FIG. 1

RAFFINATE

WASHER

EXTRACTOR

FEED

VACUUM FLASH TOWER

EXTRACT

GLYCERINE

DMF

32 46

16 18

10

12 48

26 24

36

40

38

30

28
SOLVENT EXTRACTION OF AROMATICS

Chyn Dong Shiah, 189 Nassau Ave., Manhasset, Long Island, N.Y.

Filed June 4, 1964, Ser. No. 372,577

7 Claims. (Cl. 208—321)

This application is a continuation-in-part of copending application Serial No. 96,890 filed March 20, 1961 and now abandoned.

This invention relates to a process for the separation of petroleum or petroleum products into fractions of differing chemical compositions and is more particularly concerned with a process which is applicable to petroleum distillates of all boiling ranges.

Liquid-liquid extraction is an increasingly important tool in chemical processing, especially in petroleum refining. Solvent extraction, as applied in petroleum refining, for example, serves to separate a hydrocarbon oil stock into two or more fractions of differing chemical compositions and most frequently has been applied to the separation of aromatics from other hydrocarbon types (naphthenes, paraffins and olefins). Examples of the application of liquid-liquid extractions include:

(1) Separation of benzene, toluene and xylene from catalytically reformed naphthas.

(2) Removal of aromatics from kerosene to improve smoke point.

(3) Removal of aromatics from light gas oils in order to make high-quality diesel fuel, jet fuel and rocket fuel.

(4) Removal of aromatics from catalytic cracking charge stocks in order to improve yields and reduce coke lay-down in catalytic cracking units.

(5) Separation of naphthalene precursors (alkyl naphthalenes) from petroleum fractions.

(6) Removal of aromatics from heavy straight-run gas oils to produce spray oils and transformer oils.

(7) Removal of aromatic-type compounds from lubricating oil distillates in order to produce high-quality lubricating oils.

Sulfur reduction of petroleum distillates (particularly light and heavy gas oils) is also a concomitant and desirable result of aromatics extraction, since most of the sulfur contained in middle distillates is either a part of an aromatic compound or is contained in a thiophene ring which usually responds to a selective solvent in the same manner as an aromatic compound.

A modern refinery may employ liquid-liquid extraction in one or more of the foregoing applications.

A large number of compounds have been found to exhibit selectivity for the separation of aromatics from other hydrocarbons. Of these only a few have been employed to any significant extent on a commercial scale. These include (together with their boiling points) the following:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Boiling point at 760 mm. (° F.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid-sulfur dioxide</td>
<td>325</td>
</tr>
<tr>
<td>Furfural</td>
<td>15</td>
</tr>
<tr>
<td>Phenol</td>
<td>323</td>
</tr>
<tr>
<td>Diethylene glycol</td>
<td>358</td>
</tr>
<tr>
<td>Sulfolane</td>
<td>473</td>
</tr>
</tbody>
</table>

Most of the processes which have been developed involve essentially the same processing sequence. The first step in the process is counter-current contacting of the solvent and the oil. A number of contacting devices are well known in the trade and include packed columns, mechanically-agitated columns, mixer-settler combinations and centrifugal contactors. The solvent selectively absorbs the aromatic portion of the feed stock, which portion is produced from the column as an extract phase. The less soluble (non-aromatic) portion of the feed stock is produced as a raffinate phase. The solvent is contained in both the raffinate and the extract phases, with most of the solvent recuperated in the extract phase. The usual method of recovering the solvent from the extract and the raffinate phase is to take advantage of the difference in boiling point between the hydrocarbons in the extract phase and the solvent by employing distillation procedures. The recovered solvent is then recycled to the extraction device to complete the process.

There is, however, no solvent-extraction process which can be used effectively and in a practical manner for the extraction of the full range of petroleum oil stocks. Furthermore, the existing processes employing the solvents referred to above are either relatively complicated or unduly expensive.

The customary practice in the recovery of a solvent employed in solvent extraction is by distillation, and the cost of heat required for such solvent recovery constitutes the largest item of the operating cost of the solvent extraction process. Furthermore, conventional solvent extraction process are generally operated at the same relatively elevated temperature level as the solvent stripper in an effort to effect maximum heat economy. In addition, by reason of the bulk of the extract and/or raffinate which is admixed with the solvent at the boiling temperature of the solvent, the chance of heat deterioration of the solvent and of the extract or raffinate is increased, and the chance of possible interaction between the solvent and the oil, or between the air in the system, e.g. air dissolved in the oil and solvent, with the solvent and/or oil, is also increased.

A major consideration which has heretofore been an obstacle to the provision of a solvent extraction process which can be applied to hydrocarbon stocks of all boiling ranges is the boiling point of the solvent. Customarily, as previously mentioned, the recovery of the solvent is effected by distillation. There must, therefore, be a certain temperature difference between the boiling point of the solvent and the boiling range of the stock extracted in order to effect efficient separation between the oil and the solvent upon distillation. In the event that the oil feed stock has a boiling range close to that of the solvent, it is not practicable to separate the two phases by distillation procedures. Hence, the above-mentioned solvents are limited in their applicability. For example furfural, which has a boiling point of about 323° F., is commonly used for the extraction of hydrocarbons having an initial boiling point of approximately 400° F. and higher. It cannot, however, be effectively used for oil stocks boiling much lower than about 400° F., because of the difficulty of separation of the oil from the furfural. Diethylene glycol, with a boiling point of 473° F., is suitable for the extraction of naphthas (maximum boiling point about 400° F.), but has not been used for heavier distillates because of its high boiling point.

However, the boiling points of most solvents, with the exception of sulphur dioxide, are all in or near the boiling range of the kerosene fraction, i.e. 380—550° F. As a result, none of the commercial solvent extraction processes, with the exception of the sulphur dioxide process, is applicable to oils of the kerosene boiling range. Sulphur dioxide extraction plants are inherently less expensive inasmuch as, the extraction takes place at low temperature, requiring the use of refrigeration; the solvent is recovered by evaporation and since it is a gas at normal temperatures and pressure, compressors must be employed to liquify the gas; and since sulphur dioxide is highly corrosive in the presence of water, elaborate precautions are necessary to dry the feed and prevent water from entering the plant.

In many extraction applications, it is necessary to produce a high purity extract. For example, benzene, toluene
and xylenes specifications require a purity in excess of 99%. By contracts, where removal of the aromatic-type hydrocarbons from the charging stock is the primary objective, a lower purity is acceptable. For example, in the extraction of kerosene the recovered extract phase may have an aromatic content of 70–80%. Not all the pure polar solvents which have been found to be effective in aromatic separations form Type 1 solubility diagrams with aromatics and non-aromatics. A Type 1 diagram has the following characteristic appearance when plotted by triangular coordinates:

```
E
Aromatics

Non-aromatics
Solvent
```

The maximum purity of the extract which can be produced in a Type 1 system is represented by point E, the terminus of a line starting at the solvent apex (100% pure solvent) and drawn tangent to the envelope. Typically, the extract will contain 70–80% aromatics.

