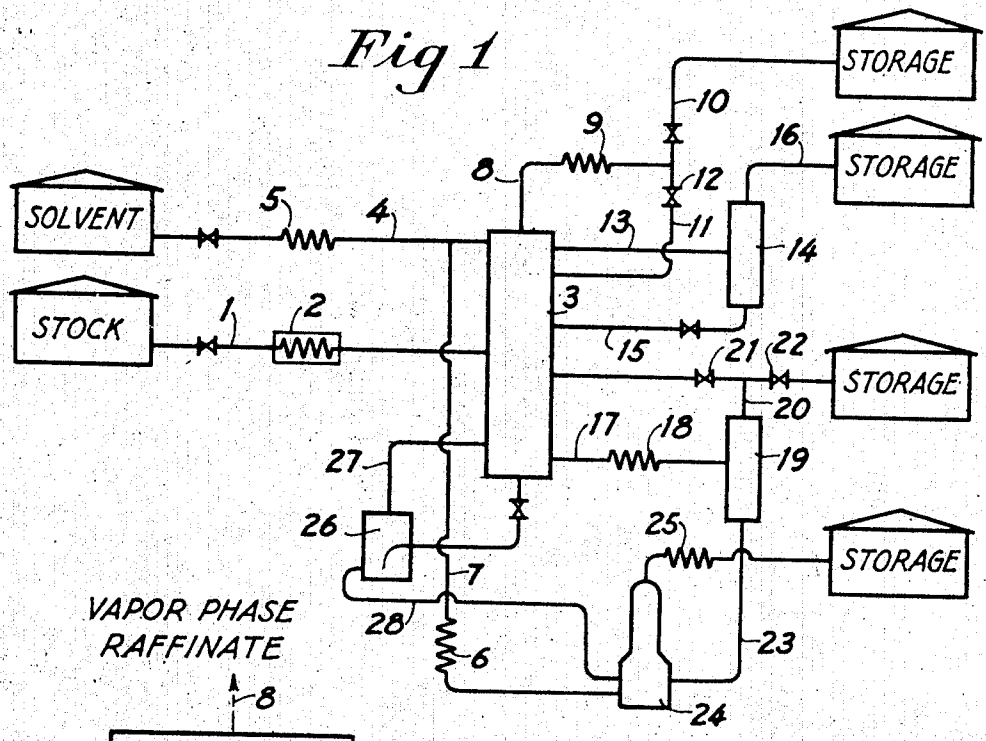
Sept. 30, 1941. A. L. SNOW 2,257,283

SOLVENT REFINING PROCESS

Filed Oct. 18, 1937 3 Sheets-Sheet 1

Fig 1



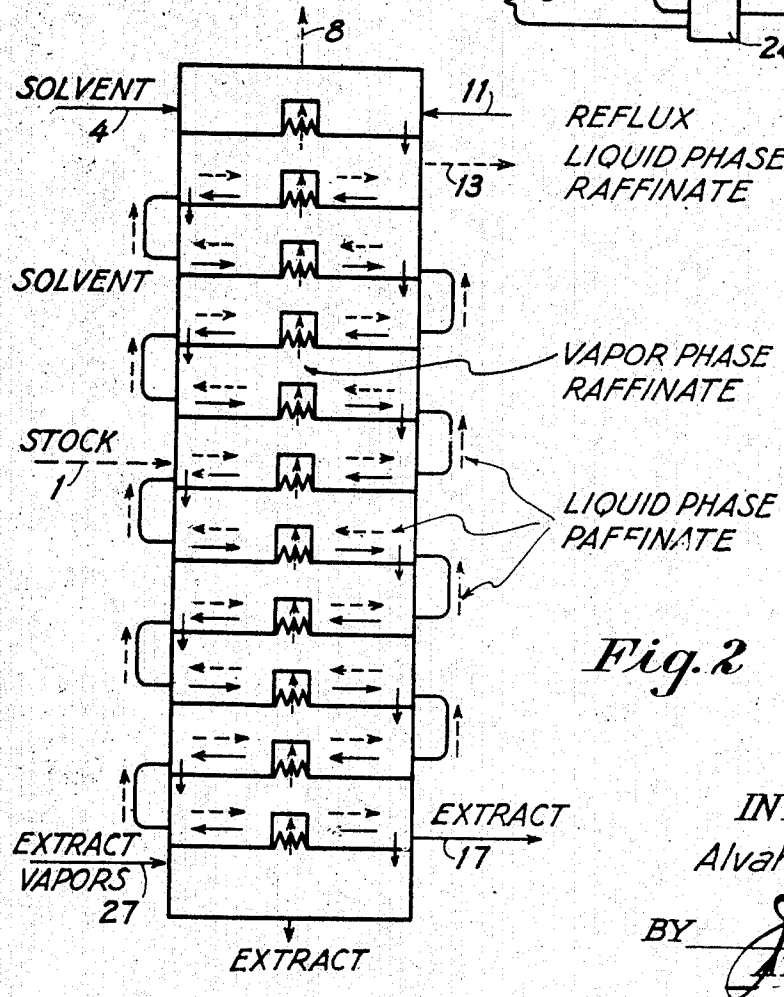


Fig. 2

