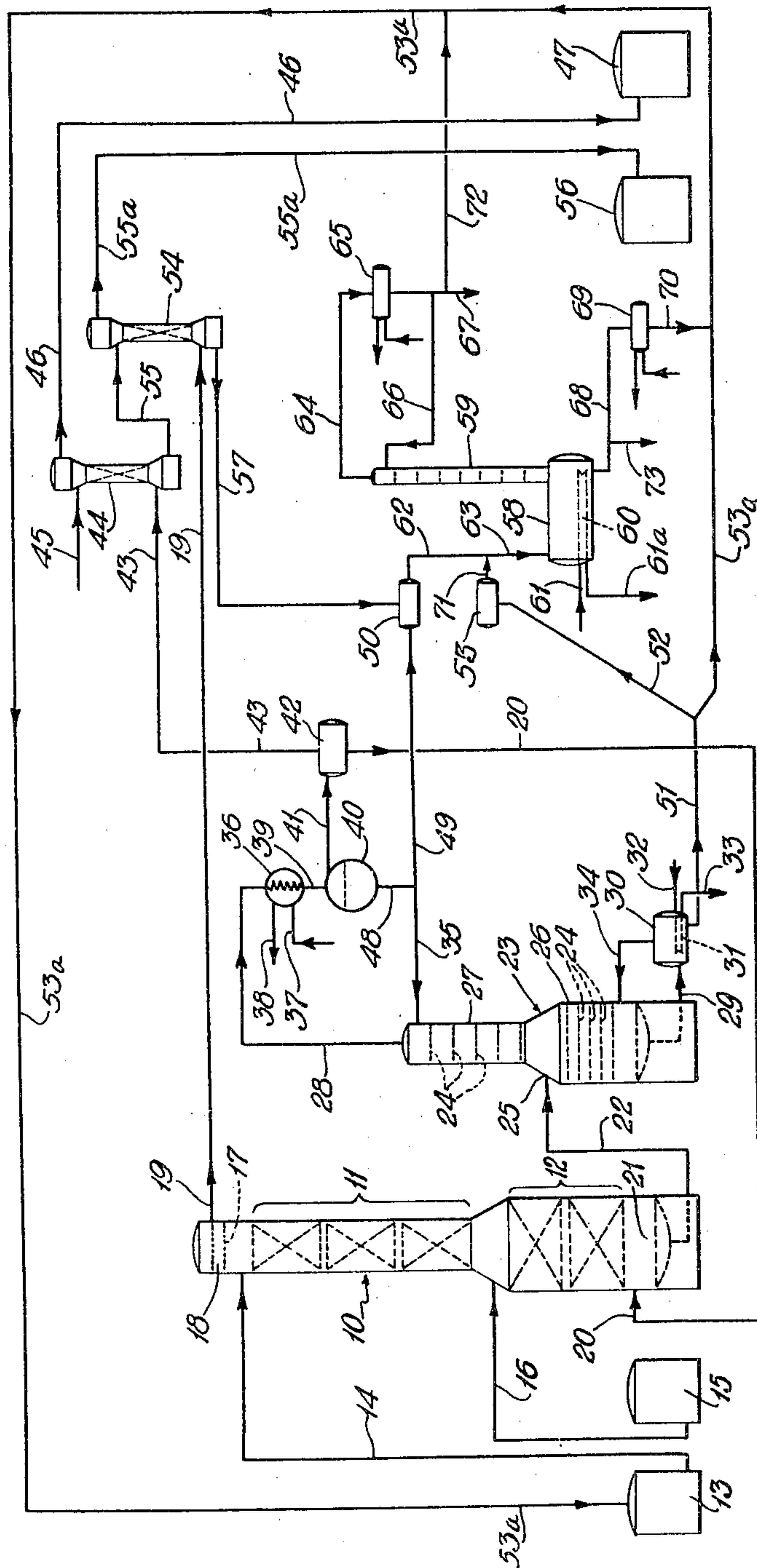


July 6, 1948.

A. S. SMITH
SELECTIVE SOLVENT TREATMENT OF LIQUID
HYDROCARBON MIXTURES FOR SEGREGATION
OF CONTAINED AROMATICS
Filed Jan. 20, 1944

2,444,582



INVENTOR
Allen S. Smith
by *Ray A. Leonard*
his ATTORNEY

UNITED STATES PATENT OFFICE

2,444,582

SELECTIVE SOLVENT TREATMENT OF
LIQUID HYDROCARBON MIXTURES
FOR SEGREGATION OF CONTAINED
AROMATICSAllen S. Smith, Ann Arbor, Mich., assignor to
Blaw-Knox Company, Pittsburgh, Pa., a cor-
poration of New Jersey

Application January 20, 1944, Serial No. 518,964

51 Claims. (Cl. 196—14.40)

1

This invention relates to selective solvent treatment of liquid hydrocarbon mixtures for segregation of contained aromatics; and it relates more particularly to continuous countercurrent selective solvent treatment of mineral oils and mineral oil fractions, especially natural or cracked petroleum distillates, having a substantial content of aromatic hydrocarbons, effected in such manner as to extract most of such aromatic content therefrom in concentrated form.

It has long been known that petroleum or petroleum distillates could be separated by various selective solvent extraction methods into (1) a more paraffinic fraction, called the raffinate, containing relatively little solvent, and (2) a more aromatic fraction, called the extract or extract solution, also containing a substantial proportion of the non-aromatic hydrocarbons present in the original stock treated, together with most of the solvent employed. Lubricating oil stocks have been thus refined to free them of aromatic and asphaltic contaminants. There have also been proposals to utilize the principles of selective solvent extraction for improving motor fuel distillates of the gasoline type in respect to anti-knock properties by eliminating a part of their paraffinic content and thus increasing proportionately their content of aromatics. Further, it has also been proposed to treat certain petroleum and other mineral oil fractions that are rich in aromatics, including cracked naphthas and the like, by selective solvent extraction with solvents selective for aromatics, for the specific purpose of separating therefrom valuable aromatic components in form suitable for the purpose, among others, of blending with gasoline to improve its octane rating.