Various methods have been used to increase extract purity. These include:

1. Subjecting the extract phase to extraction distillation to remove remaining non-aromatics.
2. Employing extract reflux.
3. Employing a high-boiling diluent which will displace the undesired non-aromatics and may later be removed by distillation.
4. Employing a low-boiling diluent which will displace the undesired non-aromatics and may later be removed by distillation.
5. Adding another solvent to the primary solvent which will modify the solvency and selectivity of the primary solvent. For example, water has been used for this purpose. In general, water will increase selectivity and reduce solvency. Adding water or similar compounds to the solvent system will often permit the production of higher purity of the pure aromatics at the expense of increased solvent circulation.

A single process which is applicable to all boiling ranges of hydrocarbons (i.e., from naphtha to lubricating oil distillates should have the following features:

1. The primary solvent should possess high solvency and selectivity.
2. The boiling point of the primary solvent should be high enough so that the vaporized solvent may be condensed with cooling water, but low enough so that excessive temperatures (which may lead to degradation of the materials being extracted) or extremely low vacuums are not required in the solvent recovery stage.
3. The solvent should be inexpensive, non-toxic, possess thermal stability and should be non-corrosive to ordinary materials of constructions, such as steel.
4. It should be possible to control the selectivity and solvency of the primary solvent to provide optimum extraction conditions for the particular stock being treated.
5. It should be possible to separate and recycle the primary solvent economically from any boiling range of stock (from naphtha to vacuum gas oil).
6. It should be possible to produce any desired purity of the extract phase (from high purity to low purity).
7. The process, once operating for a solvent combined in a single economical plant with, for example, a refinery to employ liquid-liquid extraction to a much greater extent than has heretofore been possible. Up to now, many small refineries have been unable to employ extraction in their processing schemes because, with the available processes, each possible application requires a separate small plant of an uneconomical size. However, with a single multi-purpose plant, a small refiner can take advantage of liquid-liquid extraction for a variety of applications and can produce the same range of products as a large refiner who can economically justify separate extraction plants for each type of stock.

As a result of the present invention to provide a liquid-liquid extraction process which possesses the advantageous features enumerated above and can be applied to hydrocarbon stocks of all boiling ranges.

It is a further object of this invention to provide a process for the recovery of high purity aromatics from hydrocarbon stocks of all boiling ranges.

It is a still further object of this invention to provide a process wherein the primary solvent may be recovered without subjecting the charging stock to excessive temperature.

It is another object of this invention to provide a process which does not require the use of high pressure, low temperatures or corrosion resistant materials.

In accordance with the invention, the extraction of hydrocarbon oils is effected with one or more solvents dissimilar in their solvent properties. For convenience of description, one of the components may be designated as a primary solvent and the other as a secondary solvent. The primary solvent in the process of this invention is a solvent for aromatics and must also be soluble in water. A preferred primary solvent is dimethyl formamide, but a number of other solvents possessing similar solvent properties may also be used, such as alkylamides, aroylamides, and particularly dimethyl acetamide and tetrahydrofurfuryl alcohol.

A secondary solvent is chosen, according to one aspect of the invention, in order to effect separation between the primary solvent and the hydrocarbon portion which has been selectively extracted. A secondary solvent can be a solvent which is completely miscible with the primary solvent but immiscible with hydrocarbon oil extract, or the secondary solvent can be a solvent immiscible with the primary solvent but in which the hydrocarbon oil extract is completely miscible.

In one embodiment of this invention, paraffinic hydrocarbons have been found to be effective as secondary solvents which are immiscible with the primary solvent but miscible with the hydrocarbon oil extract and when paraffinic hydrocarbons are used as the manner outlined for this invention they furnish a means of controlling aromatics recovery and purity. Paraffinic hydrocarbons of all boiling ranges are effective, and pentanes, hexanes, mineral spirits (400°F–500°F boiling range) and mineral oil have been employed successfully.

In a preferred manner of operation, the primary solvent is introduced at one end of the primary extractor, the feed at an intermediate point and the secondary solvent at the other end of the extractor. The ratio of solvent to feed may range from about 1:1 to about 5:1. The lower solvent ratios are generally applicable to lubricating oils and the higher solvent ratios to the higher stocks such as catalytic reformates. The raffinate phase, containing the non-aromatic portion of the feed together with relatively small amounts of primary and secondary solvents, flows to the raffinate solvent recovery system. The extract phase, containing most of the primary solvent, the hydrocarbon extract and some secondary solvent, flows to the extract solvent recovery system.

Since the primary raffinate usually contains a relatively small quantity of the primary solvent (ca. 3%), it is usually desirable to employ a water-wash step for recovery of the primary solvent and a distillation to separate the hydrocarbon raffinate from the secondary solvent. In order to permit separation of the secondary solvent from the hydrocarbon raffinate, the boiling range of the secondary solvent must be either higher or lower than the feed stock. The minimum difference required in the boiling points of the secondary solvent and the feed stock varies with design of the equipment, however, a difference of the order of about 50°F has been found to
be a practical minimum difference with the equipment used and described herein.

The primary extract contains aromatics, primary solvent and secondary solvent. Under suitable process conditions, the secondary solvent replaces the non-aromatics usually associated with the aromatics in the extract, the primary extract flows to a secondary extraction column where it is contacted with additional secondary solvent. The secondary extract containing largely secondary solvent and aromatics is separated by fractionation, the secondary solvent being recycled to the primary extractor or secondary extractor, and the aromatics, containing small quantities of the primary solvent, being (for example) water washed before flowing to storage.

The raffinate from the secondary extraction, containing largely the primary solvent, is recycled to the primary extractor.

From the foregoing description it is apparent that the process described possesses the desirable features of a multi-purpose extraction process outlined in earlier paragraphs. For example:

1. The primary solvent may be selected on the basis of its solvent and chemical properties, and its boiling range can be independent of the boiling range of the feed and solvent to permit separation by fractionation. In this case, the raffinate and extract produced from the naphthas are overhead products from the distillations, and the solvent is recycled to the primary extraction column. When the feed is a high-boiling hydrocarbon mixture, such as a vacuum gas oil, the secondary solvent may be recovered directly from the primary extract without distillation. In this case, the secondary solvent is the overhead product from such distillation.

2. The secondary solvent may be produced from hydrocarbon fractions available in most petroleum refineries by extraction of a fraction of the appropriate boiling range. The solvent is therefore, generally available, thermally stable and low in cost.

It is therefore apparent that this process may readily be used for a wide variety of liquid-liquid extractors.