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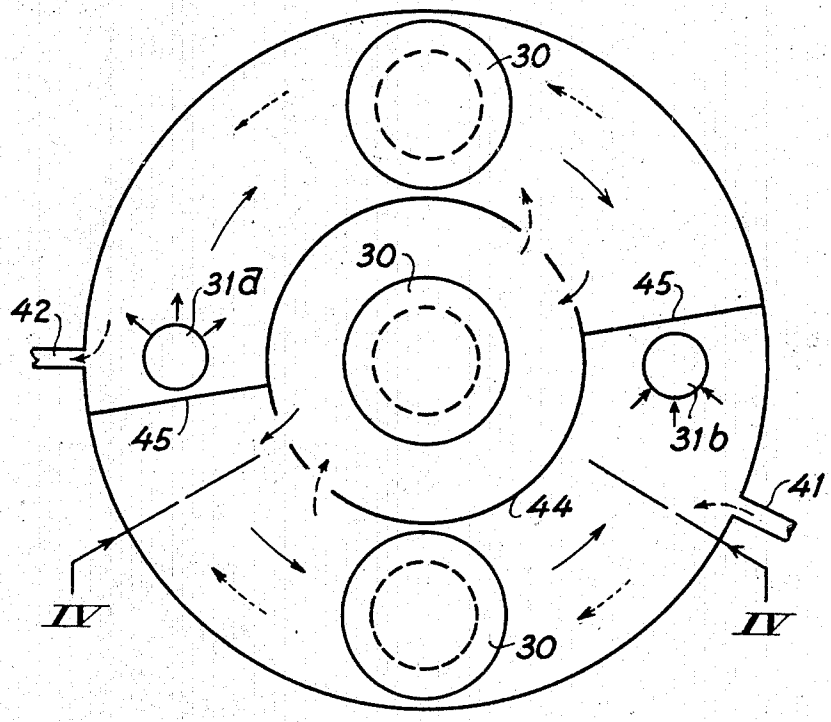

Fig. 3

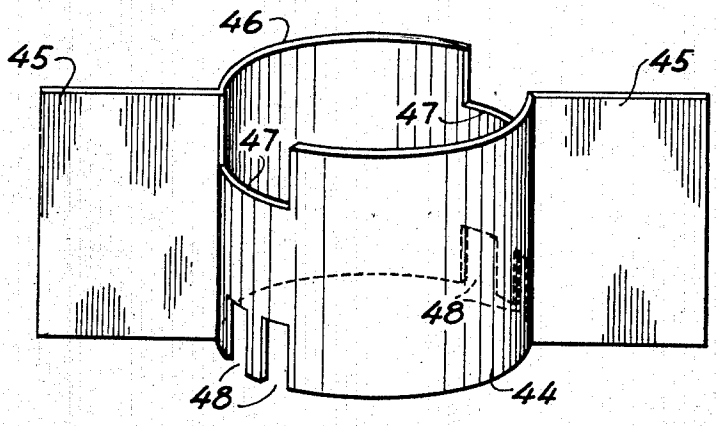

Fig. 5

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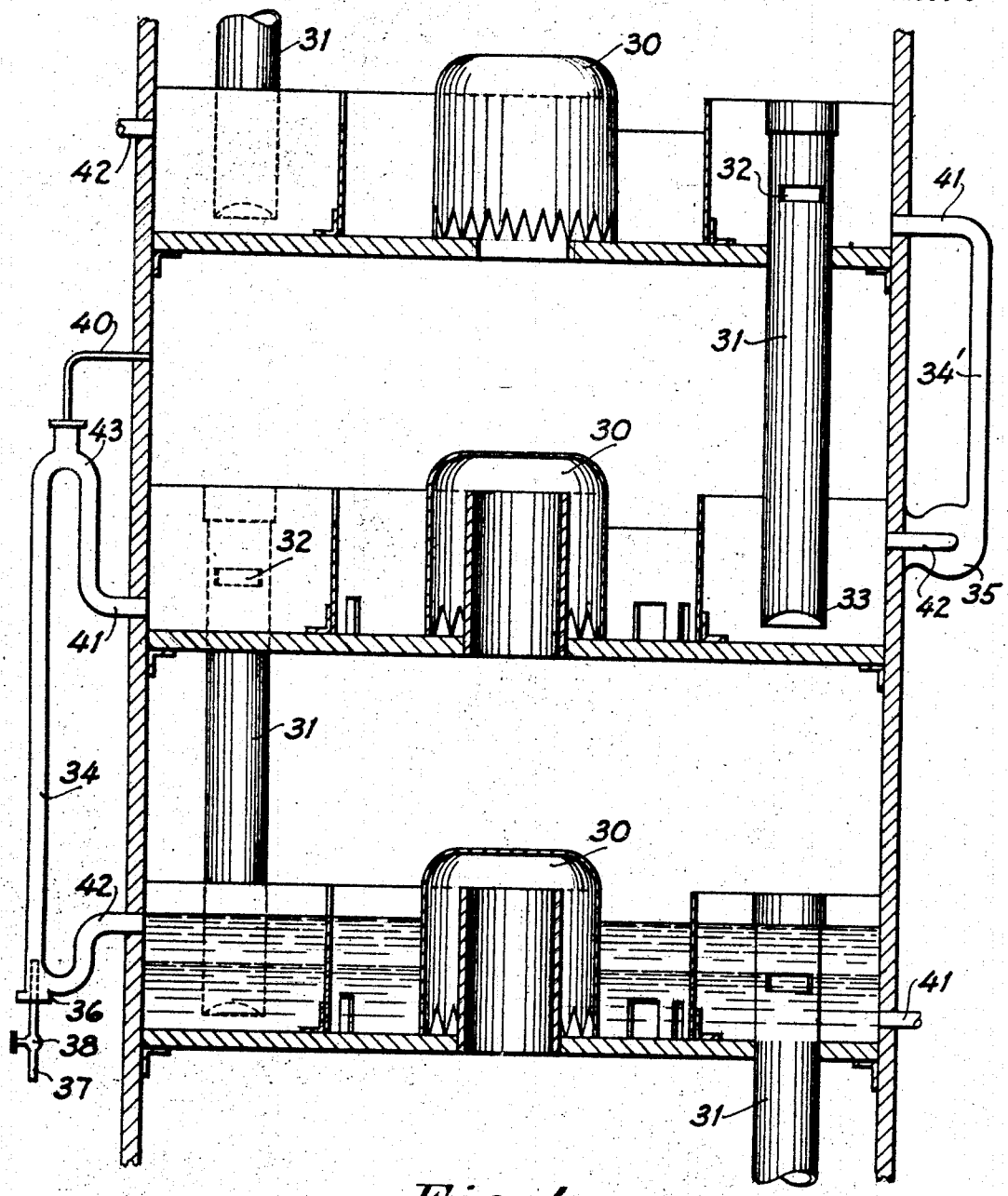

