May 3, 1966 CHYN DOUG SHIAH 3,249,532

SOLVENT EXTRACTION OF AROMATICS

Filed June 4, 1964 3 Sheets-Sheet 1

FIG. 1

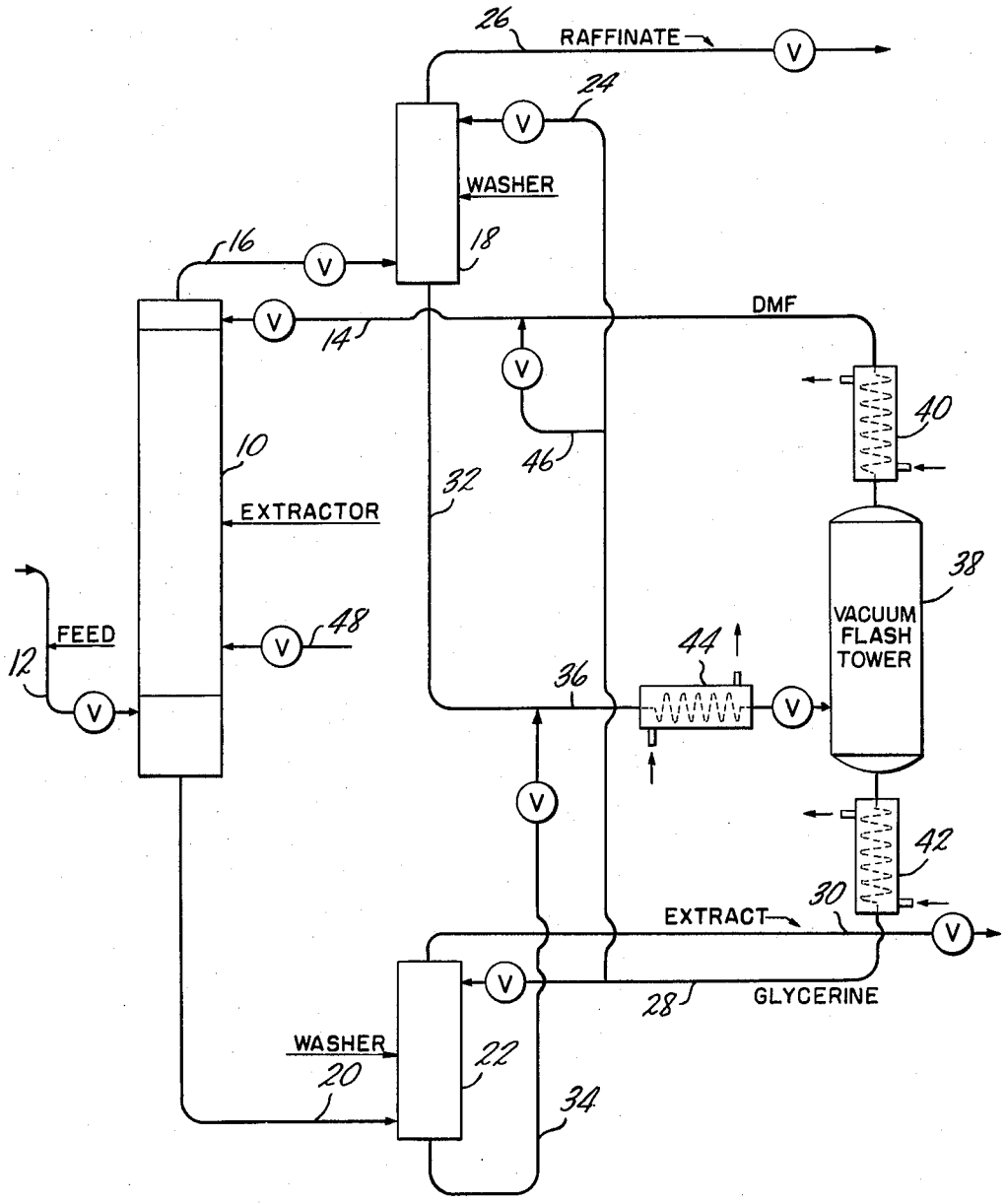
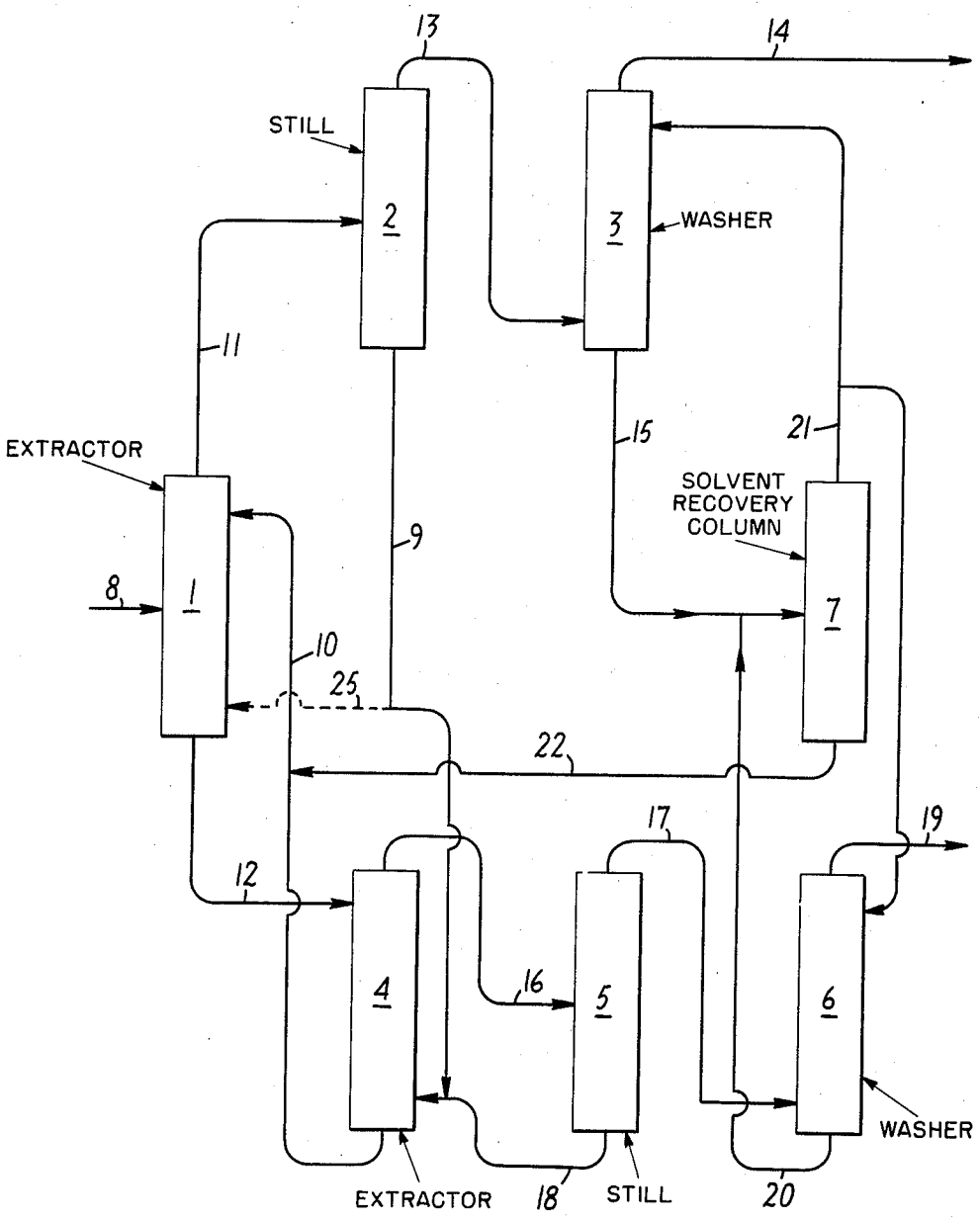