Another important feature of the process of this invention is the low heat input required for the total process. It is not necessary to distill the primary, polar solvent to separate it from the hydrocarbon extract and therefore the total heat requirement is that required to distill the hydrocarbon raffinate and extract when the secondary solvent is higher boiling than the feed stock, and the secondary hydrocarbon solvent when the secondary hydrocarbon solvent is lower boiling than the hydrocarbon feed. Inasmuch as the heat of vaporization of the polar primary solvent, is usually higher than the heat of vaporization of hydrocarbon feed or a low boiling hydrocarbon solvent, the heat of vaporization of dimethyl formamide is 248 B.t.u./lb. compared with the heat of vaporization of a typical hydrocarbon feed of 140 B.t.u./lb. It is obvious that the process of this invention requires low heat input.

In another embodiment of this invention a secondary solvent is used which is miscible with the primary solvent, but essentially immiscible with said hydrocarbon oil extract. Useful solvents of this type include mono and poly alcohols, short chain aldehydes and ketones, and other lower alkyl mono and poly hydroxy compounds. The primary and secondary hydroxy solvent pair are chosen so that a separation of primary and secondary solvent can be easily achieved. Advantageously, when the secondary solvent is miscible in the primary solvent, there should be a boiling point difference of at least 75° F. between the two solvents.

In practicing the process, wherein the primary and secondary solvents are miscible with each other, the hydrocarbon oil to be extracted is introduced as feed into the lower portion of an extraction column and the extracting fluid comprising the primary solvent (amide) and up to 90% of the total volume of the fluid of the secondary (miscible) solvent (hydroxy compound), is introduced into the upper portion of the column. The proportion of primary solvent in the extracting fluid can vary from 100 to 50 percent of the mixture.

The raffinate stream, which leaves the top of the extraction column, is a mixture of most of the paraffinic hydrocarbons from the charging stock with small amounts of the extracting fluid. The extract stream, which leaves the bottom of the column, contains most of the aromatics and olefins from the feed stock and most of the extracting fluid introduced into the column. Both the raffinate and the extract stream are then washed countercurrently in separate washers by means of further quantities of the primary solvent to remove hydrocarbon streams from the washers as the light layers from each of the washing operations. The heavier layer from both of the washing operations is composed of mixtures of the primary solvent and of the secondary (miscible) solvent with the proportion of secondary (miscible) solvent higher than the original extracted fluid used for the extraction operation. Inasmuch as the primary solvent and the secondary (miscible) solvent are selected so that their boiling points are widely spaced apart, the two are separated easily by a simple vacuum flash operation, e.g., at pressures of 2 mm. to 100 mm. Hg. A typical vacuum flash operation, carried out in a simple vacuum flash tower, is effected at a pressure of 50 mm. Hg (abs.) and at a temperature of 100° C. Such conditions are particularly suitable when the solvent is dimethyl formamide and the secondary (miscible) solvent is glycerol. The overhead from the vacuum flash operation is primarily the primary solvent and the bottoms from the vacuum flash tower is the secondary (miscible) solvent.

The overhead primary solvent stream is mixed with the desired quantities of secondary (miscible) solvent from the bottom stream and the mixtures are used over again in the main extraction column. The minute amount of oil stock which may be retained in the flash tower is recycled along with the primary solvent. The temperature of the raffinate stream entering the extraction column is conditioned by the returning bottom stock, and the bottoms from the vacuum flash tower is the secondary (miscible) solvent.

The other important feature of this invention is the low heat input required for the total process. It is not necessary to distill the primary, polar solvent to separate it from the hydrocarbon extract and therefore the total heat requirement is that required to distill the hydrocarbon raffinate and extract when the secondary solvent is higher boiling than the feed stock, and the secondary hydrocarbon solvent when the secondary hydrocarbon solvent is lower boiling than the hydrocarbon feed. Inasmuch as the heat of vaporization of the polar primary solvent, is usually higher than the heat of vaporization of hydrocarbon feed or a low boiling hydrocarbon solvent, the heat of vaporization of dimethyl formamide is 248 B.t.u./lb. compared with the heat of vaporization of a typical hydrocarbon feed of 140 B.t.u./lb. It is obvious that the process of this invention requires low heat input.

In another embodiment of this invention a secondary solvent is used which is miscible with the primary solvent, but essentially immiscible with said hydrocarbon oil extract. Useful solvents of this type include mono and poly alcohols, short chain aldehydes and ketones, and other lower alkyl mono and poly hydroxy compounds. The primary and secondary hydroxy solvent pair are chosen so that a separation of primary and secondary solvent can be easily achieved. Advantageously, when the secondary solvent is miscible in the primary solvent, there should be a boiling point difference of at least 75° F. between the two solvents.

In practicing the process, wherein the primary and secondary solvents are miscible with each other, the hydrocarbon oil to be extracted is introduced as feed into the lower portion of an extraction column and the extracting fluid comprising the primary solvent (amide) and up to 90% of the total volume of the fluid of the secondary (miscible) solvent (hydroxy compound), is introduced into the upper portion of the column. The proportion of primary solvent in the extracting fluid can vary from 100 to 50 percent of the mixture.

The raffinate stream, which leaves the top of the extraction column, is a mixture of most of the paraffinic hydrocarbons from the charging stock with small amounts of the extracting fluid. The extract stream, which leaves the bottom of the column, contains most of the aromatics and olefins from the feed stock and most of the extracting fluid introduced into the column. Both the raffinate and the extract stream are then washed countercurrently in separate washers by means of further quantities of the primary solvent to remove hydrocarbon streams from the washers as the light layers from each of the washing operations. The heavier layer from both of the washing operations is composed of mixtures of the primary solvent and of the secondary (miscible) solvent with the proportion of secondary (miscible) solvent higher than the original extracted fluid used for the extraction operation. Inasmuch as the primary solvent and the secondary (miscible) solvent are selected so that their boiling points are widely spaced apart, the two are separated easily by a simple vacuum flash operation, e.g. at pressures of 2 mm. to 100 mm. Hg. A typical vacuum flash operation, carried out in a simple vacuum flash tower, is effected at a pressure of 50 mm. Hg (abs.) and at a temperature of 100° C. Such conditions are particularly suitable when the solvent is dimethyl formamide and the secondary (miscible) solvent is glycerol. The overhead from the vacuum flash operation is primarily the primary solvent and the bottoms from the vacuum flash tower is the secondary (miscible) solvent.

