

Now, in the refining of certain types of mineral oils advantages are to be derived by distilling off a relatively light lubricating oil fraction and separately refining such distillate fraction and the residual oil. While a distillate oil may be treated or refined by the process of the above-mentioned application, it has now been found that superior results may be achieved if such oil be solvent extracted in the presence of a naphthenic fraction previously extracted from a mineral oil or preferably from a residual oil.

A feature of the present invention thus resides in the employment of a naphthenic or tarry fraction of a mineral oil or a residuum to assist in the solvent extraction of a relatively light oil, such as an overhead distillate.

Another feature resides in the provision of a novel and improved process for the efficient solvent extraction of a residual oil and of a light or non-asphaltic, low-bolling oil by solvent extracting the latter type of oil in the presence of a naphthenic or tarry fraction resulting from the solvent extraction of the former type of oil. The paraffinic fractions extracted from the distillate and residue may thus be separately recovered, while the naphthenic fractions may be combined and recovered as a unit.

Still another feature of the invention resides in providing an improved process for preparing lubricating oils having different viscosities, so that they may be blended to produce oil of various commercial viscosities, which oils shall have desired properties including a high viscosity index, or in other words a relatively small change in viscosity for a given change in temperature.

A relatively specific feature of the invention resides in providing for the recovery, as a separate by-product, of an oil which is useful for certain purposes although it does not have as good a viscosity index as the best oil produced.

A further feature resides in providing such a process which is simple and inexpensive to carry out and which can be practised without the need for heating or cooling the fluids during the extraction operations, and preferably without the need for excessive, costly apparatus.

Other features, objects and advantages will become apparent as the following detailed description of illustrative processes in accordance with the invention proceeds, reference being had to the accompanying drawings, wherein:

Fig. 1 is a diagrammatic flow sheet indicating one such process.

Fig. 2 is a diagrammatic flow sheet showing certain additional steps in accordance with the invention.

Referring to Fig. 1, a crude or charge oil may first be topped in the usual manner to take off gasoline, kerosene, and gas oil. A light oil fraction may then be distilled, for instance in a manner similar to present refinery practice, the end point temperature preferably being kept below that at which constituents desired as lubricants would be decomposed. The residual oil may then be introduced to a solvent extraction apparatus 5 where it is intimately mixed with solvents which are selective for the paraffinic oil and for the naphthenic oil, respectively. Preferably, the paraffinic and naphthenic solvents are counterflowed and the preferable oil is introduced in the middle of the system under conditions such that the solvents are miscible to only a limited extent, so that the oil is separated into paraffinic and naphthenic fractions carried by the respective solvents.

In this manner it is possible to dissolve the entire residual oil and at the same time to provide for efficient extraction from each fraction of constituents which belong in the other fraction. However, while such process is especially advantageous for reasons indicated and others, the present invention in its broader aspects is not limited to any particular type of extraction.

The solvents employed may be such as disclosed in my Patents No. 1,912,348 and No. 1,912,349 and in copending applications Serial No. 623,483, filed July 20, 1932 and Serial No. 688,271, filed September 6, 1933. For instance, 55
propane or natural gas fractions liquefied by pressure, are useful as paraffinic solvents, while nitrobenzene and cresylic acid, alone or in mixture with pyridine, phenol, furfural, or sulnine are examples of useful naphthenic solvents. The selective paraffinic and naphthenic solvents are preferably miscible to only a limited extent under the temperature conditions prevailing during the extraction, so that a good separation may be secured. The amounts of solvents employed may be different in several preceding fractions of oil are generally preferred for efficient extraction to avoid excessively long periods of extraction or slow rates of separation as well as as extreme intimate mixing of the solvents and oil to produce the desired contact between them.

In one manner of conducting the extraction, the oil may be continuously introduced into the middle of a tower, the lighter solvent near the bottom, and the heavier solvent near the top. The immiscible solvents and dissolved constituents are withdrawn from top and bottom of the tower. When the paraffinic solvent solution is lighter than the naphthenic solvent solution, the former will be withdrawn at the higher level, the latter at the lower level. The temperature in the extractor should preferably be maintained below the critical temperature at which the solvents will prove aseptic.

Vents are miscible, and where a normally gaseous paraffinic solvent is used the materials are maintained under adequate pressure to keep the solvent liquid. If desired, the extraction may be accomplished by batch treatment instead of continuously, preferably in countercurrent stages.