FIG. 2

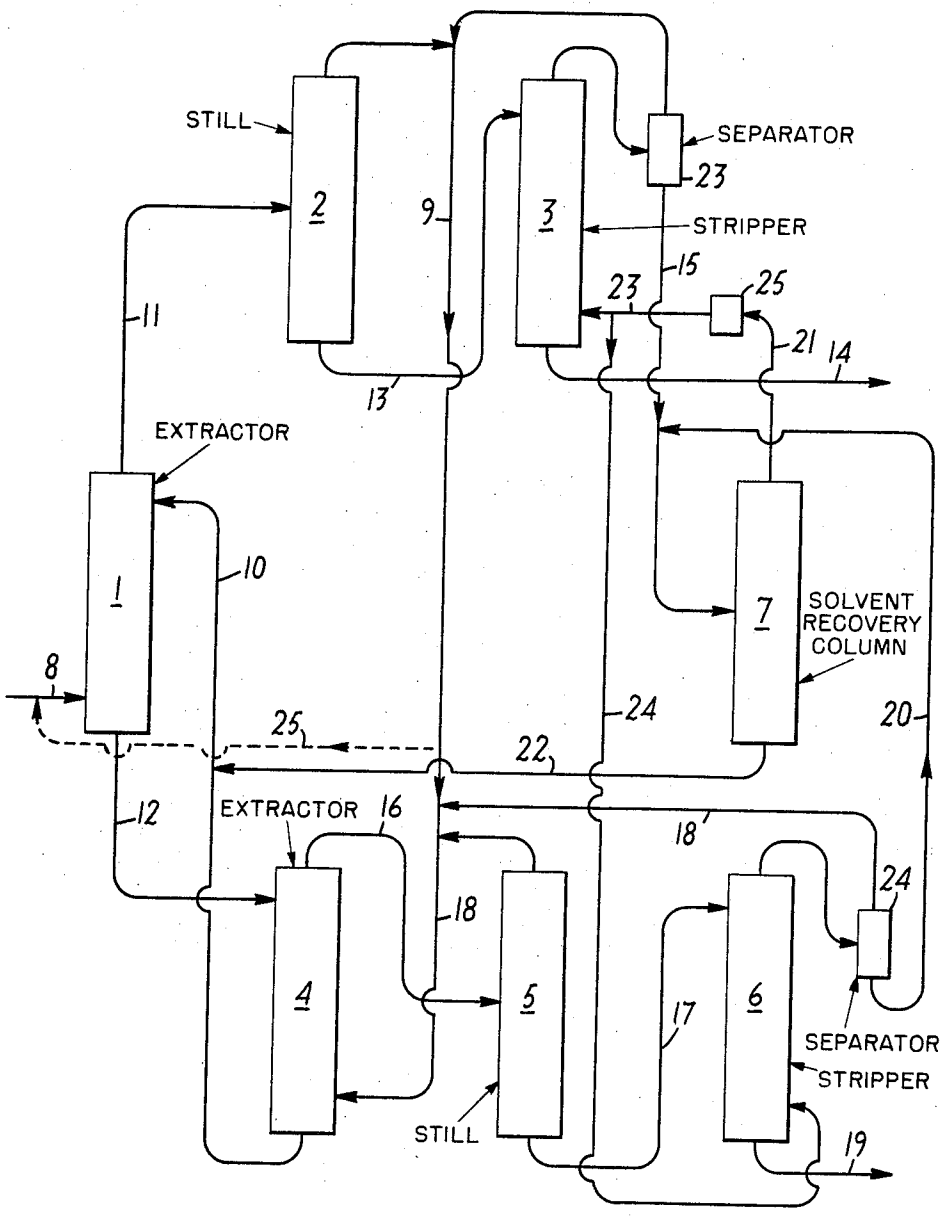

13
14
STILL
2
3
WASHER
11
EXTRACTOR
15
21
SOLVENT
RECOVERY
COLUMN
9
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1
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25
22
17
19
12
4
16
5
6
WASHER
EXTRACTOR
18
STILL
20

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SOLVENT EXTRACTION OF AROMATICS

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FIG. 3



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3,249,532

SOLVENT EXTRACTION OF AROMATICS

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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 xylenes 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:

	Boiling point at 760 mm. (° F.)
Liquid-sulfur dioxide	15
Furfural	323
Phenol	358
Diethylene glycol	473
Sulfolane	550

Most of the processes which have been developed involve essentialy 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, mechanicaly-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 occurring 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.

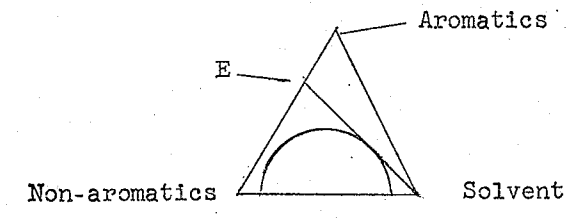
A major consideration which has heretofore been an obstacle to the provision of a solvent extraction process which can be applied to hydrocarbon stocks of all boiling ranges is the boiling point of the solvent. Customarily, as previously mentioned, the recovery of the solvent is effected by distillation. 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-listed solvents are limited in their applicability. For example furfural, which has a boiling point of about 323°, 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 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 liquefy the gas; and since sulfur 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%.