The overhead primary solvent stream is mixed with the desired quantities of secondary (miscible) solvent from the bottom stream and the mixtures are used over again in the main extraction column. The minute amount of oil stock which may be retained in the flash tower is recycled along with the primary solvent. The other important feature of this invention is the low heat input required for the total process. It is not necessary to distill the primary, polar solvent to separate it from the hydrocarbon extract and therefore the total heat requirement is that required to distill the hydrocarbon raffinate and extract when the secondary solvent is higher boiling than the feed stock, and the secondary hydrocarbon solvent when the secondary hydrocarbon solvent is lower boiling than the hydrocarbon feed. Inasmuch as the heat of vaporization of the polar primary solvent, is usually higher than the heat of vaporization of hydrocarbon feed or a low boiling hydrocarbon solvent, the heat of vaporization of dimethyl formamide is 248 B.t.u./lb. compared with the heat of vaporization of a typical hydrocarbon feed of 140 B.t.u./lb. It is obvious that the process of this invention requires low heat input.

In another embodiment of this invention a secondary solvent is used which is miscible with the primary solvent, but essentially immiscible with said hydrocarbon oil extract. Useful solvents of this type include mono and poly alcohols, short chain aldehydes and ketones, and other lower alkyl mono and poly hydroxy compounds. The primary and secondary hydroxy solvent pair are chosen so that a separation of primary and secondary solvent can be easily achieved. Advantageously, when the secondary solvent is miscible in the primary solvent, there should be a boiling point difference of at least 75° F. between the two solvents. 
theoretical plates or stages depending on the separation desired. The ratio of primary solvent to oil is suitable 0.2-1 to 15:1.

Other objects and features of the invention will be apparent from the following detailed description of il- lustrative embodiments thereof and from the accompanying drawings which show diagrammatically on the nature of flow sheets, apparatus systems which are particularly suitable for use in carrying out the process of the invention.

The flow of materials in the above-described operations wherein the secondary solvent is miscible with the primary solvent is readily seen from the drawing in FIG. 1 which illustrates diagrammatically a typical apparatus layout suitably used. In the drawing, the hydrocarbon oil to be treated enters the extraction column 10 through line 12 while the extracting fluid enters through line 14. The raffinate stream leaves the top of column 10 through line 16 and passes to the raffinate washer 18. At the same time, the extract stream leaves the bottom of column 10 through line 20 and is conducted to the extract washer 22. In the washer 18, the raffinate stream is brought into contact with a stream of the secondary (miscible) solvent which enters through line 24 and the hydrocarbon raffinate, freed from primary solvent and secondary (miscible) solvent, leaves the system through line 26. In the extract washer 22, the extract stream is countercurrently washed with further quantities of the secondary (miscible) solvent which enters through line 28, and the hydrocarbon extract, free from solvent and secondary (miscible) solvent, leaves the system through line 30. The non-hydrocarbon streams issuing from washer 18 and washer 22 pass into lines 32 and 34, respectively, which merge into line 36 which leads to the vacuum flash tower 38. In the vacuum flash tower 38, the primary solvent is separated from the secondary (miscible) solvent with the former passing through a condenser 40 into line 38 and the latter passing through a cooler 42 into line 28. The only heat supplied is in heater 44 which adds only sufficient heat to cause vaporization of the primary solvent under the pressure conditions prevailing in the vacuum flash tower 38. A branch line 46 provides communication between secondary (miscible) solvent line 24 and primary solvent line 14 to permit regulation of the ratio between primary solvent and secondary (miscible) solvent passing to the extracting column 10. As indicated in the drawing, the several fluid lines are provided with valves to permit control of flow, and pumps (not shown) may be supplied to insure desired movement of the several fluid streams.

As will be apparent from the foregoing, the highest temperature encountered in the entire system is the inlet temperature to the vacuum tower 38 and this generally needs to be no higher than 150° C. At all times the contacts between the hydrocarbon oils and the extracting fluid occur at a low temperature level much below the normal boiling point of the primary solvent. The only process heat requirement is the heat of vaporization of the low boiling component of the extracting fluid, i.e., the solvent, which, in the case of dimethyl formamide, is 248°F. Rtu. per lb. at 760 mm. Hg, plus a small amount of sensible heat to bring the primary solvent-secondary (miscible) solvent mixture to a boil at the pressure existing in the vacuum tower.

Preferably, and to improve the selectivity of the separation, a paraffinic hydrocarbon with a much higher or a much lower boiling point than the feed stock is suit- ably injection into the lower portion of the extraction column, e.g. through line 48, to serve as a counter-solvent. For this purpose, normal butane and/or normal pentane have been found to be particularly effective. A typical flow of materials wherein the secondary solvent is immiscible with the primary solvent but miscible with the hydrocarbon feed oil, for processing a light hydrocarbon feed, such as a refinery reformate stream, and a typical apparatus layout is illustrated diagrammatically in FIG. 2.

The hydrocarbon oil to be treated enters near the center of the primary extractor 1, through line 8. Recycled primary solvent enters the top of the primary extractor 1, through line 10 and, when used, recycled secondary solvent enters the bottom through line 25. Primary paraffinic raffinate, containing the primary paraffinic fraction of the feed oil, a small amount of the primary solvent and secondary solvent (the amount depending upon whether secondary solvent was added to the primary extractor) leaves the extractor through line 11 and enters the raffinate still 2. Primary gross extract, containing the more aromatic fraction of the feed oil, a small amount of the secondary solvent, and a major part of the primary solvent, leaves the primary extractor 1, through line 12 and enters the secondary extractor 4.

Secondary solvent is recovered as the bottom product from the raffinate still 2, and is recycled to the secondary extractor 4, through line 9, or to the primary extractor through line 25. The paraffinic fraction of the feed and a minor amount of primary solvent are recovered as the top product from the raffinate still 2, and pass through line 13 to the raffinate washer 3.

The primary solvent is removed from the paraffinic fraction of the feed by water washing in the raffinate washer 3. Raffinate product flows from the system through line 14. Water and primary solvent leave the bottom of the raffinate washer 3, through line 15 and enter the solvent recovery column 7.

The primary gross extract enters the secondary extractor 4, and is contacted with secondary solvent entering the extractor through line 18. Primary solvent recovered from the secondary extractor 4, is recycled to the primary extractor 1, through line 10. Secondary gross extract, containing the more aromatic fraction of the feed oil, secondary solvent and, minor amounts of primary solvent leave the secondary extractor 4, through line 16 and enter the extract still 5.

Secondary solvent is recovered from the extract still 5, and is recycled to the secondary extractor 4, through line 28. The aromatic fraction of the feed and minor amounts of primary (and secondary) solvents leave the extract still 5, through line 17 and enter the extract washer 6.

The minor amount of primary solvent is removed from the aromatic fraction of the feed by water washing in the extract washer 6. Extract product flows from the system through line 19. Water and primary solvent leave the bottom of the extract washer 6, through line 20 and enter the solvent recovery column 7.

Primary solvent is separated from water in the solvent recovery column 7. The recovered solvent is recycled to the primary extractor 1, through line 22. Water leaves the recovery column 7, through line 21 and is recycled to the raffinate and extract washers.