The paraffinic oil fraction, including paraffinic solvent and some entrained naphthenic solvent and possibly some naphthenic oil, may then be passed to a solvent evaporator 6 where the paraffinic solvent is evaporated and recovered for reuse. Where some naphthenic solvent is entrained in the upper layer, this may be separated, fractionally distilled, and returned to storage for reuse. The paraffinic oil thus produced, after dewaxing (which may be accomplished before or after the extraction), will be found to have excellent properties as a lubricating oil. The process is especially advantageous for producing oils having a high viscosity index (i.e., a relatively small reduction in viscosity when heated from 100°F. to 210°F.). For example, oils having a viscosity index of over 100 may be produced from residual oils in a simple and efficient manner. Moreover, a higher yield of oil is obtained than has heretofore been possible with residua.

A rather remarkable feature of this solvent extraction process is that it is particularly suited to extracting relatively heavy or residual oils containing considerable or even high amounts of asphaltic type constituents, and excellent results have been achieved when operating on such oils. However, the process is less efficient for light oil distillates, for instance, from common overhead from Pennsylvanian or Appalachian crudes. It has now been found that improved results may be achieved by solvent extracting such a distillate, or similar light oil, in the presence of the naphthenic or tarry material removed from a relatively heavy or residual oil.

While it would ordinarily be possible to solvent extract the whole crude in a single operation, it is highly desirable under certain circumstances to remove a light oil from the crude charging stock by distillation, for one reason to obtain a light fraction useful for blending. For another reason, it may be desirable to dewax, or remove wax from, the light oil by a somewhat different procedure than is most suitable for dewaxing heavy oils. There are other advantages to this practice, but suffice it to say that when a distillate is to be treated with a solvent or solvents, excellent results may be achieved by mingling a naphthenic layer from a relatively heavy oil with the light distillate either prior to or after introducing them into the extraction system or during the extraction operations. For instance, a naphthenic layer and solvent drawn off from the bottom of extractor 5, may be introduced into an extractor 5 at a point above the point where light oil is introduced, and paraffinic and naphthenic solvents may be counterflowed as in the extractor 5. If in some instances sufficient naphthenic solvent is present in the naphthenic (tar) fraction, it may be unnecessary to add more of such solvent to the extractor 5.

The paraffinic oil and paraffinic solvent are withdrawn from the top of extractor 5 and passed to suitable apparatus 6 for evaporating the solvent. Some naphthenic solvent may also be carried over and recovered, as described in connection with the paraffinic fraction from extractor 5. The extract there will prove aseptic.

Like the oil produced from the residuum, but will have a lower viscosity, and be suitable for blending with the oil from evaporator 6 to produce a full line of motor lubricants from say S. A. E. viscosity 10 to 80.

The residual fraction from the extractor 7 may be withdrawn and further treated, or disposed of as a by-product. It will contain the naphthenic oil from both the residual charging stock and the light distillate, as will most of the naphthenic solvent and generally some paraffinic solvent, which solvents can be readily recovered by evaporation, decantation or otherwise, for reuse in the process.

Through the employment of a naphthenic oil fraction in connection with the solvent extraction of a heavy crude, certain advantages are secured. For one thing, the critical solution temperature, at which the paraffinic solvent solution and the naphthenic solvent solution become immiscible to such extent that a separation occurs, is raised, thus avoiding the need for cooling the mixture to a low temperature. Moreover, the character of the naphthenic fraction is such as to increase the selectivity of the solvents for type of constituents each is designed to dissolve. A superior separation results, both in respect to the purity of the products and the mechanical efficiency (speed and so forth) of the extraction. Furthermore, while distinct paraffinic or lubricating oils are produced well adapted for blending, the entire naphthenic oil and tar fractions are recovered as a unit. Furthermore, savings in apparatus may be effected due to the ability to obtain a highly efficient extraction of both the light oil and the residual oil under conditions best suited to the treatment of each.

Merely by way of example, one may take a typical Appalachian crude and distill off the gasoline, kerosene and gas oil fractions, after which a lubricating oil fraction may be obtained which is preferentially removed under vacuum, until an end point temperature, commonly considered satisfactory in refining of such oils, is reached. The balance of the oil may then be extracted with a solvent for paraffinic oil and a solvent for naphthenic oil.
to separate the residuum into a lubricating oil fraction and a naphthenic fraction in accordance with the foregoing or the disclosure of the invention, the residuum may be introduced into an extractor 11', into which the intermediate oil distillate is also admitted, and the extraction is effected preferably in the manner previously described by means of one or both of the solvents for paraffinic oil and for naphthenic oil. The high-grade paraffinic oil, resulting mainly from the intermediate distillate and solvent treated to pass to solvent evaporator 16', and otherwise treated, if desired, as pointed out in connection with the high-grade oil from the residuum.