However, it is well known that such previously proposed methods accomplish only a comparatively rough qualitative separation at best. The extract, although richer in aromatics (and naphthenes) than the original stock, still contains paraffins; while the raffinate, although definitely more paraffinic than said stock, includes also a very considerable proportion of the original aromatics content. Attempts to better the extraction of aromatics by increasing the operating temperature, in order thus to increase the solvent power of the selective solvent employed, are of no avail, generally speaking, because this ordinarily results, at the same time, in increasing its solvent power for paraffins and other non-aromatics present, such as olefins and naphthenes.

Recognizing the great desirability of devising

2

some commercially feasible way of applying selective solvent extraction principles to the production, from mineral oil materials of the character mentioned, of valuable aromatics in highly concentrated form, and thus importantly supplementing the supply of such hydrocarbons available from other sources, various attempts have been made to overcome the aforesaid difficulties and objections. For example, a fairly recent proposal is to selectively solvent-treat the stock in liquid phase, next to separate the resultant extract into several aromatic-rich fractions by distillation, and finally to subject the individual fractions, while in vapor phase, to further extraction with a high-boiling selective solvent. Aside from other objections to this procedure, the recovery asserted for it is only from 50 to 70 per cent of the aromatics originally present in the stock. Another and more recent suggestion is to subject aromatic stock to selective solvent extraction, using as the selective solvent a dihydric alcohol characterized by having at least two ether groups, such as triethylene glycol or tetraethylene glycol. This method appears to be even more inefficient, the extract obtained evidently containing only a relatively small proportion of the total aromatic content of the stock.

From a consideration of these and other proposals, it is apparent that attempts heretofore made to solve the problem leave much to be desired. Aside from their generally characteristic low recovery of aromatics, some of the prior proposals have been impractical because of prohibitively high cost of the specific solvent employed or of its recovery for re-cycling, or because of other expensive operational features that rendered them uncommercial. So far as this applicant is aware, no commercially feasible selective solvent extraction method has heretofore been devised which enables approximating substantially complete recovery of valuable aromatic hydrocarbons in concentrated form from a mineral oil feed stock containing them.

The importance of finding a satisfactory solution of the problem is obvious in view of the wide variety of essential purposes for which benzene, and its alkyl homologues such as toluene, xylenes, mesitylene, cumene, etc., are greatly needed. Benzene is a raw material used in numerous syntheses of benzene derivatives as, for example, in the manufacture of such compounds as styrene and phenol. Toluene is the hydrocarbon raw material for the manufacture of high explosives, such as trinitrotoluene. The more highly alkylated aromatics are likewise used in

3

syntheses, but they are also used for blending purposes as additions to motor fuel, particularly for production of aviation gasoline, in order to improve the octane number and particularly the power characteristics of the fuel. Some of them, such as xylene, may serve as special reserve fuels employed directly, unblended, for temporary or emergency purposes, as where a plane is required under certain conditions to develop exceptionally high speed for a brief period. In addition, there is great need for a practical method of solvent-treating a mineral oil stock containing aromatics, in such manner as to recover therefrom all or a high percentage of such aromatics content in the form of an extract product much enriched in aromatics, without necessarily separating individual aromatics as such. As examples of this may be mentioned the production, by selectively extracting a gasoline feed stock having a low or medium octane number, of an extract richer in aromatics than the gasoline feed stock and consequently higher in octane number; as well as the production of high solvency naphthas from feed stock of lower solvent power.

Accordingly, it is a primary object of the present invention to provide an efficient and industrially practicable selective solvent extraction process whereby a high proportion, commonly 90 to 95 per cent and frequently as much as 98 to 99 per cent, of the valuable aromatic hydrocarbons present in mineral oil charging stocks or feed mixtures of various specific kinds can be recovered in the form of products which, while still containing non-aromatics in proportion which may vary widely, are commercially valuable products for various purposes. A further and more specific object is to provide such a process whereby the hydrocarbon components of the stock or feed mixture may be separated into an aromatic portion or extract exceptionally low in paraffins and naphthenes, and a paraffinic portion or raffinate substantially free from aromatics and containing nearly all the paraffins and naphthenes initially present in the stock. A further object of the invention is to accomplish the foregoing in a relatively simple and economical manner, in a continuously operating system, at ordinary temperatures, that is, within a normal temperature range of, say, 70° to 90° F., and with temperatures of 60° and 100° as extreme limits in practice. Other objects of the invention will appear in connection with the further detailed description of the invention to be given hereinafter.

Liquid mineral oil charging stocks or feed mixtures adapted to be processed in accordance with the invention are of wide variety, obtainable from many different sources. In general, however, they are essentially complex liquid mixtures or solutions of hydrocarbons both aromatic and non-aromatic, the latter frequently including naphthenes and olefins in addition to paraffins. Examples of suitable stocks are gasolines, naphthas, burning oils, or similar fractions derived from crude petroleum by "straight-run" distillation; corresponding or other distillates produced by the thermal decomposition or cracking of petroleum or other mineral oils, or cuts therefrom; as well as fractions separated from cracked distillates, light oils, or the like. "Light oils" are fractional distillates from coal-tar consisting of mixtures of benzene, pyridine, toluene, xylene, phenol and cresols. The lower-boiling fractions separated from crude petroleum, such as gasolines, naphthas and burning oils, when produced

4

by straight-run or non-cracking distillation, are composed mainly of paraffins, naphthenes, and aromatics. Olefin hydrocarbons are normally present in relatively negligible proportion, if at all. On the other hand, the lower-boiling distillates produced through reactions of thermal decomposition and polymerization, that is, through the use of processes known broadly in the art as cracking, contain not only paraffins, naphthenes and aromatics, but also olefin hydrocarbons and, to a lesser degree, hydrocarbons of the diolefin and acetylene series.