A procedure and apparatus for processing lube stocks with a primary solvent and a secondary paraffinic-hydro- carbon solvent is illustrated in the flow diagram, FIG. 3. Lube stock feed enters near the bottom of the primary extractor 1, through line 8. Recycled primary solvent passes through line 10 and enters the top of the primary extractor 1. When secondary solvent is added to the primary extractor 1, it is fed through line 25 and mixed with the lube stock feed in line 8 before entering the extractor 1. Primary paraffinic raffinate, containing treated lube oil, secondary solvent and a major part of the primary solvent, leaves the extractor through line 11 and enters the raffinate still 2. Primary gross extract, containing lube oil extracts, trace amounts of the secondary solvent, and a major part of the primary solvent, leaves the primary extractor through line 12 and enters the secondary extractor 4.

The secondary solvent is recovered as the overhead product from the raffinate still 2, and is returned to the secondary extractor 4, through line 9 or to the primary extractor through line 25. Treated lube oil and minor
3,249,532

amounts of primary and secondary solvents are recovered as the bottom product from the raffinate still 2 and pass through line 13 to the raffinate still 2 and pass through line 13 to the raffinate stripper 3. The minor amounts of primary and secondary solvents are recovered from the treated lube oil by steam stripping in the raffinate stripper 3. Treated lube oil flows from the system through line 14. Condensed steam and primary solvent flow overhead from the raffinate stripper 3, through the separator 23, and line 15 to the solvent recovery column 7. Secondary solvent flows overhead from the raffinate stripper 3, through the separator 23 and 3 is recycled to the secondary extractor through line 9 or to the primary extractor through line 25. The primary gross extract enters the secondary extractor 4, and is contacted with secondary solvent entering the extractor through line 18. Primary solvent recovered from the secondary extractor 4 is recycled to the primary extractor 1 through line 10. Lube oil extract, secondary solvent and minor amounts of primary solvents leave the secondary extractor 4 through line 16 and enter the extract still 5. Secondary solvent is recovered from the extract still 5, and is recycled to the secondary extractor 4 through line 18. Lube oil extract and minor amounts of primary and secondary solvents leave the extract still 5 through line 17 and enter the extract stripper 6. The minor amounts of primary and secondary solvents are removed from the lube oil extract by steam stripping in the extract stripper 6. Lube extract flows from the system through line 19. Condensed steam and primary solvent flow overhead from the extract stripper 6 through the separator 24 and line 20 to the solvent recovery column 7. Secondary solvent flows overhead from the extract stripper 6 through the separator 24 and is recycled to the secondary extractor 4 through line 18. Primary solvent is separated from stripping steam condensate in the solvent recovery column 7. The recovered solvent is recycled to the primary extractor 1 through line 22. Water from the solvent recovery column 7 passes through line 21 and the vaporizer 25 and is recycled to steam to the raffinate and extract stripper through lines 23 and 24 respectively.

In processing the process and advantageously, the extraction temperature in all of the columns is usually in the ambient range. The primary extraction is usually carried out in a column having from 6 to 22 theoretical stages and the secondary extractions are carried out in columns having from 6 to 11 theoretical stages. The temperature of the process, are normally limited when carried out with a paraffinic secondary solvent, so as not to go above 500°F. at any point, and this temperature is reached only in the bottom of the fractionators in which the secondary solvent is recovered. Very little of the primary solvent is exposed to temperatures higher than ambient. An important feature of the invention in using both types of secondary solvents is low heat input. When the secondary solvent is a paraffinic type the only important heat input is in separation of the secondary paraffinic hydrocarbon solvent from the primary hydrocarbon oil extract. In this case, the substantial and major portion of the primary solvent is recovered solely by treatment with the paraffinic secondary solvent, and a very minor portion is recovered by distilling off the water resulting from the water washings. When the secondary solvent is an organic hydroxy compound, the only important heat input in the process is the distillation to separate the primary and secondary solvents. In this case, both the aromatic hydrocarbon oil portion and the paraffinic hydrocarbon oil portion are obtained solely by treatment with solvents. Although the invention has been described by references to particular embodiments thereof, it is obvious that many modifications may be employed without departing from the spirit and scope of the invention. Hence, the invention is not to be construed as limited in any manner except by the appended claims.

EXAMPLE 1
A 450-550°F. cut from a catalytic cycle gas oil, with a specific gravity of 0.900 at 25°C., containing 59 vol. percent of aromatics including 25.7 vol. percent naphthylene and naphthalene homologues was counter-currently extracted in a 1" x 4" glass Scheibl column containing eleven stages. Dimethyl formamide (DMF) was introduced at the top of the column at a DMF/feed ratio of 3.76/1; pentane (secondary solvent) was introduced at the bottom at a pentane/feed ratio of 4.49/1. The gas oil was added near the center of the column. After equilibrium had been established the pentane solution of raffinate was withdrawn from the top. After solvent removal a raffinate was isolated constituting 77 vol. percent of the charge, with specific gravity (25°C.) of 0.839 and analyzing 36 vol. percent aromatics but only 3.2 vol. percent bicyclic aromatics.

EXAMPLE 2
A xylene-rich cut from a refinery stream containing 90 volume percent aromatics and having a specific gravity of 0.846 at 60°F. was extracted using the apparatus of Example 1. The solvent, a mixture of DMF and glucose was introduced at the top of the column at a solvent/feed ratio of 5.3/1. Feed was added near the center of the column, and pentane, at a pentane/feed ratio of 1.6/1, was introduced at the bottom. An extract stream was recovered that contained 99.6% of the aromatic feed hydrocarbons, these hydrocarbons having an aromatics content of 99.5 vol. percent after removal of the pentane.

EXAMPLE 3
A kerosene, containing 23.6 vol. percent aromatics, and having a specific gravity of 0.835 at 60°F., was extracted using the apparatus of Example 1. DMF was introduced at the top of the column at a DMF/feed ratio of 2/1. Feed was added near the center of the column and pentane, at a pentane/feed ratio of 0.75/1, was introduced at the bottom. An extract stream was recovered from the bottom of the column that contained 23% of the kerosene fed, this fraction of the kerosene having an aromatics content of greater than 99 vol. percent. The composition of the gross extract stream was 74.6 vol. percent DMF, 20 vol. percent pentane, and 5.5 vol. percent kerosene. The remainder of the kerosene fed was recovered in a raffinate stream, this fraction of the kerosene having an aromatics content of 7 vol. percent. The composition of the gross raffinate stream was 6 vol. percent DMF, 18.8 vol. percent pentane, and 75.2 vol. percent kerosene.