Fig. 4

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UNITED STATES PATENT OFFICE

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SOLVENT REFINING PROCESS

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Application October 18, 1937, Serial No. 169,687

17 Claims. (Cl. 196—13)

This invention relates to a process and apparatus for treating complex mixtures of carbon compounds with a selective solvent. More particularly, it involves a process of treating such complex mixtures with a liquid phase selective solvent at a temperature above the initial boiling point, but below the dew point of the mixture being extracted to effect an efficient separation of the carbon compounds into fractions of different chemical types.

As is well known, normally liquid petroleum contains a complex mixture of hydrocarbons of different types. For example, certain natural petroleums are known to contain a minor percentage of aromatic hydrocarbons and a major proportion of paraffins or naphthenes having 5, 6 and 7 carbon atoms in the naphthene ring. Because of close similarity in properties it has been very difficult to separate these hydrocarbons according to their chemical types. Liquid phase extraction of petroleum oils with selective solvents at temperatures substantially below the initial boiling point of the oils constitutes one known method of refining petroleum and separating aromatic and/or naphthenic hydrocarbons from the remaining oil. Although such a process produces an extract containing relatively more aromatic and more naphthenic hydrocarbons and a raffinate relatively more paraffinic in nature, the separation is only qualitative and yields fractions containing substantial quantities of hydrocarbons which it is desired to eliminate from the particular fraction in question.

It is a well accepted general rule in the art of selective solvent refining that an increase in the temperature of extraction, although it increases the yield of extract obtained, decreases the selectivity of a given solvent and yields an extract in which the separation between aromatics and/or naphthenes on the one hand and paraffins on the other hand is less sharp than obtained at lower temperatures. That is, as temperature of extraction is increased, the yield of raffinate is lowered and the extract contains more and more of the hydrocarbons which it is desired to keep in the raffinate. When the temperature of extraction is lowered, the yield of raffinate increases but it contains an increased amount of the type of hydrocarbons (e. g. aromatic and/or naphthenic) which it is desired to retain in the extract. Accordingly it has heretofore been regarded as necessary to adopt a temperature intermediate the above mentioned high and low extremes such that a given solvent will yield a satisfactory quantity of raffinate and yet also give a reasonably efficient separation or refinement of the petroleum oils.

In the present process selective solvent extraction is carried out under conditions such that the selective solvent is above the initial boiling point but below the dew point of the stock being treated. Remarkable and unpredictable increase in the effectiveness of the selective solvent extraction process is obtained by this high temperature operation. The process gives three phases in the extraction zone, namely, a vapor phase raffinate, a liquid phase raffinate, and a liquid phase extract comprising the selective solvent with its dissolved components. Thus a single stock can be separated into three components by a single extraction step.

Accordingly, an object of the invention is to provide an improved and effective process and apparatus for treating complex mixtures of carbon compounds with a selective solvent.

Another object is to provide a process and apparatus for countercurrently contacting a normally liquid mixture of carbon compounds with a liquid phase selective solvent having a preferential solvent action for one class of the carbon compounds such as aromatics, the temperature of the solvent being above the initial boiling point of the mixture and below the dew point thereof under the conditions of extraction.

A further object is to provide a treating process for continuously separating petroleum into a plurality of separate portions comprising an extract fraction, a lower boiling vapor phase raffinate fraction, and a higher boiling liquid phase raffinate fraction.

Another object is to provide a process of selective solvent extraction capable of effecting separation of a substantially pure component from a mixture of carbon compounds having overlapping boiling ranges and a relatively wide range between the boiling point of the lowest boiling compound and that of the highest boiling compound of said mixture.

A further object of the invention is to provide a process capable of separating substantially pure aromatic hydrocarbons from a petroleum fraction containing paraffinic compounds having boiling points which overlap with those of the aromatics and also containing paraffinic compounds having boiling points more than 60° F. higher than the lowest boiling aromatic compound present.

In the drawings, Figure 1 is a diagrammatic flow sheet illustrating a single stage treating process embodying the principles of this inven-

tion. Figure 2 is a diagrammatic illustration of the path of flow of the various components through one form of treating column and Figure 3 illustrates the path of the solvent and liquid phase stock through a single plate of such a treating column. Figure 4 is a section on line IV—IV of Figure 3 and shows an arrangement of bubble caps and baffle plates for producing the flow of the fluids as illustrated in Figures 2 and 3. Figure 5 is a perspective view of a baffle plate for the apparatus of Figure 4.

Briefly, the specific embodiment of this invention involves intimately contacting a liquid mixture of carbon compounds, such as petroleum hydrocarbons, with a higher boiling selective solvent maintained in liquid phase and at a temperature above the initial boiling point of the mixture being treated. In order that there may be a liquid raffinate phase the solvent should also be at a temperature below the dew point of the stock in the treating zone. During the intimate contacting of the selective solvent and the stock being treated the solvent preferentially dissolves one type of carbon compounds, for instance aromatics, and this solution is separated to give one of the desired fractions. The more volatile less soluble compounds such as lower boiling paraffinic hydrocarbons are converted to vapor phase and separated as such to give a second component from the treating process. The less volatile less soluble types of compounds, such as higher boiling paraffinic hydrocarbons having a boiling point more than 60° F. above that of the lowest boiling dissolved aromatics, form a separate liquid phase and comprise the third component separated from the treating zone.