In extracting valuable aromatic hydrocarbons from any feed stock of the character above indicated in accordance with the process of the present invention, the procedure is essentially as follows:

The feed stock is subjected to continuous selective solvent extraction in an extraction column, both feed and solvent being in liquid phase, by a procedure which, insofar as concerns what may be termed its general mechanics of operation, is in the main already well known. That is to say, the solvent is introduced into the column at one end of the extraction zone, the liquid feed is introduced at a location intermediate the ends of the column, and extract solution comprising nearly all of the solvent together with the extracted hydrocarbons dissolved therein, is removed at or near the other end of the extraction zone; while a solvent-poor liquid raffinate comprising the undissolved hydrocarbons leaves the column at a point near where the solvent is introduced.

In accordance with the present invention, however, the solvent employed is a composite or mixed solvent of a particular type not heretofore employed, it is believed, which has been found to be outstandingly effective for the purposes hereinabove stated, and which is also believed to be novel as a composition. Such novel type of mixed solvent comprises two component solvents now to be identified. Both are aliphatic oxygenated polar compounds. One of them, which may be termed the primary solvent, or the primary component of the mixed solvent, must be at least partially miscible with the hydrocarbon mixture as a whole that is to be solvent-treated, and must also be selective for the aromatic component or content of that mixture. The primary solvent must contain at least one hydroxyl group in the molecule; and it may contain two or more hydroxyl groups, in which latter case it must also contain at least one ether group. With respect to the other component solvent, which may be termed the modifying, auxiliary or secondary solvent, the essential requirements are that it shall be completely miscible with the primary solvent but only partially miscible, at most, with each of the components (aromatic and non-aromatic) of said hydrocarbon mixture; also that it shall contain at least two hydroxyl groups in the molecule, accompanied or not either by one or more ether groups or else by nitrogen. In respect to both solvents, it is to be understood that the above specified requirements for miscibility apply to operating temperatures within the range at which the extraction is to be conducted.

Within the foregoing definitions of the primary and secondary solvents to be used in mixture in accordance with the principles of the invention, it is found that particularly desirable results are obtainable, especially when operating at from 70° to 90° F., if the primary solvent is selected from the group consisting of methyl alcohol, ethyl alcohol, isopropyl alcohol, dipro-

pylene glycol, tetraethylene glycol, hexaethylene glycol, nonaethylene glycol and a product available under the trade name "Carbowax 1500", which is a commercial mixture of glycols having a molecular weight of about 1500 and a melting point of about 35°-37° C.; and if the secondary solvent is selected from the group consisting of ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, and triethanolamine.

It will be noted that tetraethylene glycol is included both as a primary solvent and as a secondary solvent in the two groups of solvents just specifically designated hereinabove. This exemplifies the occasional instance where, within the scope of the invention in its broader aspects, a solvent compound can be employed in either capacity, subject to certain limitations. If tetraethylene glycol is used as a primary solvent, only a very small amount of secondary solvent (e. g., ethylene glycol) can be tolerated in mixture therewith; if used as a secondary solvent, a large amount of it must be added to the primary solvent (e. g., dipropylene glycol) to provide a mixture suitable for practicing the invention. For the purposes of the invention, tetraethylene glycol is useful chiefly as a secondary solvent. The commercially available form of tetraethylene glycol known as "Polyethylene Glycol 200" may be employed. Because of its physical properties, triethanolamine is less desirable as a secondary solvent, generally speaking, than a glycol.

In actual practice of the invention, it has been found usually most desirable that both the primary and secondary solvents shall be alcohols, with the secondary solvent a dihydric alcohol. More specifically, use of a mixed solvent in which both the primary and secondary solvents are glycols, and especially one consisting of dipropylene glycol as the primary solvent and ethylene glycol as the secondary solvent, has outstanding advantages in some of the most important practical applications of the new process. In addition to the glycols that have been specifically referred to, there are also other glycols suitable for use either as primary or secondary solvents in a solvent mixture to be used in practicing the invention, including other propylene glycols, as well as methylene glycols and butylene glycols.

Relatively slight miscibility of the secondary solvent with both aromatics and non-aromatics is a practical advantage. It is highly desirable also that such solvent action as the secondary solvent exerts shall be selective for the aromatic hydrocarbons, although, in the broader aspects of the invention, this is not an indispensable characteristic. Ethylene glycol and propylene glycol are found to be especially satisfactory in this respect.

While either the primary solvent or the secondary solvent may itself consist of more than one member of the indicated group of compounds to which it belongs, practice of the invention is simpler and generally more satisfactory where each consists of but one such member.

It has been found that, by making use of a mixed solvent consisting of primary and secondary components of the types herein designated, the selective solvent extraction of valuable aromatics from mineral oil feed stock, which has heretofore been commercially impracticable because of excessive cost of plant and operation or for other reasons, can be carried out with such

efficiency and economy as to be commercially feasible.

The proportioning of the components of the mixed solvent must be so adjusted that this composite solvent and the liquid mixture or solution of hydrocarbons constituting the feed stock are only partially miscible with each other, with the result that, at the operating temperature, they form in the extraction column two distinct liquid phases, the solvent or extract phase and the hydrocarbon phase; the composition of each phase varying, of course, as it progresses from one level to another in the column, corresponding to different stages of the extraction. More specifically, the mixed solvent components must be present in such ratio that two separate liquid phases are formed upon mixing the composite solvent with the most soluble aromatic component to be extracted. It is essential to the practical operation of the system that there be sufficient difference in density between the solvent phase and the hydrocarbon phase, at all points in the column, to cause effective counterflow of the two phases throughout the extraction zone as well as adequate separation of the phases in suitable settling zones from which raffinate and extract, respectively, are removed; and this requirement is readily met when using a mixed solvent of the type herein disclosed.