EXAMPLE 4
A kerosene containing 0.53 wt. percent sulfur and having a smoke point of 18 mm. and a specific gravity of 0.849 at 60°F., was extracted using the apparatus of Example 1. DMF was introduced at the top of the column at a DMF/feed ratio of 0.86/1, and the feed was introduced at the bottom of the column. The raffinate stream consisted of 80.7 vol. percent of the kerosene fed, and 3.5 vol. percent of DMF. This kerosene contained 0.35 weight percent sulfur and had a smoke point of 21 mm. and a specific gravity of 0.837. The extract stream consisted of the balance of the kerosene and DMF, 18.9 vol. percent kerosene. The kerosene from the extract stream contained 1.13 wt. percent sulfur and had a specific gravity of 0.899.

EXAMPLE 5
A gas oil containing 3.23 wt. percent sulfur and having a specific gravity of 0.895 at 60°F. was extracted using the apparatus of Example 1. DMF was introduced at
the top of the column at a DMF/feed ratio of 2.5/1 and 
the feed was introduced six stages lower in the column. 
The raffinate stream consisted of 64.5 vol. percent of the 
gas oil fed and 2.5 vol. percent of DMF. This gas oil 
contained 1.81 wt. percent sulfur and had a specific 
gravity of 0.829. The extract stream consisted of the 
balance of the gas oil and DMF.

EXAMPLE 6
A lube stock having a viscosity of 100 Saybolt universal 
seconds at 100° F., a viscosity index of minus 10.4, and a 
specific gravity of 0.920 at 60° F. was extracted using the 
apparatus of Example 1. DMF was introduced at the 
top of the column at a DMF/feed ratio of 1.5/1, and 
the feed was introduced six stages lower in the column. 
The raffinate stream consisted of 74.8 vol. percent of the lube 
stock fed and DMF to the extent of 3.8 vol. percent of the 
stream. This oil had a viscosity index of 36.5 and a 
specific gravity of 0.895. The extract stream consisted of 
the balance of the oil and DMF.

EXAMPLE 7
A lube stock having a viscosity of 300 Saybolt universal 
seconds at 100° F., a viscosity index of 10.4, and a specific 
gravity of 0.943 at 60° F. was extracted using the apparatus 
of Example 1. DMF was introduced at the top of the column at 
a DMF/feed ratio of 1.3/1, and the feed was introduced six stages lower in the column. 
The raffinate stream consisted of 35.7% of the oil fed, 
and DMF to the extent of 3 vol. percent of the stream. 
This oil had a viscosity index of 54.9 and a specific gravity 
of 0.902. The extract stream consisted of the balance of 
the oil and DMF.

EXAMPLE 8
A lube stock having a viscosity of 900 Saybolt universal 
seconds at 100° F., a viscosity index of minus 42.2, and a 
specific gravity of 0.956 at 60° F. was extracted using the 
apparatus of Example 1. Before being fed to the 
extractor the lube stock was diluted with hexane to 25 vol. 
percent hexane. DMF was introduced to the top of the column at a DMF/feed ratio of 1.3/1, and 
the diluted feed was introduced six stages lower in the column. 
The raffinate stream consisted of 74.5% of the oil in the feed, 
part of the hexane, and DMF to the extent of about 3 vol. percent of the stream. This oil had a viscosity index of 49.9 and a specific gravity of 0.926. The extract stream consisted of the balance of the oil, hexane, and 
DMF.

EXAMPLE 9
A solution containing 30 vol. percent toluene in normal 
heptane was extracted using an apparatus similar to that 
of Example 1, except that it employed 22 stages. DMF 
was introduced at the top of the column at a DMF/feed ratio of 1.2/1.0. Feed was added near the center of the column, 
and odorless mineral spirits (OMS), a paraffinic material, 
boiling in the range of a heavy kerosene, was 
introduced at the bottom at an OMS/feed ratio of 0.3/1.0.
Essentially 100% of the toluene fed was recovered in 
the extract stream. The light hydrocarbons, separated 
from the DMF-free extract by distillation, proved to be essentially 100% toluene. Similarly, the light hydrocarbons recovered from the raffinate stream proved to be essentially 100% heptane.

EXAMPLE 10
A lube stock having a viscosity of 72 centistokes at 
100° F., a viscosity index of 71, and a specific gravity 
of 0.949 at 60° F. was extracted using the apparatus of 
Example 4. Before being fed to the extractor the lube 
stock was diluted with 15 vol. percent OMS. DMF was 
introduced to the top of the column at a DMF/feed ratio 
of 1.5/1.0, and the diluted feed was introduced six stages 
lower in the column. The raffinate stream consisted of 
73 vol. percent of the oil in the feed, part of the OMS, 
and DMF to the extent of 4 vol. percent of the stream. 
This oil had a specific gravity of 0.913 at 60° F., and a viscosity index of 88. The extract stream consisted of the balance of the oil, OMS, and DMF.

The extract stream from this primary extraction containing 86 vol. percent DMF was subjected to a secondary 
extraction to recover the DMF. The same apparatus 
was used as for the primary extraction, except that all 11 
stages were employed. Primary extract was introduced to the top of the column, and OMS was introduced at the 
bottom of the column, using an OMS to feed ratio of 1.5/1.0. The bottom product stream contained 95.4 vol. percent 
of the DMF fed, and had a composition of 8 vol. percent hydrocarbon, 92 vol. percent DMF. The 
overhead product stream contained 95.7 vol. percent 
of the hydrocarbon fed, and had a composition of 2.5 vol. 
percent DMF and 97.5 vol. percent hydrocarbon.

EXAMPLE 11
The following table presents binodal curve data for 
the system DMF-medium viscosity white mineral oil-
toluene at 75° F.

<table>
<thead>
<tr>
<th>Vol. percent DMF</th>
<th>Vol. percent Toluene</th>
<th>Vol. percent MO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>95</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>85</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>75</td>
<td>25</td>
</tr>
<tr>
<td>7</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>8</td>
<td>65</td>
<td>35</td>
</tr>
<tr>
<td>9</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>10</td>
<td>55</td>
<td>45</td>
</tr>
</tbody>
</table>

EXAMPLE 12
The following table presents binodal curve data for 
the system DMF-OMS heavy-neutral lube extract (HNX) 
at 80° F.

<table>
<thead>
<tr>
<th>Vol. percent DMF</th>
<th>Vol. percent HNX</th>
<th>Vol. percent OMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>92.2</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>87.5</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>82.8</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>78.1</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>73.5</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>69.0</td>
<td>25</td>
</tr>
<tr>
<td>7</td>
<td>64.5</td>
<td>30</td>
</tr>
<tr>
<td>8</td>
<td>60.0</td>
<td>35</td>
</tr>
<tr>
<td>9</td>
<td>55.5</td>
<td>40</td>
</tr>
<tr>
<td>10</td>
<td>51.0</td>
<td>45</td>
</tr>
</tbody>
</table>

EXAMPLE 13
A solvent mixture was prepared by mixing 20 parts 
of dimethyl formamide with 7 parts of U.S.P. grade glyc-
erine. One part of this solvent mixture was shaken 
vigorously with one part of pure normal-heptane. The 
mixture separated into two layers immediately and there 
was no change in the volume of the normal-heptane, indi-
cating that normal-heptane was completely immiscible 
with the solvent mixture. One part of this solvent mix-
ture was shaken with one part of pure benzene. The mixture 
became a single homogeneous phase. Ten parts of a 1:1 mixture of benzene and normal-heptane were 
brought into contact with 10 parts of the solvent mixture. 
The mixture separated into two distinct layers. The upper 
layer amounted to five parts which consisted almost 
entirely of normal-heptane. The lower layer represented 
15 parts and consisted of the original solvent mixture 
and benzene. To this mixture were added 15 parts of glyc-
erine, whereupon 5 parts of benzene separated from 
the mixture as an upper layer. The lower layer was a mix-
ture of dimethyl formamide and glycerine.