In the process as illustrated by the flow sheet of Figure 1, the petroleum stock to be treated is passed from storage through valve controlled pipe 1 and heater 2 to treating column 3. The temperature of the stock is raised by heater 2 to a point above its initial boiling point and preferably below the dew point thereof. Temperatures above the dew point of the stock may be utilized where the temperature of the incoming solvent is properly controlled so that the mean temperature in the column is below the dew point of the stock. Since the stock is heated to a temperature above its initial boiling point the mixture admitted to the treating column will contain both liquids and gases which are to be intimately contacted with the selective solvent admitted to the treating tower through valve controlled line 4. The temperature of the entering solvent is controlled by heater 5 or by cooler 6 in recirculating line 7. The preferred temperature of the solvent is from the boiling point of the stock to the dew point of the petroleum stock being treated. The solvent temperature may be higher than the dew point of the stock when it is necessary to compensate for low temperatures of the stock fed to the column. Likewise, the temperature of the solvent may be lower when the temperature of the incoming stock is higher than its dew point. In other words, the temperature of the stock and solvent should be correlated so that the temperature in the column is above the initial boiling point, but below the dew point of the mixture being extracted and at pressures existing in the column.

Vapor phase compounds pass upwardly through the treating column and are extracted by the down-flowing selective solvent. The vapor phase hydrocarbons pass out the top of the column through line 8, condenser 9 and valve controlled conduit 10 to storage. A portion of the condensed vapors may be returned as reflux through pipe 11 controlled by valve 12. Liquid phase hydrocarbons may flow either upwardly or downwardly or in both directions through extraction tower 3. If the selective solvent has a specific gravity greater than that of the compounds being extracted, then the liquid phase compounds will tend to float on the selective solvent and the direction of flow of the solvent will be predominantly downward. This is the normal situation, although in some instances mixtures which have a specific gravity greater than that of the selective solvent being used will be extracted and the direction of flow of the solvent will be predominantly upward. In any event, the liquid phase stock can be separated from the selective solvent and is passed through the column in the proper direction. If the stock comprises the top of the two liquid phase layers then the inlet and outlet ports will have one position; if the stock is on the bottom of the two layers than the inlet and outlet ports will have an inverted position. The liquid phase stock which reaches the top of the treating column 3 is removed through conduit 13 to separator 14 where any entrained selective solvent is allowed to separate from the liquid phase stock. The separated solvent is returned to the extraction column through valve controlled line 15 and the separated stock passed to storage through conduit 16.

The selective solvent together with its dissolved compounds passes down through the tower and is removed from the bottom of the column through line 17, cooler 18, to separator 19. As previously pointed out, in some instances liquid phase raffinate hydrocarbons may flow to the bottom of the column and be removed through this same path to the separator 19. Such liquid phase compounds as are contained in admixture with the selective solvent and are separable therefrom will be removed in separator 19 and flow through line 20 either by way of valve 21 to the column or by way of valve 22 to storage or both as desired.

In the specific illustration given in this specification the petroleum fraction is lighter than the solvent and the direction of flow of the petroleum stock is therefore predominantly upward. However, because the separation between the two liquid phases is not absolutely complete a portion of the petroleum is carried down the column wtih the solvent by entrainment. The stock may therefore be said to flow both upwardly and downwardly in the tower. The amount of flow in each direction depends of course on the amount of entrainment. In order to obtain countercurrent extraction it is preferred to have the solvent flow down the tower and the stock flow up the tower in the oppostie direction. This is accomplished by removing liquid phase raffinate from the top of the tower only. Stock which is entrained in the solvent then serves merely as a kind of reflux inasmuch as it in effect is merely recirculated downwardly from an upper plate to a lower plate from which it ultimately returns as an extracted liquid phase raffinate.

Cooler 18 in line 17 also serves to reduce the temperature of the solvent in order to free some of the less soluble compounds which are actually dissolved in the solvent and thereby enable them to be mechanically separated in separator 19 and returned through line 20 and valve 21 to the treating column as a type of reflux. The selective solvent together with the compounds which remain dissolved therein is removed from the bottom of separator 19 through line 23 to still 24.

The dissolved compounds are vaporized from the solvent in still **24** and the vapors pass to condenser **25** from which they are removed to storage. The selective solvent is recirculated through cooler **6** and line **7** to the inlet of treating column **3**.

Vaporizer **26** is provided to receive a portion of the selective solvent together with high boiling dissolved compounds from the bottom of treating column **3**. The vaporized compounds from heater **26** pass through pipe **27** to the bottom of treating column **3** and serve as a source of heat for the treating tower. Solvent from vaporizer **26** is removed through line **28** to still **24** where the remaining dissolved compounds are vaporized and pass to storage in the manner previously described.

To insure intimate contacting in the extraction column between the mixture being treated and the liquid phase selective solvent, various means may be adopted. A tower filled with suitable packing of refractory earthenware, glass, etc., comprises one effective form of apparatus for this purpose. When such an apparatus is utilized the vapor phase raffinate is taken off as overhead and the liquid phase raffinate is removed from the bottom of the tower as is also the selective solvent with its extract when the solvent is heavier than the mixture being treated. Another form of apparatus which is adapted for treatment, according to the present invention, is a staged counter-flow in which a series of contacting zones for the vapor phase hydrocarbons and liquid phase selective solvent are provided. After thorough contacting in each of the zones the extract and raffinate are separated and pass to succeeding contacting zones. It is apparent that hydrocarbons being extracted should flow in one direction through the series of contacting zones and the selective solvent in an opposite direction through the zones.