Employment of a mixed solvent of the character specified enables notably high recovery, as an aromatic-rich extract, of the total aromatics content of a mineral oil feed, without carrying the extraction beyond what, by analogy to distillation, may be termed a stripping operation; and such practice is within the scope of the invention, broadly considered. However, much higher concentration of the aromatics and much more complete separation therefrom of paraffins and naphthenes is effected if the aromatic-rich product obtained in the stripping operation is subjected to rectification by counter-current contact with a highly aromatic reflux. In its most desirable practical embodiments, therefore, the invention is characterized by inclusion of this further treatment, with resultant production of an extract representing not only an exceptionally high recovery of the aromatics present in the feed, but also a more complete separation therefrom of paraffins and naphthenes than has been attainable by prior methods. Also, if the feed contains olefins and diolefins, the proportion of these hydrocarbons remaining in the extract may be considerably reduced by the rectifying operation. Although it is not broadly new to employ a reflux in selective solvent countercurrent extraction, the use thereof in the recovery of valuable aromatics from a mineral oil feed stock containing them is new, so far as this applicant is aware, particularly in the manner and procedural combination herein disclosed.

In order to explain further the principles of the invention, certain practical embodiments thereof will be hereinafter described in detail by way of specific illustrative example, but without implying limitation of the invention to those particular embodiments or to the specific details thereof.

One important typical practical application of the invention consists in employing it for the selective solvent extraction of a mineral oil feed stock containing a more or less wide series or range of aromatic compounds, for production of an extract which contains either the entire series aforesaid or a desired portion thereof, in amount

7

representing a recovery of 85 to 90 per cent, or better, of the total amount of the corresponding aromatic compounds originally present in the feed stock, and at relatively high concentration. For example, assume that the feed stock is a whole cracked gasoline analyzing, approximately, 29% aromatic compounds, substantially all in the C₇—C₁₀ range (i. e., toluene and higher benzene homologues), and 71% non-aromatics; this total percentage of non-aromatics consisting of 15% olefins and 42% paraffins plus naphthenes, in the C₇—C₁₀ range, and 14% non-aromatics below C₇ and above C₁₀. Assume further that the extraction is to be carried out at operating temperatures between 70° and 90° F. Assume also that the mixed solvent to be used is a mixture consisting of dipropylene glycol as the primary solvent and ethylene glycol as the secondary solvent.

Although it is feasible to vary considerably the proportioning of the primary and secondary components of the mixed solvent in any mixture of the solvents herein designated as suitable, while in all cases realizing the benefits of the invention in at least substantial degree, practical considerations usually render optimum a certain particular proportioning of the specific component solvents employed in any instance for extraction of a given type of mineral oil feed within a given temperature range. Thus, where the mineral oil feed to be solvent-treated is comparable in general character to the whole gasoline of the present illustrative example, it is found that a mixture consisting of approximately 65% dipropylene glycol and 35% ethylene glycol, by weight, which has a specific gravity of about 1.04 and boils at about 412° F. (at 760 mm.), gives excellent results and may generally be regarded as optimum. With this proportioning any benzene present in the feed will be largely obtained in the extract, along with the toluene and higher homologues; whereas, if the proportion of ethylene glycol be materially less than 35%, a mixture of the composite solvent with benzene produces but one homogeneous phase, with no separation of a benzene-rich phase. Nevertheless considerable latitude is permissible in this respect. In general, the proportioning of the mixed solvent may, for practical purposes, range from 25% dipropylene glycol and 75% ethylene glycol as one limit, to 80% dipropylene glycol and 20% ethylene glycol as the other; nor is it to be understood that operability of the process is confined strictly to this stated range. But better results are usually obtainable by staying within it. The factor of viscosity also has to be considered in proportioning the mixed solvent, especially when the operating temperature is relatively low.

Among the advantages of using a mixed solvent of the character described, whatever specific type of mineral oil feed is being extracted, are the following: Each of the component solvents is miscible to only a very limited extent with paraffins and naphthenes. Thus, in the specific mixed solvent used in this illustrative example, the dipropylene glycol is miscible in all proportions with the typical aromatic (toluene); while the ethylene glycol is only somewhat more miscible with the aromatics than with paraffins and naphthenes. The mixed solvent is almost completely immiscible with paraffins and naphthenes, and only partially miscible with the most soluble hydrocarbon component of the feed, but is selective for aromatics. In using the mixed solvent to extract a solution of mixed hydrocarbons, therefore, two immiscible phases coexist, which phases

8

are of widely differing densities and hence capable of separating quickly in a suitable settling zone. The boiling points of the glycols, as well as that of triethanolamine, are much higher than those of the dissolved hydrocarbons, thereby permitting ready separation and recovery of the extracted material by distilling it from the extract solution, leaving virtually all the mixed solvent, which is stable at the distilling temperatures involved, for re-use in cycle. Furthermore, the ready solubility of the mixed solvent in water renders very simple the removal and recovery of the small amount contained in the extract distillate, as well as the still smaller amount carried out of the extraction zone by the raffinate.

The presence of more than a relatively very small proportion of water in the mixed solvents employed in practicing the invention reduces their solvent power for aromatics to an extent that is undesirable or excessive, and is accordingly to be avoided so far as is practicable. Therefore, since small amounts of water, including that normally contained in the feed (a few hundredths of one per cent), unavoidably enter the extraction system from various sources and contaminate the solvent, although in a single passage of the solvent through the system such contamination does not occur to a degree that cannot be tolerated commercially, it is desirable that the solvent, at the point where it is introduced into the system, be as nearly anhydrous as is practicable. However, if the water content of the mixed solvent, as introduced, does not materially exceed 1 per cent, the efficiency of the process remains relatively high and, for the purposes of this invention, is properly to be regarded as carried out substantially in the absence of water; although it is much better practice, and entirely feasible as a rule, to keep well below this indicated maximum.