EXAMPLE 14
A 375°-585° F. kerosine cut from a 31.5° API Kuwait 
crude oil was extracted with dimethyl formamide counter-
currently in an extraction column with 4 theoretical stages. The solvent oil ratio was 1:1, the temperature was 25°C, and the pressure was atmospheric. The extract and raffinate were separated by addition of glycine and then the components of the solvent mixture were recovered by vacuum flashing. The yield and quality of the raffinate and of the extract were comparable to those obtained by SO₂ extraction as shown in the following table.

<table>
<thead>
<tr>
<th>Extraction</th>
<th>Raw Stock</th>
<th>Raffinate</th>
<th>Extract</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂ extraction:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Antline point</td>
<td>150</td>
<td>120.3</td>
<td>8.3</td>
</tr>
<tr>
<td>Yield</td>
<td>100</td>
<td>84.5</td>
<td>15.5</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.90</td>
<td>0.57</td>
<td>4.20</td>
</tr>
<tr>
<td>Gravity (AP)</td>
<td>34.3</td>
<td>34.5</td>
<td>15.5</td>
</tr>
<tr>
<td>DMP extraction:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Antline point</td>
<td>157.4</td>
<td>175.5</td>
<td>Below 50</td>
</tr>
<tr>
<td>Yield (calculated)</td>
<td>100</td>
<td>82</td>
<td>18</td>
</tr>
<tr>
<td>Sulphur</td>
<td>729</td>
<td>503</td>
<td>28.4</td>
</tr>
<tr>
<td>Gravity (AP)</td>
<td>41.0</td>
<td>43.3</td>
<td>21.2</td>
</tr>
</tbody>
</table>

EXAMPLE 15
A 430–565°F cut from a catalytic cycle gas oil was extracted countercurrently with dimethyl formamide with a weight ratio of 1.65 dimethyl formamide to 1.0 of oil at 92°F. and at atmospheric pressure. During the extraction, the max. velocity was 752 lb/hr.-sq. ft. in the case of the oil feed, 1260 lb/hr.-sq. ft. for the extracting fluid stream, 372 lb/hr.-sq. ft. for the raffinate stream and 1650 lb/hr.-sq. ft. in the case of the extract stream. The extract contained 21.3% by volume of oil and was extracted countercurrently with 3 volumes of U.S.P. grade glycine. The glycerine-dimethyl formamide mixture was vacuum flashed at 14°F. (13 mm. Hg abs.) and the dimethyl formamide was recovered overhead.

The raffinate contained 3.2% by volume of solvent which was removed by contact with 10% by volume of glycerine. The resulting solvent-glycerine mixture was vacuum flashed together with that from the glycerine extraction of the extract.

The net extract obtained was 45% by volume of the feed and the raffinate was 55%. The property changes were as follows:

```
<table>
<thead>
<tr>
<th>Feed</th>
<th>Wt. percent of Sulphur</th>
<th>Wt. percent of Olefin</th>
<th>Wt. percent of Aromatics</th>
</tr>
</thead>
<tbody>
<tr>
<td>30.4</td>
<td>0.18</td>
<td>6.31</td>
<td>36.69</td>
</tr>
<tr>
<td>Extract</td>
<td>18.00</td>
<td>6.79</td>
<td>71.27</td>
</tr>
<tr>
<td>Raffinate</td>
<td>44.1</td>
<td>6.92</td>
<td>7.47</td>
</tr>
</tbody>
</table>
```

EXAMPLE 16
A full range platformate with a specific gravity of 0.775 at 25°C. containing 30% of aromatics was countercurrently extracted with a solvent mixture consisting of 87% by weight dimethyl formamide and 13% by weight of glycine. The extraction column was a 1" glass pipe packed with 4 1/2" raschig rings to a depth of 8 feet, which was equivalent to 4 theoretical contact stages. The flow rate for the platformate was 2350 ml per hour and that for the extracting fluid stream was 3250 ml per hour, i.e., the solvent to oil ratio was 1.38 to 1 by volume. The raffinate, amounting to 1210 ml per hour, was extracted countercurrently with 213 ml per hour of glycine in a washing column. This produced a raffinate of 1163 ml per hour of washing column, yielding an oil product at the rate of 982 ml per hour with a specific gravity of 0.804. This oil contained 71% aromatics. The glycine-dimethyl formamide solution, together with a small amount of dissolved oil from both washing columns were combined and vacuum flashed at 90°F (100 mm. Hg). The overhead from the vacuum flash was dimethyl formamide with about 185 ml per hour of oil. The bottom stream from the vacuum flash tower was essentially all glycine, which was mixed with the overhead to provide the 87–13 solvent mixture, and reused in the main extraction column. The balance of the vacuum flash tower bottoms stream was used as solvent in the two secondary extraction columns.

EXAMPLE 17
A solvent mixture was prepared by mixing 75 parts by volume of tetrahydrofurfuryl alcohol with 25 parts by volume of pure glycine. One part by volume of this solvent was shaken vigorously with one part by volume of pure normal-heptane. The mixture separated into two layers immediately and there was no change in the volume of normal-heptane, which indicated that normal-heptane is completely immiscible with the solvent mixture. One part of this solvent mixture was shaken with one part of pure benzene. The mixture became one homogeneous phase, which indicated that benzene is completely miscible with the tetrahydrofurfuryl alcohol-glycine mixture. To a homogeneous solution of 5 parts by volume of benzene and 5 parts by volume of tetrahydrofurfuryl alcohol were added 8 parts by volume of glycine. After vigorous shaking and settling the mixture separated into two layers. Five parts by volume of benzene separated out as an upper layer. To a homogeneous solution of 5 parts by volume of normal-heptane, 5 parts by volume of benzene and 10 parts of the above-mentioned solvent mixture were added 6 parts of glycine. Ten parts by volume of oil separated out as an upper layer.