A column constructed in a manner analogous to an ordinary fractionating column of the bubble cap type is also an efficient means of insuring effective contact between the vapor phase mixture, the liquid phase mixture, and the liquid phase extracting solvent. In such a preferred form of apparatus the path of flow is shown diagrammatically in Figure 2 of the drawings, and is as follows:

Solvent is admitted to the column at the top by line **4**, passed across the first bubble plate downwardly through an overflow pipe, back across the second bubble plate in the opposite direction from that in the first, through an overflow pipe to the third contacting plate, etc., as shown diagrammatically by the arrows in the solid lines of Figure 2. The stock being treated is admitted through line **1** as indicated by the dotted line arrows in this figure of the drawings. Since the stock comprises a liquid phase portion and a vapor phase portion these two fractions follow different paths. The vapor phase portion passes upwardly through the bubble caps in the same manner as in an ordinary fractionating column and as shown by the dotted line arrows in the center of column of Figure 2. The liquid phase stock flows horizontally across the plates countercurrently to the selective solvent and vertically through the pipes outside of the column from one plate to the other as shown by the dotted line arrows in Figure 2. Extract is removed from the bottom of the tower through line **17**, as shown, and liquid phase raffinate from the top of the tower through line **13**. A portion of the extract is also removed from the bottom of the tower to a vaporizer and the vapors returned to line **27**. Vapor phase raffinate passes from the top of the tower through line **8** after being thoroughly extracted with the selective solvent.

A form of extraction column especially adapted for use in the present process is shown in Figures 3 and 4. The column is provided with a series of bubble caps **30** and a series of down-spouts **31**. Orifices **32** in down-spouts **31** serve to admit selective solvent to the down-spout through which the solvent passes to the next lower bubble plate. The upper end of each of the down-spouts is closed to prevent entry of the stock being treated which floats on the solvent layer. In the lower end of the down-spout a section is cut out as shown at **33** in order to direct the selective solvent in the general direction desired.

Lift conduits **34** and **34'** are provided for conveying liquid phase raffinate from a lower bubble plate to an upper bubble plate. The inlets, that is, the lower ends of the lift conduits, are at the top of the level at which it is desired to keep the liquid phase raffinate layer. The outlet ends of the lift conduits are preferably below the selective solvent level so that the liquid phase raffinate will be intimately contacted with the selective solvent as it rises therethrough.

Two different types of means have been illustrated for causing the liquid phase raffinate to flow upwardly through the lift conduits. The first is a centrifugal pump **35** and the second a gas lift arrangement **36**. When a gas lift is utilized various inert gases may be used, e. g. methane, ethane, propane, a mixture thereof such as obtained in petroleum refinery gases, nitrogen or steam where condensed water does not interfere with the extraction process or render the selective solvent useless by reason of dilution. In those cases where water is miscible with the solvent and where the selective solvent is relatively non-selective at the high temperatures used in this process, steam will be found particularly desirable since the presence of water or water vapor decreases the miscibility of the solvent and oil. Phenol is an example of a selective solvent which is relatively non-selective at high temperatures and which can be rendered more selective by the addition of water by this or other methods. Another gas which may be utilized in the gas lift comprises the raffinate vapors themselves which may be removed from the top of the extraction tower, compressed and introduced into the gas lift device.

Pipe **37** controlled by valve **38** is provided for introducing the lifting gas into the liquid in lift conduit **34**. The bottom end of conduit **34** is U-shaped as shown in order that the liquid phase raffinate will flow into the U and have an upper level above the gas inlet. The upper end of conduit **34** comprises a goose-neck portion which serves simultaneously as a gas trap and siphon breaker. The lifting gas accumulates in the top of the U and is removed through line **40** in order to prevent formation of a gas pocket. Also line **40** acts as a breather to prevent siphoning of fluid from the upper plate through inlet **41** downwardly to the lower plate.

The level of the solvent and liquid raffinate phase relative to the various inlet and outlet conduits is illustrated at the bottom bubble plate of Figure 4. The lower layer as represented in this figure is selective solvent and the upper layer of liquid is the raffinate being extracted.

Figure 3 shows the arrangement of parts and path of liquid flow on a single bubble plate. Three bubble caps **30** are provided and are separated by a baffle plate having a cylindrical portion **44** surrounding the center bubble cap and wing portions **45** extending from the cylindrical portion to the sides of the column. Slots **47** (see Figure 5) are provided in the top edge of the baffle to direct the upper liquid phase through the desired path of flow. Likewise, slots **48** are placed in the bottom edge of the baffle to cause the selective solvent to flow around the several bubble caps as shown by the solid line arrows of Figure 3. Specifically, the selective solvent flows from overflow pipe **31***a* around and under the first bubble cap (top of Figure 3) through slot **48** into the cylindrical portion of the baffle around the center bubble cap and out through the second of slots **48** around and under the third bubble cap to outlet overflow pipe **31***b*. As indicated by the dotted line arrows the upper layer liquid phase raffinate flows countercurrently to the selective solvent and passes from inlet pipe **41** over and around the lower bubble cap through slot **47** across the center bubble cap out second slot **47** and around the third bubble cap to outlet conduit **42**. The wings **45** and higher portions **46** of the baffle plate serve to prevent the liquid phase raffinate from flowing directly across the bubble plate from inlet to outlet. The vapor phase raffinate passing through the bubble caps is extracted by the lower solvent layer and simultaneously the vapors act as an efficient means for agitating the two liquid phases passing across the bubble plate. Thus intimate contact between all three phases is effected in a simple and efficient manner.