In extracting the aromatics from the above-described whole cracked gasoline in accordance with the principles of the invention, using a 65—35 mixture of dipropylene glycol and ethylene glycol, one desirable type of apparatus plant or system practical to employ is shown diagrammatically in the accompanying drawing, which is largely in the form of a simplified flow-sheet. It is to be understood that, in order to avoid unnecessarily complicating the drawing and description, numerous parts and accessories such as pumps, valves, thermostatic and other types of automatic level and flow controls or regulators, heat exchangers, coolers, vapor-liquid separators, auxiliary tanks, and the like, which are commonly employed in systems of this general character as is well understood by those skilled in the art, and which are actually included in the system as employed in practicing the novel process, are not here illustrated.

Referring to the drawing, the extraction column 10 comprises upper and lower packed sections 11 and 12, the packing material employed in these sections being of any suitable type that will provide a relatively large contacting surface such, for example, as Raschig rings or Berl saddles. The solvent is pumped into the extraction column from solvent storage tank 13 through line 14, entering the column at a level just above upper packed section 11. Although, in this instance, the solvent is to constitute the continuous phase and the feed the discontinuous or disperse phase, this is not an essential condition. It is feasible, and within the scope of the invention, to operate with this phase relationship reversed.

In the present example, the solvent fills the void space around the packing, flowing downwardly as a continuous liquid phase. The whole gasoline constituting the feed, containing about 29% aromatics, is pumped from storage tank 15 through line 16 into the column at an intermediate point, substantially the midpoint in this instance, immediately below the aforesaid upper packed section 11 and above the lower packed section 12. The respective rates at which the gasoline feed and solvent enter the column are so coordinated and controlled as to maintain a suitable predetermined ratio between them. In the present instance the volume ratio of solvent to feed is 4.7 to 1. The feed is so introduced into the column as to cause it to be dispersed in fine droplets uniformly distributed over the whole cross sectional area of the column. Various devices for effecting such dispersal, any of which may be employed in practicing this invention, are well known in the art and therefore none requires specific description here. Being of much lower specific gravity than the solvent, the feed thus dispersed as droplets rises through the packed section, flowing countercurrently to the descending solvent introduced above the packed section 11. In this way a large interface, at which the mixed hydrocarbons of the gasoline are in intimate contact with the mixed solvent, is produced. By this process of the counterflow of the ascending hydrocarbon phase and descending solvent phase, opportunity is afforded at each point for a mutual interchange of material between the two phases.

As the gasoline feed material enters the column and is dispersed in contact with the solvent phase, it loses hydrocarbons to the solvent phase, but preferentially aromatic hydrocarbons rather than paraffins and naphthenes. The equilibrium proportion of olefins also passes into the solvent phase. As the hydrocarbon phase ascends through packed section 11, it continues to lose hydrocarbons to the solvent phase, progressively, in the manner stated, so that, by the time it has reached the top of said section, it has lost all but a small part of its aromatic hydrocarbons to the solvent phase.

When the solvent or extract solution phase initially contacts the ascending hydrocarbon phase at the top of the packed section, hydrocarbons from the hydrocarbon phase dissolve into the solvent and an extremely small amount of solvent dissolves into the hydrocarbon phase. As the solvent phase descends the upper section of the column, it becomes progressively richer in its content of aromatic hydrocarbons, while at the same time dissolving paraffin, naphthene, and olefin hydrocarbons, but to a lesser extent than aromatic hydrocarbons.

At any desired predetermined level in the column suitably distant from the feed inlet, an interface is established between the lighter raffinate solution and the heavier solvent phase, in order to permit separation of one phase from the other. The predetermined level of this interface is maintained constant by properly coordinating the rates at which the several liquids enter and leave the column. In the present instance this separation interface, indicated at 17, is located near the upper end of the extraction column in settling zone 18, and may be maintained constantly at this level by appropriate constant-level means acting automatically to control the rate at which aromatic extract solution is led from the column. If the hydrocarbon feed stock

constituted the continuous phase and the solvent the disperse phase, as is practicable, the interface might be maintained in a settling zone below the feed.

The raffinate, poor in aromatics and containing only a very small proportion of the solvent, typically on the order of 0.25% by weight, leaves the top of the column through line 19; while the extract phase, when it arrives at the feed level in its downward flow, is rich in aromatics.

By the countercurrent contacting operation thus far described, which, as previously stated, may be called a stripping treatment, removal of nearly all the aromatic hydrocarbons from the feed material can be effected, and a raffinate produced which contains only a very small percentage of the aromatic hydrocarbons that were contained in the feed. This assumes, of course, that the upper packed section is of sufficient length to allow effective contacting of solvent and feed to occur for the length of time necessary to attain substantial equilibrium between the solvent phase and the hydrocarbon phase at each successive level in the stripping zone. It further assumes operation of the column at a rate below "flooding velocity," i. e., that flow velocity at which turbulence of the two liquid phases becomes so great as to prevent proper counterflow thereof. Concentration, in the extract solution leaving the base of the upper packed section 11, of from 90 to 95 per cent or more of the total aromatics contained in the gasoline feed stock is readily attainable in practice. As has already been pointed out, this extract solution also contains a minor proportion of the paraffins and naphthenes that were contained in the feed, as well as some olefins.

If, as is contemplated by the invention in its broader aspects, the aforesaid extract solution obtained in the stripping operation is withdrawn from the column at this stage without being subjected to the hereinafter described further countercurrent contacting treatment in the nature of rectification, and is freed of solvent, the resultant extract constitutes a product useful and valuable in itself for various purposes. It consists largely of aromatic hydrocarbons which are in the C₇—C₁₀ range for the most part, together with lesser proportions of paraffins, naphthenes and olefins. It represents, moreover, a more nearly complete separation of aromatics from a feed of the general type here involved than has been achieved, so far as this applicant is aware, in any commercially feasible solvent extraction process heretofore proposed.

However, a product much more concentrated in respect to aromatics can be obtained by subjecting the product of the stripping operation to such rectifying treatment, in the lower packed section 12 of the extraction column, whereby to reduce its content of paraffins and naphthenes especially. Such rectifying treatment therefore constitutes an important part of the novel process where such a more concentrated extract product is desired.