What I claim is:

1. A process of treating a hydrocarbon oil for the purpose of separating said oil into fractions of differing chemical compositions which comprises contacting hydrocarbon oil feed with dimethyl formamide to produce a primary raffinate containing the portion of said hydrocarbon oil feed rich in non-aromatic components together with a minor portion of the dimethyl formamide primary solvent and a primary extract containing the aromatic hydrocarbon oil together with a major portion of said dimethyl formamide, whereby the product hydrocarbon stream rich in non-aromatic components is produced solely by treatment with dimethyl formamide and water, contracting said primary extract with a secondary paraffinic hydrocarbon solvent, said secondary hydrocarbon solvent being substantially insoluble in said said dimethyl formamide having a boiling range differing by at least 50°F. from the boiling range of said hydrocarbon oil feed, thereby producing a secondary raffinate consisting essentially of said dimethyl formamide and a secondary extract consisting essentially of said partial of said hydrocarbon oil feed rich in aromatic components, said secondary solvent, and a minor portion of said dimethyl formamide, distilling said secondary extract to separate said secondary hydrocarbon solvents from said portion of hydrocarbon oil rich in aromatic components, water washing said product hydrocarbon oil rich in aromatic components, water washing the product hydrocarbon oil rich in aromatic components obtained as a secondary product from said distillation, to remove said minor portion of said dimethyl formamide, recycling thus recovered secondary hydrocarbon solvent, and recycling said primary solvent, whereby said primary solvent is recovered substantially as secondary raffinate solely by treatment with secondary solvent, and whereby the major heat input is that required for said distillation to separate said secondary hydrocarbon solvent from said portion of hydrocarbon oil rich in aromatic components.

2. A process of treating a hydrocarbon oil for the purpose of separating said oil into fractions of differing chemical compositions which comprises contacting hydrocarbon oil feed with dimethyl formamide as a primary selective solvent to produce a primary raffinate contain-
ing the portion of said hydrocarbon oil feed rich in non-
aromatic components and a minor portion of said di-
methyl formamide, and a primary extract containing the
portion of said oil rich in aromatic components together
with a major portion of said dimethyl formamide, wash-
ing the primary raffinate with water to remove said minor
portion of primary solvent, contacting said primary ex-
tract with a secondary paraffinic hydrocarbon solvent,
said secondary hydrocarbon solvent being substantially
insoluble in said primary solvent and having a boiling
range differing from said hydrocarbon oil feed, thereby
producing a secondary raffinate consisting essentially of
said primary solvent, and a secondary extract consisting
essentially of said portion of hydrocarbon oil feed rich
in aromatic components, said secondary solvent, and a
minor portion of said primary solvent, distilling said sec-
ondary extract to separate said secondary hydrocarbon
solvent from said primary hydrocarbon extract, water
washing the overhead product from said distillation to re-
move said minor portion of primary solvent, recycling the
thus-recovered secondary hydrocarbon solvent, and re-
cycling said primary solvent whereby said primary solvent
is recovered substantially as secondary raffinate solely
by treatment with secondary solvent.

3. A process as defined in claim 2 wherein said sec-
ondary paraffinic hydrocarbon solvent has a boiling range
differing by at least about 50° F. from the boiling point
of said hydrocarbon oil feed.

4. A process of treating a hydrocarbon oil for the pur-
pose of separating said oil into fractions of differing
chemical compositions which comprises contacting hy-
drocarbon oil feed with dimethyl formamide to produce a
primary raffinate containing the portion of said hydrocar-
bon oil feed rich in non-aromatic components and a pri-
mary extract containing the portion of said hydrocarbon
oil feed rich in aromatic components together with a
major portion of said dimethyl formamide, contacting said
primary extract with a secondary paraffinic hydrocarbon
solvent, said secondary hydrocarbon solvent being sub-
stantially immiscible with said dimethyl formamide and
having a boiling range differing from the boiling range
of said hydrocarbon oil feed, thereby producing a sec-
ondary raffinate consisting essentially of said dimethyl
formamide, and a secondary extract consisting essentially
of said portion of said hydrocarbon oil feed rich in aro-
matic components, said secondary solvent, and a minor
portion of said dimethyl formamide, distilling said sec-
ondary extract to separate and recover said secondary hy-
drocarbon solvent from said portion of hydrocarbon oil
feed rich in aromatic components, recycling recovered
secondary hydrocarbon solvent, and recycling said pri-
mary solvent, whereby said primary solvent is recovered
substantially as secondary raffinate solely by treatment
with secondary solvent and whereby the only major heat
input is that required for said distillation to separate said
secondary hydrocarbon solvent from said portion of hy-
drocarbon oil rich in aromatic components.

5. A process as defined in claim 4 wherein said second-
ary paraffinic hydrocarbon solvent has a boiling range
differing by at least about 50° F. from the boiling point
of said hydrocarbon oil feed.

6. A process of treating a hydrocarbon oil for the pur-
purpose of separating said oil into fractions of differing
chemical compositions which comprises contacting hy-
drocarbon oil feed with dimethyl formamide as a pri-
mary selective solvent and with a secondary paraffinic
hydrocarbon solvent, said secondary hydrocarbon solvent
being substantially insoluble in said dimethyl formamide
and having a boiling range differing from said hydrocar-
on oil feed to produce a primary raffinate containing the
portion of said oil rich in non-aromatic components to-
gether with said secondary hydrocarbon solvent and, a
minor portion of said primary solvent, and a primary ex-
tract containing the portion of said hydrocarbon oil oil feed
rich in aromatic components together with a major portion
of said primary solvent, water washing said primary raf-
finate to remove said minor portion of primary solvent,
contacting said primary extract with said secondary hydro-
carbon solvent, thereby producing a secondary raffinate
consisting essentially of said primary solvent, and a sec-
ondary extract consisting of said portion of said hy-
drocarbon oil rich in aromatic components, said second-
ary solvent, and a minor portion of said primary solvent,
distilling said secondary extract to separate said secondary
hydrocarbon solvent from said product hydrocarbon
oil rich in aromatic components, water washing the
overhead product from said distillation to remove said
minor portion of primary solvent, recycling thus-recover-
ed secondary hydrocarbon solvent, and recycling said
primary solvent, whereby said primary solvent is recov-
ered substantially as secondary raffinate solely by treat-
ment with secondary solvent.

7. A process as defined in claim 6 wherein said second-
ary paraffinic hydrocarbon solvent has a boiling range
differing by at least about 50° F. from the boiling point
of said hydrocarbon oil feed.

References Cited in the file of this patent

UNITED STATES PATENTS
2,167,632 8/1939 Browncombe et al. 260—674
2,176,396 10/1939 Fesske et al. 208—321
2,261,799 11/1941 Franklin 208—321
2,307,242 1/1943 Savelli et al. 208—321
2,337,344 9/1944 Morris et al. 260—674
2,646,387 7/1953 Francis 208—328

DELBERT E. GANTZ, Primary Examiner.
ALPHONSO D. SULLIVAN, PAUL M. COUGHLAN, Examiners.