The efficiency of separation of the two liquid phases on each of the bubble plates is subject to control by design of the size of the column, gas rates through the bubble caps, rate of flow of the liquid phases, etc. However, it should be noted that perfect separation is not absolutely essential since entrainment of either solvent in the stock or stock in the solvent, or both, merely acts as a reflux in that it feeds back a portion of the liquid entrained to the bubble plate from which it came. This entrainment of course decreases the net rate of flow through the treating zone, but up to a certain degree may be found to increase the efficiency of extraction as is the case with any reflux.

In its broad aspects the present invention is applicable to a great number of mixtures of chemical compounds which are difficult to separate because of similarity of boiling points, solubility characteristics, or because of formation of constant boiling mixtures. For example, the selective solvent extraction process may be applied to mixtures of compounds such as phenols, aromatics, sulfur compounds, olefines, naphthenes and paraffins, which commonly occur in petroleum distillates. These mixtures can be passed through a single extraction zone or a series of extraction zones under conditions of temperature and pressure such that the mixture is separated into different components, one component or group of components being removed from the bottom of each extraction zone as an extract phase, the more volatile component or group of components being removed from the top of the extraction zone as a vapor phase overhead and the less volatile less soluble component or group of components being removed from the top of the extraction zone as a liquid phase raffinate. It will be necessary of course to provide at least one extraction zone for each three components or groups of components to be separated. However, the process at present is regarded as having its greatest utility for the extraction of substantially pure aromatic hydrocarbons from extremely complex mixtures of aromatics, naphthenes or paraffins which occur in natural gasolines of relatively wide boiling range such as 360° F. end point distillates.

Repeated reference has been made throughout this specification to the use of "selective solvents" in the process. This generic term is used to define a solvent which has greater solvent power for at least one component of a multi component system than it has for other components of that system. Stated conversely, the term "selective solvent" designates a solvent which has less tendency to dissolve one component of a mixture than other components thereof. The greater the differential in solvent power of a selective solvent for different components of the mixture, the greater is its selectivity and the more efficient it will be in the extraction of the component for which it has the greatest solvent power.

A selective solvent useful for the present process should be highly selective and should have a boiling point well above the dew point of the stock to be treated. The selective solvent must also be of incomplete miscibility with the stock being treated at the temperature of extraction. In other words, the suitability of a known selective solvent for the process of this invention can be primarily determined by two physical characteristics, namely, boiling point and miscibility temperature. Since the process is operated at temperatures above the initial boiling point of the stock, but below its dew point, the temperature of complete miscibility of solvent and stock must be above the dew point of the stock under the conditions of extraction. This property can be readily ascertained by a simple miscibility test at elevated temperature. It should of course be recognized that by the terms "dew point" and "boiling point" used above, one means the dew point or boiling point in the presence of the selective solvents and under the conditions of extraction. For example, vacuum may be utilized on the extraction tower and thereby permit use of a selective solvent which would be miscible with the stock being treated at its ordinary initial boiling point, but which is of incomplete miscibility with the stock at the initial boiling point of the stock and the dew point of the stock under the conditions of extraction, namely, high vacuum. The use of vacuum is therefore contemplated as falling within the broad scope of the present invention.

The following compounds are illustrative of high boiling selective solvents which have high temperatures of miscibility with most petroleum stocks and which are therefore operative for separating aromatics such as benzene or toluene from natural petroleum distillates containing the same: triethylene glycol, diethylene glycol, acetamide, monoacetin, diethanolamine, diaminopropanol. In general polar compounds selected from the group consisting of hydroxy benzenes, amides, chlorinated hydrocarbons and esters of polycarboxylic acids which have boiling points and solubility characteristics such as above discussed are contemplated as falling within the broad scope of the invention. The solvents selected from this group preferably should have a

boiling point above approximately 300° F. in order that they can be readily maintained in liquid phase under ordinary conditions of extraction with the usual normally liquid petroleum fractions.

Those selective solvents which are miscible with the mixture of compounds being extracted can be utilized in some instances by adding to the solvent a diluent which is miscible with the solvent, but immiscible with the stock being treated. For example, in the treatment of very volatile stocks, phenol may have a suitable boiling point, but have a miscibility temperature below the dew point of the stock. In such instances the phenol may be diluted with water to render it operative in the process of this invention. Other diluents which are characteristically immiscible with hydrocarbons or petroleum fractions and which are often miscible with the solvents are carbon compounds having a large number of hydroxy groups. Glycerol is an example of a poly-hydroxy alcohol having high miscibility temperatures with petroleum fractions and which is operative as a diluent in the above suggested combinations.

Obviously, specific conditions of operation such as temperature, pressure, relative solvent to stock volumes, and proportion of vapor phase raffinate to liquid phase raffinate will vary with the particular mixture being treated and with the selective solvent used. As previously pointed out, a critical feature of the invention comprises operation of the process at a temperature above the initial boiling point, but below the dew point of the stock. The entire process will usually be carried out at atmospheric pressures, although super-atmospheric pressures may be used. Sub-atmospheric pressures will be found sufficiently desirable in some instances to justify the additional cost occasioned by operation under vacuum.

It will be observed that the present process is fundamentally different from ordinary selective solvent extraction processes in that it operates at temperatures above the boiling point of the stock being treated. The process is also fundamentally different from ordinary distillation processes in that three phases are present and three components are simultaneously separated from the treating zone.