By this further treatment of the intermediate extract solution, removal of most of its content of paraffins and naphthenes, together with a substantial part of its content of olefins, can be accomplished. The extract solution continues to descend through the column, constituting a continuous liquid phase filling the voids in the mass of packing material in said lower or rectifying section 12. It travels downward countercurrent to and in intimate contact with an ascending dis-

11

continuous phase formed by dispersed droplets of an aromatic liquid reflux introduced into the column through line 20 at a point just below the lower packed section 12, and there dispersed as fine droplets in the same general manner as is the feed material introduced through line 16. Said liquid reflux contains aromatic hydrocarbons in higher concentration than does the extract solution phase leaving the base of the lower packed section 12. More specifically, this reflux liquid consists in this instance of a suitable quantity of the aromatic extract product obtained by removing most of the mixed glycol solvent from said extract solution phase at a later stage of the complete process, as will more fully appear hereinafter. In other words it comprises the same mixture of hydrocarbons contained in said extract solution phase, in the same relative proportions, but is substantially undiluted with solvent. Since it has a much lower specific gravity (0.85 e. g.) than said extract solution or solvent phase, the dispersed droplets of this aromatic reflux rise through and in intimate contact with such downwardly flowing solvent or extract phase. As the latter descends, it becomes progressively richer in aromatics dissolved from the reflux phase; also poorer in paraffins and naphthenes and, in some degree, poorer in olefins, dissolved from it by and into the reflux phase. The reflux phase, in turn, becomes progressively richer in paraffins, naphthenes and olefins, while at the same time becoming progressively poorer in aromatics. By the time it leaves the top of the lower packed section 12, the composition of the reflux phase has become substantially the same, in respect to content of aromatics, as that of the feed material, with which it merges to constitute the disperse hydrocarbon phase ascending through the stripping section.

At the base of the column, a settling zone 21 is provided in order to permit gravity separation of any entrained droplets of reflux from the final extract solution. The final extract solution, saturated at the operating temperature with hydrocarbons, mainly aromatic, flows from the base of the column through line 22. Freeing this extract solution of solvent in the manner to be presently described gives a finished extract product which, even when operating with a column having a relatively short stripping section, regularly represents a recovery of at least 90% to 92% of the total amount of aromatic hydrocarbons in the feed stock. Thus, when conducting the extraction of the gasoline stock specifically described hereinabove in a 40-foot column having a 12-foot stripping section, operating within a temperature range of 70°–90° F. with a feed of 86.3 gallons per minute, a solvent ratio of 4.7 to 1, and a reflux of 71.8 gallons per minute, approximately 92% of the aromatics of the feed are recovered in a finished extract product analyzing approximately 66% aromatics, 7% paraffins and naphthenes taken together, and 9% olefins, all in the C₇–C₁₀ range; together with 18% non-aromatics in the ranges below C₇ and above C₁₀.

Assuming, by way of example, employment of a column such as that illustrated in the drawing, having an upper packed section 11 that is 6.5 feet in diameter and 27 feet high, and a lower packed section that is 8 feet in diameter and 15 feet high, a recovery of materially better than 92% of the aromatic hydrocarbons of that same gasoline feed stock can be achieved under operating conditions otherwise substantially the same, as those just mentioned. By employing a longer rectifying

12

section, separation of paraffins and naphthenes from the aromatic extract can be effected to virtually any desired extent, as well as some further separation of olefins.

It will be seen that, as a result of the complete countercurrent selective solvent extraction and rectification procedure hereinabove described, not only has there been accomplished the substantially complete separation or recovery from the feed material of nearly all its entire content of aromatic hydrocarbons—which separation is achieved in the upper or stripping packed section 11—but in addition the extract solution or phase containing the separated aromatic hydrocarbons has been concentrated with respect to its aromatic hydrocarbon content, while its content of other hydrocarbons has been reduced to a predeterminable extent, in what amounts to a rectifying treatment in the lower packed section 12 of the column. Subject only to practical limitations of extraction column design, and of the ratio between solvent and feed, and ratio of reflux to end product, the proportion of paraffinic and naphthenic hydrocarbons contained in the extract solution leaving the extraction column can be reduced by this procedure to virtually any desired minimum. For example, it is often entirely practical, in carrying out the process of the invention, to produce an extract solution in which the content of the paraffinic and naphthenic hydrocarbons combined amounts to only 5% or even somewhat less of the entire hydrocarbon content, by weight. In such case, the aromatic reflux introduced into the lower end of the lower packed section must of course contain only such low percentage of paraffinic and naphthenic hydrocarbons. Where, as is often the case, it is permissible that the proportion of paraffinic and naphthenic hydrocarbons in the finished extract be 10%, for example, the aromatic reflux will be characterized by that same percentage content of paraffinic and naphthenic hydrocarbons.

It is not feasible in practice, however, to reduce the content of olefinic hydrocarbons to a similar extent by the described procedure. This is because of the fact that the equilibrium conditions between the mixed glycol solvent, however proportioned, and the olefins of the feed, are such that it is not practicable to make a clean separation of the olefins from the feed. The best that can be done, practically, is to effect a distribution of the olefins between raffinate and extract such that much the greater proportion goes into the raffinate, say two-thirds or more, while the remainder goes into the extract.

Where it is desired to obtain a final aromatic product substantially free of olefins, chemical treatment of the solvent-free aromatic extract with 66° Bé. sulphuric acid in the well-known manner, followed by fractional distillation, removes the olefin hydrocarbons substantially completely.