Nearly all of 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:



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 darwn 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) Emplyoing a high-boiling wash oil 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 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).

The foregoing features combined in a single economical plant will permit a refiner to employ liquid-liquid extraction to a much greater extent than has heretofore been possible. Up to now, many small refiners 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 product as a large refiner who can economically justify separate extraction plants for each type of stock.

It is, accordingly, an object 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 two solvents dissimilar in their solvent properties. For convenience of description, one of the two 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, arylamides, 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 in the manner outlined in 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 either 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. Moreover, it is not necessary to employ distillation for primary solvent recovery, thereby contributing to the heat economy of the process.

(2) The secondary solvent may be employed to control the purity and recovery of the extract hydrocarbons to any desired extent. When processing highly viscous feed stocks, the secondary solvent may be used to reduce the viscosity of the feed.

(3) The characteristics of the secondary solvent are readily modified to suit the particular process requirements. For example, when the feed is a naphtha, the secondary solvent should be somewhat higher boiling than the feed and the solvent to permit separation by fractionation. In this case, the raffinate and extract produced from the naphthas are overhead products from the distillations. When the feed is a high-boiling hydrocarbon mixture, such as a vacuum gas oil, the secondary solvent may be lower boiling than the feed to permit separation by distillation. In this case, the secondary solvent is the overhead product from such distillation.

(4) 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 of low cost.

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

Another important feature of the process of this invention is the low heat imput 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 major heat requirement of this process 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 varporiaztion 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 a relatively low heat imput.

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 such as methanol, glycerol and glycol 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 paraffinate 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 secondary (miscible) solvent. Pure hydrocarbon streams issue 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 extraction 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 amounts of oil stock which may be carried over along with the primary solvent are, of course, recycled through the main extraction column. The secondary (miscible) solvent used for the washing of the raffinate and extract streams from the main extraction column is obtained from the bottom stream of the vacuum flash tower. Inasmuch as the extracting fluid used in the main extraction step can be a mixture of the solvent and the secondary (miscible) solvent, sharp separation in the vacuum flash operation is not necessary and generally a one-stage vacuum flash will suffice. It will be understood, of course, that if sharper separation is desired, it can be achieved without difficulty by conventional techniques.

The amount of secondary (miscible) solvent used in the main extraction step can vary from 0 to 90% of the extracting fluid, depending upon the boiling range of the hydrocarbon oil stock to be extracted. The lighter the stock, the more secondary (miscible) solvent in the fluid. For instance, in extracting a light naphtha cut. e.g. having a boiling range of 140° to 400° F., as much as 20% of the secondary (miscible) solvent will be needed. On the other hand, in the extraction of heavy lubricating cuts, no secondary (miscible) solvent is needed. The extraction, is carried out at a temperature of 15–200° C. but preferably at 25° C. and at a pressure of from 0–200 lbs. per sq. in. gage, but preferably at 14.7 lbs. per. sq. in. gage, using a countercurrent extraction column with 2–20

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 illustrative embodiments thereof and from the accompanying drawings which show diagrammatically on the nature of flow sheets, appartus 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 **14**, 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 provided 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° B.t.u. 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 suitably injected 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 gross raffinate, containing the 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 minor amount of 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-hydrocarbon 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 gross raffinate, containing treated lube oil, secondary solvent and a minor 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 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

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 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 solvent 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 as steam to the raffinate and extract stripper through lines **23** and **24** respectively.

In practicing 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 naphthalene and naphthalene homologs was counter-currently extracted in a 1" x 4' glass Scheibel 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 glycerine was introduced at the top of the column at a solvent/feed ratio of 3.3/1. 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 at 160° F. using the apparatus of Example 1. DMF was introduced to the top of the column at a DMF/feed ratio of 1.33/1, 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 lub 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 19.3 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.