The following principal advantages of the invention will be readily apparent. Mixtures of paraffins, aromatics, etc. having much wider boiling ranges can be separated according to chemical types by the process of this invention. Heretofore it has been possible to separate pure aromatics from paraffins by treatment of relatively narrow fractions in a large number of carefully controlled fractionating steps. The present invention avoids such complex multi-stage operations. By utilizing the present process it is unnecessary to operate at temperatures above the end point of the stock since the high boiling, less soluble components, e. g., paraffins, are not vaporized as is the case with ordinary distillation processes carried out in the presence of a solvent. By operating at these lower temperatures the efficiency of extraction of the more soluble components, e. g. aromatics, is increased since there is less tendency to distil them out of the solvent. The process herein described effectively separates the less soluble paraffinic compounds having boiling points nearest those of the aromatics. Normally these very similar components are the most difficult to separate and cause the greatest difficulties in distillation operations. After treatment by the present process any paraffinic constituents which happen to remain dissolved in the extract with the aromatics are found to have a boiling point sufficiently different from the aromatics (as much as 60° F. or more) that they can readily be removed by ordinary distillation and fractionation after separation from the solvent.

The actual distillation operation is more efficient by reason of the fact that the paraffins remain in a separate liquid phase than is the case where the paraffins are dissolved in a solvent. This is believed to result from the fact that a greater differential in boiling points is produced by the selective solvent when only one component is dissolved in the solvent than when the entire mixture is dissolved therein. This greater differential in boiling points in turn increases the efficiency of separation by the fractionation process. Other numerous advantages will be apparent to those skilled in the art.

While the character of this invention has been described in detail this has been done by way of illustration only and with the intention that no limitation should be imposed upon the invention thereby. Likewise, the drawings are to be regarded as diagrammatical, no attempt having been made to show all the necessary details such as pumps, valves, pressure control devices and the like. It will be apparent to those skilled in the art that numerous modifications and variations may be adopted in the apparatus and method of the invention which is of the scope of the appended claims.

I claim:

1. A process of separating a multi-component mixture of carbon compounds into more than two components which comprises passing said mixture through a treating zone, passing through said treating zone a selective solvent which remains in liquid phase and is of incomplete miscibility with said mixture, converting a portion only of said multi-component mixture to vapor phase whereby the solvent phase, a vapor phase raffinate and a liquid phase raffinate are simultaneously present in said zone, passing said vapor phase components through said treating zone, intimately contacting said three phases while passing said liquid phase raffinate in a direction opposite to that of said liquid solvent phase to selectively dissolve one type of carbon compound in said solvent, removing the treated vapor phase, and separating the two liquid phases to obtain at least three different fractions from said treating zone.

2. A process of separating aromatic hydrocarbons from mixtures containing aromatic and non-aromatic carbon compounds of similar boiling range which comprises passing said mixture through a treating zone, passing through said treating zone a liquid phase selective solvent for said aromatic compounds, which solvent is of incomplete miscibility with said mixture, converting a portion only of the mixture of carbon compounds to vapor phase whereby a solvent phase, a vapor phase raffinate and a liquid phase raffinate are simultaneously present in said zone, passing said vapor phase components through said treating zone, intimately contacting said three phases and passing said liquid phase raffinate countercurrently to said solvent phase to selectively dissolve aromatic compounds in said solvent, and separately removing the vapor phase,

the liquid raffinate phase and the solvent phase from said treating zone.

3. In a process of separating a normally liquid, multi-component mixture of carbon compounds into a plurality of components the steps which comprise passing said mixture through a treating zone, passing through the treating zone a liquid phase selective solvent which is of incomplete miscibility with said mixture at the dew point thereof, maintaining the temperature in the treating zone above the initial boiling point but below the dew point of the mixture under the conditions of extraction whereby a vapor phase raffinate, a liquid phase raffinate and a liquid phase extract are simultaneously present in said zone, intimately contacting the said three phases while flowing said liquid phase raffinate through said treating zone in one direction and flowing said liquid phase extract through said treating zone in the opposite direction, and separately removing the treated vapor phase, the liquid raffinate phase and the liquid extract phase from the treating zone.

4. A process of separating aromatic hydrocarbons from petroleum distillates which comprises extracting said distillate with a liquid phase selective solvent at a temperature above the initial boiling point but below the dew point of said distillate and under such conditions of extraction that a vapor phase raffinate, a liquid phase raffinate, and a liquid phase extract are simultaneously present, said selective solvent being in liquid phase and of incomplete miscibility with the distillate at the temperature of extraction, passing said liquid phase raffinate countercurrently with respect to said liquid phase extract, and separating three different phases comprising a vapor phase raffinate, a liquid phase raffinate and a liquid phase extract.

5. A process as defined in claim 4, in which the selective solvent is an hydroxy ether having a boiling point above approximately 300° F.

6. A process as in claim 4, in which the selective solvent is a poly-ethylene glycol.

7. A process of treating a normally liquid petroleum fraction containing hydrocarbons of the aromatic and paraffinic types and in which the boiling point of the highest boiling paraffinic hydrocarbon is more than approximately 60° F. above the boiling point of the lowest boiling aromatic hydrocarbon contained therein, which comprises passing said normally liquid petroleum fraction through a treating zone, passing through said treating zone a liquid phase selective solvent which is of incomplete miscibility with the petroleum fraction at the dew point thereof, maintaining the temperature in the treating zone above the initial boiling point but below the dew point of the fraction under the conditions of extraction whereby a vapor phase raffinate, a liquid phase raffinate and a liquid phase extract are simultaneously present in the zone, intimately contacting said three phases, passing said liquid phase raffinate countercurrently to said liquid phase extract, and separately removing the treated vapor phase, the liquid phase raffinate and the liquid phase extract from the treating zone.