In the complete process, the extract solution passing from the lower part of the extraction column is appropriately treated to separate the solvent from the extracted matter. The separated solvent is recovered and re-cycled, while a portion of the concentrated extract is also returned to the column as reflux for the rectifying section. Most desirably, the raffinate is likewise treated for solvent separation and recovery, notwithstanding the fact that it carries only a relatively very small proportion of the mixed glycol solvent out of the column. In accomplishing this separation and recovery, the separated solvent is

13

also freed from moisture to an extent ensuring that, when reintroduced into the extraction column, it is substantially anhydrous in the sense that it contains less, most desirably much less, than 1% of moisture. Furthermore, in the continuous re-use of the solvent, there is a tendency for the solvent gradually to become contaminated with high-boiling substances dissolved from the hydrocarbon stock extracted, or formed from the solvent itself. An effective way to prevent these impurities, as well as the moisture content, from building up in the recycled solvent to an undesirable extent, is to divert a certain proportion of the solvent from the main stream of recovered solvent before returning it to the column, and to distil the diverted portion of solvent in such manner as to leave the impurities as a higher-boiling residue which is removed from the cycle. Accordingly, in its best practical embodiments, the novel process includes recovery and purification of the solvent, most desirably by the procedure now to be described.

After leaving the base of extraction column or tower 10 through line 22 at a temperature of about 85° F. (e. g.), the extract solution, containing the extracted hydrocarbons at a concentration of around 16%, for example, is suitably heated to 180° F. or higher, as by passing it through a heat exchanger, and is then delivered into vacuum distillation tower or evaporator 23 provided with plates or trays 24 of any suitable type, at a level 25 intermediate the lower or stripping section 26 and the upper or rectifying section 27 of said tower. The separating distillation accomplished in tower 23 is conducted under operating conditions such that, as a final result, virtually all the extracted hydrocarbons, together with virtually all the moisture present and a small proportion of the mixed glycols (e. g., 2%), are separated as overhead vapors which are led from the top of the tower through vapor line 28; leaving as stripped bottoms nearly the whole of the mixed glycols solvent containing a minute proportion of hydrocarbons (e. g., 0.1%).

Such a substantially clean separation of extract and moisture from solvent is readily attainable under proper operating conditions now to be described. With the aid of suitable vacuum-producing means (not shown), such as a steam jet ejector, connected in the system in a manner well understood in the art, the distilling operation and the condensation of the separated overhead vapors occur at low absolute pressure. Thus, a vapor pressure of about 85 millimeters mercury absolute is desirably maintained in the vapor space below the stripping section 26 of the tower; which, employing a tower of typical design, means maintaining an absolute vapor pressure of about 65 millimeters in the top of the tower. The liquid residuum or bottoms produced in the distilling operation and having a temperature of about 300° F. leave the base of the column through line 29 and pass to reboiler 30. The reboiler is heated by closed steam coils 31, the supply and return connections for which are shown at 32, 33. The vapor space of the reboiler is at about the same absolute pressure as that of the tower below section 26. Steam at 125 pounds gauge pressure (e. g.) is supplied to heating coils 31 in such quantity that vapors of the mixed solvent are delivered through vapor line 34 into the tower at a sufficient rate to supply the heat units necessary to accomplish the desired stripping and fractionation in the column, the re-

14

quired amount of glycol-rich liquid reflux being introduced into the upper part of the tower through line 35 from a source to be presently pointed out.

The extract solution delivered into tower 23 descends through the lower or stripping section thereof, being countercurrently contacted by ascending hot vapors of the mixed glycols entering below said section from the reboiler and being thereby stripped of its hydrocarbon content, as well as of water. The resultant hydrocarbon vapors and water vapor, together with a small proportion of vapors of the mixed glycols, ascend through the column and are fractionated in section 27 by countercurrent contacting with the descending glycol-rich liquid reflux aforesaid. The composition of the vapors leaving the top plate of the fractionating section is approximately 97 to 98% hydrocarbons (mostly aromatics), together with some solvent and water in the proportions given hereinabove.

The vapor product leaving the top of column 23 passes through line 28 to condenser 36, provided with cooling water intake and discharge connections 37, 38. Uncondensed vapor and gas are sucked away by the vacuum-producing means, while the condensate, at a temperature of, say, 85° F., flows from the condenser through line 39 to decanter 40. There the condensate separates into two layers of which the upper comprises practically 99% of the condensate and consists of the hydrocarbon extract, wholly freed of the mixed solvent except for a minute proportion, on the order of 0.1% by weight, dissolved therein. The lower layer consists principally of the mixed glycols but contains about 5% of water and 2% of hydrocarbons, by weight.

The nearly pure extract is decanted through line 41 into extract receiver 42. From this receiver, the amount required to provide the aromatic reflux for the rectifying section 12 of the extraction column is pumped through line 20 at a properly controlled rate, and introduced below said section 12 as already described hereinabove. If the remainder of the extract is to be treated for removal of its very small content of solvent, it may be passed from receiver 42 through line 43 to washer 44, entering at the base of the washer and passing upwardly therein through suitable packing or the like adapted to ensure thorough contacting with down-flowing wash water introduced through line 45 into the upper part of the washer. From the top of the washer, the extract, washed free of solvent, is conducted through line 46 to finished extract storage 47.

The aqueous mixture of glycols constituting the lower liquid layer in decanter 40 is drawn off through line 48, part of it going through branch line 35 to provide the glycol-rich liquid reflux introduced into the upper part of distillation tower 23, as previously described; while the rest is passed through branch line 49 to aqueous solvent storage 50, there to be accumulated for subsequent dehydrating treatment to be described hereinafter.

The main body of mixed solvent, constituting the liquid residuum or bottoms produced in the distillation tower 23, is withdrawn from reboiler 30 through line 51. Its temperature is approximately 300° F. or somewhat higher. A small portion of the anhydrous solvent may be diverted, continuously or intermittently, through branch line 52 to impure solvent storage 53, there to be accumulated for purification by removal of high-boiling components in a manner to be de-

scribed presently. The remainder is returned through line 53a to solvent storage 13, after utilizing it in a suitable heat exchanger (not shown) to preheat extract solution that is being introduced into tower 23 from extraction column 10, as described hereinabove, and then further cooling it in any convenient manner to the temperature, say 85° F., at which the mixed solvent is to be introduced into extraction column 10.