	Vol. percent DMF	Vol. percent Toluene	Vol. percent MO
1	100	0	0
2	0	0	100
3	8.3	33.0	58.7
4	30.3	45.4	24.3
5	44.6	44.6	10.8
6	56.6	37.7	5.7
7	78.5	19.6	1.9
Tie Line a	1.0	7.8	91.2
Tie Line b	94.7	4.6	0.7

EXAMPLE 12

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

	Vol. percent DMF	Vol. percent HNX	Vol. percent OMS
1	92.2	0	7.8
2	2.4	0	97.6
3	3.0	6.1	90.9
4	4.5	15.9	79.6
Tie Line a	85.3	6.5	8.2
Tie Line b	4.0	7.5	88.5

EXAMPLE 13

A solvent mixture was prepared by mixing 20 parts of dimethyl formamide with 7 parts of U.S.P. grade glycerine. 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, indicating that normal-heptane was completely immiscible with the solvent mixture. One part of this solvent mixture 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 glycerine, whereupon 5 parts of benzene separated from the mixture as an upper layer. The lower layer was a mixture of dimethyl formamide and glycerine.

EXAMPLE 14

A 375°–585° F. kerosene 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 glycerine 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 SO_2 extraction as shown in the following table.

	Raw Stock	Raffinate	Extract
SO_2 extraction:			
Aniline point	156	176.3	8.3
Yield	100	84.5	15.5
Sulphur	0.90	0.37	3.32
Gravity (API)	39.3	43.5	19.3
DMF extraction:			
Aniline point	157.4	175.5	Below 30
Yield (calculated)	100	82	18
Sulphur	.729	.332	2.84
Gravity (API)	40.5	43.3	21.2

EXAMPLE 15

A 430–565° F. cut from a catalytic cycle gas oil was extracted countercurrently with dimethyl formamdie 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 mass velocity was 762 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 glycerine. The glycerine-dimethyl formamide mixture was vacuum flashed at 140° 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:

	API	Wt. percent of Sulphur	Wt. percent of Olefins	Wt. percent of Aromatics
Feed	30.4	0.18	6.31	38.69
Extract	19.5	0.40	7.00	71.00
Raffinate	44.1	0.012	5.74	12.35

EXAMPLE 16

A full range platformate with a specific gravity of 0.775 at 25° C. containing 30 percent of aromatics was countercurrently extracted with a solvent mixture consisting of 87% by weight dimethyl formamide and 13% by weight of glycerine. The extraction column was a 1" glass pipe packed with ¼" 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 glycerine in a washing column. This produced a raffinate of 1163 ml. per hour of water-white oil stock with a specific gravity of 0.735. The extract from the main extractor column amounted to 4390 ml. per hour and was also extracted countercurrently with 2630 ml. per hour of glycerine in another 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 glycerine-dimethyl formamide solution, together with a small amount of dissolved oil from both washing columns were combined and vacuum flashed at 90° (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 glycerine, 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 glycerine. 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-glycerine mixture. To a homogeneous solution of 5 parts by volume of benzene and 5 parts by volume of tetrahydrofurfuyl alcohol were added 8 parts by volume of glycerine. 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 glycerine. 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 together with a major portion of said dimethyl formamide, water washing said primary raffinate to remove said minor 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 dimethyl formamide and 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 dimethy formamide and a secondary extract consisting essentially of said portion 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 the product hydrocarbon oil rich in aromatic components obtained as overhead 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 only 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 dimethyl formamide, and a primary extract containing the portion of said oil rich in aromatic components together with a major portion of said dimethyl formamide, washing the primary raffinate with water to remove said minor portion of primary solvent, contacting said primary extract 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 secondary extract to separate said secondary hydrocarbon solvent from said primary hydrocarbon extract, water washing the ovehead product from said distillation to remove said minor portion of primary solvent, recycling the thus-recovered secondary hydrocarbon solvent, and recyling 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 secondary 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 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 and a primary 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 substantially immiscible with said dimethyl formamide and having a boiling range differing 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 portion 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 and recover said secondary hydrocarbon solvent from said portion of hydrocarbon oil feed rich in aromatic components, recycling 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 only 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.

5. A process as defined in claim 4 wherein said secondary 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 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 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 hydrocarbon oil feed to produce a primary raffinate containing the portion of said oil rich in non-aromatic components together with said secondary hydrocarbon solvent and, a minor portion of said primary solvent, and a primary extract containing the portion of said hydrocarbon oil feed rich in aromatic components together with a major portion of said primary solvent, water washing said primary raffinate to remove said minor portion of primary solvent, contacting said primary extract with said secondary hydrocarbon solvent, thereby producing a secondary raffinate consisting essentially of said primary solvent, and a secondary extract consisting of said portion of said hydrocarbon oil rich in aromatic components, said secondary 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-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.

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

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