The naphthenic oil from the extractor 11" may be solvent-treated to produce a second-grade oil in extractor 12", or be bypassed by proper operation of valve 13' and 14', to extractor 11", where the light oil distillate is solvent-treated in the presence of the naphthenic or tarry fractions from previous operations. A high-grade lubricating oil fraction is drawn off from the top of extractor 11" and the solvent is removed from this fraction in evaporator 16". The resulting fraction may be treated to further purify or improve it as mentioned in connection with the previously described high-grade oil fractions. By operating valves 13' and 14', as desired, the naphthenic or asphaltic fraction from extractor 11" may be treated or not in extractor 12" to produce a second-grade oil.

The several high-grade oil fractions may then be passed to blending apparatus 15 where the high viscosity oil from the extractor 11 may be mixed in suitable proportions with one or both of the high-grade oils from extractors 11" and 11", to produce a full line of lubricating oils. The second-grade oils from the several extractors 12, 12' and 12" may be treated similarly to the high-grade oils, to remove solvents from them and otherwise improve their properties, and be blended, if desired, in suitable apparatus (not indicated on the flow sheet).

From the bottom of extractor 11" or 12", as the case may be, there are withdrawn the total for naphthenic oil from the various extractions. The entire naphthenic oil contained in this fraction may be recovered by evaporation or by settling and decantation, or both, in suitable apparatus (not indicated on the flow sheet).

It will thus be understood that there is provided a simple and convenient process for producing a series of high-grade lubricating oils having different viscosities. At the same time, the present process provides for extracting a light oil in the presence of a naphthenic or tar fraction, which results in a superior extraction of the light oil and permits the extraction to be carried out at a higher temperature than would otherwise be feasible. That is to say, the solvent extraction must be carried out at a temperature at which the solutions tend to separate efficiently, so that the paraffinic fraction may be drawn off from the naphthenic fraction. When given solvents are employed, the critical temperatures at which the layers become immiscible, or miscible to but a limited extent, is found to be higher where an asphaltic oil is present than where only a light oil is present. The need for refrigeration or cooling apparatus is thereby eliminated, where the solvents employed are propane and cresylic acid, for example, the process may be conducted at around 75° F.

Moreover, a high yield of lubricating oil is
produced, since any lubricating oil not extracted from the residuum in the extractor II is carried down into extractor II' and again treated with paraffinic solvent. So, in extractor II' a further washing is carried out to recover additional paraffinic oil.

In addition, provision is made for recovering oils of lower viscosity index than the high-grade oils, if desired, and much flexibility is permitted. The tars or asphaltic and naphthenic oils are all recovered as a unit and the recovery of naphthenic solvent from them may be effected in a single operation. Thus the apparatus required is minimized, while at the same time provision is made for the separate production of lubricating oils of various viscosities. The process is particularly advantageous in connection with plants where apparatus is already in use for distilling crude oils, where a further saving in apparatus results.

In short, a high yield of superior lubricating oils of varying viscosities may be produced in a simple and efficient manner. The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no intention, in the use of such terms and expressions, of excluding any equivalents of the features shown and described, or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed.

What is claimed is:

1. In a process for extracting a mineral oil by means of solvents, the steps comprising distilling a crude charging stock to produce a light oil distillate, extracting the residual oil from the stock by means of paraffinic and naphthenic solvents which are miscible to only a limited extent, to produce a paraffinic layer and a naphthenic layer, separating the layers, adding at least a portion of the naphthenic layer to the distillate, and separating the distillate into relatively paraffinic and naphthenic fractions by means of a paraffinic solvent.

2. In a process for extracting a mineral oil by means of solvents, the steps comprising distilling a crude charging stock to produce a light oil distillate, extracting the residual oil from the stock by means of paraffinic and naphthenic solvents, which are miscible to only a limited extent, to produce a paraffinic layer and a naphthenic layer, separating the layers, adding the entire naphthenic layer to the distillate, and separating the distillate into relatively paraffinic and naphthenic fractions by means of a paraffinic solvent.