8. A process of separating a multi-component mixture of carbon compounds into a plurality of components which comprises, continuously introducing said mixture into a frictionating column at a point intermediate the ends thereof, continuously introducing a high boiling selective solvent of incomplete miscibility with the mixture at the dew point thereof into said fractionating column at a point above that at which said mixture is admitted, maintaining the temperature in said column above the initial boiling point but below the dew point of said mixture and under such conditions that a vapor phase raffinate, a liquid phase raffinate, and a liquid phase extract are simultaneously present, passing said liquid phase raffinate countercurrently to said liquid phase extract, and continuously removing vapor phase raffinate and liquid phase raffinate from the top of said column and continuously removing liquid phase extract from the lower portion of said fractionating column.

9. A process as defined in claim 8, further characterized in that entrained raffinate is separated from the liquid phase extract and returned to the fractionating column.

10. A process as defined in claim 8, further characterized in that entrained selective solvent is separated from the liquid phase raffiinate and returned to the fractionating column.

11. A process of treating a multi-phase mixture of carbon compounds having more than one liquid phase which comprises, forming a multi-phase system having heavier and lighter liquid phases by only partially dissolving said mixture in a selective solvent, separating said liquid phases into a lighter and a heavier portion, passing the lighter portion through an extraction system in one direction, passing the heavier portion through said extraction system in a different direction, partially vaporizing undissolved carbon compounds of said mixture without substantial vaporization of said solvent and contacting the vapors with at least one of said liquid phases different from said partially vaporized undissolved liquid phase.

12. A process of separating according to chemical type a multi-component mixture of carbon compounds which comprises passing said mixture through a selective solvent extraction zone, forming an undissolved vapor phase fraction and an undissolved liquid phase fraction in said zone, passing said undissolved fractions in said zone countercurrently to a liquid phase selective solvent having a boiling point substantially above the end point of said mixture of carbon compounds, contacting said undissolved phases with said selective solvent, withdrawing a liquid phase selective solvent extract from said extraction zone at one point, withdrawing a liquid phase raffinate from said extraction zone at a second point remote from said first point, maintaining the temperature in said zone at said second point below the dew point but above the initial boiling point of said mixture of carbon compounds, and maintaining said selective solvent incompletely miscible with said mixture of carbon compounds substantially throughout the extraction zone.

13. A process of separating according to chemical type a multi-component mixture of carbon compounds which comprises passing said mixture through a selective solvent extraction zone, forming an undissolved vapor phase fraction and an undissolved liquid phase fraction in said zone, passing said undissolved fractions in said zone countercurrently to a liquid phase selective solvent having a boiling point substantially above the end point of said mixture of carbon compounds, contacting said undissolved phases with said selective solvent, withdrawing a liquid phase selective solvent extract from said extraction zone at one point, withdrawing a liquid phase raffinate from said extraction zone at a second point re-

mote from said first point, maintaining the temperature in said zone at said second point below the dew point but above the initial boiling point of said mixture of carbon compounds, and maintaining said selective solvent incompletely miscible with said mixture of carbon compounds substantially throughout the extraction zone by adding to said solvent a diluent immiscible with said mixture of carbon compounds.

14. A process of treating a normally liquid petroleum fraction containing hydrocarbons of the aromatic and paraffinic types and in which the boiling point of the highest boiling paraffinic hydrocarbon is more than approximately 60° F. above the boiling point of the lowest boiling aromatic hydrocarbon contained therein, which comprises passing said petroleum fraction through a selective solvent extraction zone, forming an undissolved vapor phase hydrocarbon fraction and an undissolved liquid phase hydrocarbon fraction in said zone, passing said undissolved fractions in said zone countercurrently to a liquid phase selective solvent having a boiling point substantially above the end point of said mixture of carbon compounds, contacting said undissolved phases with said selective solvent, withdrawing a liquid phase selective solvent extract from said extraction zone at one point, withdrawing a liquid phase raffinate from said extraction zone at a second point remote from said first point, maintaining the temperature in said zone at said second point below the dew point but above the initial boiling point of said mixture of carbon compounds, and maintaining said selective solvent incompletely miscible with said mixture of carbon compounds substantially throughout the extraction zone.

15. A process as defined in claim 14 in which the selective solvent is an hydroxy ether having a boiling point above approximately 300° F.

16. A process of separating according to chemical type a multi-component mixture of carbon compounds which comprises passing said mixture through a selective solvent extraction zone, forming an undissolved vapor phase fraction and an undissolved liquid phase fraction in said zone, passing said undissolved fractions in said zone countercurrently to a liquid phase selective solvent comprising a liquid phase hydroxy benzene having a boiling point substantially above the end point of said mixture of said carbon compounds, contacting said undissolved phases with said selective solvent, withdrawing the liquid phase hydroxy benzene together with its dissolved carbon compounds from said zone at one point, withdrawing a liquid phase raffinate from said extraction zone at a second point remote from said first point, maintaining the temperature in said zone at said second point below the dew point but above the initial boiling point of said mixture of carbon compounds, and maintaining said selective solvent incompletely miscible with said mixture of carbon compounds substantially throughout the extraction zone.

17. A process of separating according to chemical type a multi-component mixture of carbon compounds which comprises passing said mixture through a selective solvent extraction zone, forming an undissolved vapor phase fraction and an undissolved liquid phase fraction in said zone, passing said undissolved fractions in said zone countercurrently to a liquid phase selective solvent comprising a liquid phase ester of a polycarboxylic acid having a boiling point substantially above the end point of said mixture of said carbon compounds, contacting said undissolved phases with said selective solvent, withdrawing the liquid phase ester of a polycarboxylic acid together with its dissolved carbon compounds from said zone at one point, withdrawing a liquid phase raffinate from said extraction zone at a second point remote from said first point, maintaining the temperature in said zone at said second point below the dew point but above the initial boiling point of said mixture of carbon compounds, and maintaining said selective solvent incompletely miscible with said mixture of carbon compounds substantially throughout the extraction zone.

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