3. In a process for extracting a mineral oil by means of solvents, the steps comprising distilling a crude charging stock to produce a light oil distillate, extracting the residual oil from the stock by means of paraffinic and naphthenic solvents, which are miscible to only a limited extent, to produce a paraffinic layer and a naphthenic layer, separating the layers, adding the entire naphthenic layer to the distillate, and separating the distillate into relatively paraffinic and naphthenic fractions by means of a paraffinic solvent and additional naphthenic solvent.

4. In a process for extracting a mineral oil by means of solvents, the steps comprising distilling a crude charging stock to produce a light oil distillate, extracting the residual oil from the stock by means of paraffinic and naphthenic solvents which are miscible to only a limited extent, to produce a paraffinic layer and a naphthenic layer, separating the layers, extracting a paraffinic oil from the naphthenic layer by means of a paraffinic solvent, adding the remainder of the naphthenic layer to the distillate, and separating the distillate into paraffinic and naphthenic fractions.

5. In a process for extracting a mineral oil by means of solvents, the steps comprising distilling a crude charging stock to produce a light oil distillate, extracting the residual oil from the stock by means of paraffinic and naphthenic solvents, which are miscible to only a limited extent, to produce a paraffinic layer and a naphthenic layer, separating the layers, extracting a paraffinic oil from the naphthenic layer by means of a paraffinic solvent, adding the remainder of the naphthenic layer to the distillate, and separating the distillate into paraffinic and naphthenic fractions by means of a paraffinic solvent.

6. In a process for extracting a mineral oil by means of solvents, the steps comprising distilling a crude charging stock to produce a light oil distillate, extracting the residual oil from the stock by means of counterflowing paraffinic and naphthenic solvents, which are miscible to only a limited extent, to produce a paraffinic layer and a naphthenic layer, separating the layers, adding at least a portion of the naphthenic layer to the distillate, and separating the distillate into relatively paraffinic and naphthenic fractions by means of counterflowing solvents which are miscible to only a limited extent.

7. In a process for refining mineral oils, separating a crude into a plurality of portions by distillation, extracting the resulting residue by means of paraffinic and naphthenic solvents, adding at least a portion of the naphthenic portion thus produced to one of said distilled portions, extracting the resulting mixture with paraffinic and naphthenic solvents, and extracting another of said distilled portions with a solvent in the presence of at least a portion of the naphthenic oil resulting from the extraction of the first-named distillate portion.

8. Method of refining a mineral oil which comprises extracting at least a portion of said oil with paraffinic and naphthenic solvents to produce a high-grade paraffinic oil and a relatively naphthenic oil, treating said naphthenic oil with paraffinic solvent, removing the paraffinic solvent and dissolved constituents from the said naphthenic oil, mixing the balance of said naphthenic oil with a light mineral oil distillate, extracting the mixture thus produced with a solvent to produce a high-grade paraffinic oil, and extracting the balance of the mixture to produce another paraffinic oil.

9. Method of refining a mineral oil which comprises distilling said oil to produce a light oil, distilling said mineral oil to produce an intermediate distillate, treating the light oil with paraffinic and naphthenic solvents, removing a naphthenic fraction from the light oil and introducing said fraction to the intermediate distillate in the presence of paraffinic solvent, removing a naphthenic fraction from said intermediate distillate, conducting said intermediate distillate with a second naphthenic fraction to the residue of the mineral oil in the presence of a paraffinic solvent, and withdrawing a naphthenic fraction from said residue, whereby the naphthenic portions of said light oil, said intermediate distillate and said residue are paraffinic and naphthenic solvents.

10. In a process for refining a crude mineral oil by means of solvents, the steps comprising distilling a crude charging stock to produce a
relatively light oil distillate, extracting the residual oil from said stock by means of a naphthenic solvent to produce a raffinate phase and an extract phase, and extracting the aforementioned distillate with at least a portion of said extract phase containing naphthenic constituents of the residue and naphthenic solvent.

11. In a process for refining a crude mineral oil by means of solvents, the steps comprising distilling a crude charging stock to produce a relatively light oil distillate, extracting the residual oil from said stock by means of paraffinic and naphthenic solvents which are miscible to only a limited extent to produce a raffinate phase and an extract phase, and extracting the aforementioned distillate with at least a portion of said extract phase containing naphthenic constituents of the residue and naphthenic solvent.

MALCOLM H. TUTTLE.