Where, as in the present example, the small amount of mixed solvent contained in the raffinate leaving the top of column 10 is to be recovered, the raffinate is conducted through line 19 to the lower part of washer 54, which is similar to washer 44. Through washer 54, the raffinate ascends in countercurrent contact with wash water introduced into the upper part of the water through line 55. Most desirably, the water used for this washing is that which was used in washer 44 and which, therefore, already contains the mixed glycols solvent dissolved from the distilled extract collected in decanter 40. Accordingly, line 55 is here shown as connected to the base of washer 44 and conducting used wash water therefrom for re-use in washer 54. Solvent-free raffinate leaves the top of washer 54 through line 55a which conducts it to raffinate storage 56. Wash water carrying the mixed glycols picked up in washers 44 and 54 leaves the base of washer 54 through line 57, by which it is delivered to aqueous solvent storage 50.

Suitable distilling means are provided for separating water from the aqueous mixed solvent collected in storage 50, and for separating high-boiling impurities from the anhydrous mixed solvent in storage 53. In the present example, a single distillation unit is employed for these purposes, the aqueous and non-aqueous bodies of solvent to be purified being handled separately therein, of course, and under different operating conditions. The distillation unit is here shown in simplified conventional form as a batch still comprising still pot 58 and plate column 59. The still pot is heated by closed steam coils 60, having high-pressure steam supply and return connections indicated at 61, 61a.

In dehydrating aqueous mixed solvent, the charge is introduced into the still from storage 50 through lines 62—63. The distillation system is maintained under reduced pressure which may be, for example, about 125 millimeters mercury absolute at the top of column 59 and about 145 millimeters in the vapor space of the still pot; the temperature in the latter being, say, 300° F. The vapors leaving the top of the fractionating tower through vapor line 64 pass to water-cooled condenser 65, yielding a condensate which is 98–99% water, the remainder being hydrocarbons and mixed glycols. Part of this condensate is returned to the still column as reflux through line 66, the remainder being run to waste through line 67. The dehydrated mixed solvent, left as bottoms, is run off through line 68 and, after having its temperature reduced to around 85° F. by passage through heat exchange and cooling means indicated generally at 69, is returned to the solvent circuit by line 70 which is connected to main solvent line 53a. This returned solvent contains on the order of 0.5% water, typically; and the quantity thereof being small as compared to the whole body of solvent sent back through line 53 to solvent storage 13, the water content of the mixed glycols solvent delivered through line 14 into the extraction column at no time exceeds a

small fraction of 1%, commonly on the order of 0.1% or less, in normal operation of the process.

When using the distillation unit 58—59 to purify the impure anhydrous solvent collected in storage 53, the impure solvent is charged into the still through lines 71—73. Since the mixed glycols solvent is to be distilled overhead in this case, leaving the high-boiling impurities as residuum, the distillation is conducted under higher degree of vacuum ranging, say, from 65 millimeters absolute at the top of column 59 to 85 millimeters in the still pot. The resultant mixed glycols condensate is returned through line 72 to main solvent circuit line 53a; while the residuum, consisting of the separated high-boiling impurities, may be discharged to waste through line 73.

It will be understood that the extracting and rectifying operation in the extraction column 10 is continuous, as is also most desirably, the the primary or principal separation and recovery of solvent which is performed in distillation tower 23; flow of material through the various lines being automatically controlled and coordinated in a manner generally well understood in the art. The operations of dehydrating and purifying minor portions of the solvent, carried out in the distilling system 58—59, may also be continuous to such extent as is desired.

The same procedure hereinabove described for treating a whole gasoline for recovery of a wide range of valuable aromatics may be employed with great advantage in treating some particular fraction thereof to obtain an extract predominantly rich in some one aromatic compound. One particularly useful practical application of the invention consists in subjecting a xylene-rich fraction of a cracked gasoline or naphtha to selective solvent extraction with the hereinabove described mixed or composite solvent composed of dipropylene glycol and ethylene glycol, for production of a concentrated xylene product. Such a fraction is obtainable, for example, from certain commercially available gasolines produced by vapor-phase cracking. In a typical instance, such a gasoline can be distilled into the following cuts:

Cuts or fractions:	Percent by weight
Forerunnings	11.0
Benzene fraction	10.0
Benzene-toluene intermediate	2.0
Toluene cut	14.5
Toluene-xylene intermediate	3
Xylene plus cut	47.5
Bottoms	12
	100.0

In a typical instance, the "xylene plus" cut obtained in the above distillation has an approximate boiling range of 250°–350° F. and a specific gravity of 0.796, and contains about 23% of C₈ to C₁₀ aromatic hydrocarbons by weight. These aromatic hydrocarbons are mostly xylenes (chiefly meta and para), together with some cumene, ethyl toluene and mesitylene. The remainder of the cut consists substantially of 60.6% paraffins plus naphthenes, and 16.4% olefins.

Employing as solvent the same 65–35 mixture of dipropylene glycol and ethylene glycol as before, and carrying out the process in the apparatus system shown in the drawing and under the same conditions of operation already described hereinabove, the rectified extract solution

leaving the base of the extraction column consists of about 84% mixed solvent and 16% hydrocarbons. The hydrocarbon content analyzes, typically, about 80% to 85% aromatics, 4% to 6% paraffins and naphthenes taken together, and the remainder substantially all olefins. The raffinate, which contains a minor fraction of 1% of solvent, consists almost wholly (98-99%) of non-aromatic hydrocarbons. The net result of the operation, in a typical instance, is a recovery, in the extract solution, of better than 95% of the aromatic hydrocarbons contained in the "xylene plus" fraction constituting the feed.

Where the production of a toluene-rich extract is desired, similarly good results are obtainable by selective solvent extraction in the same manner, with a mixed glycols solvent, of a toluene-rich feed such, for example, as the 14.5% toluene cut distillable from the vapor-phase cracked gasoline already mentioned. Such toluene cut may contain, in a typical instance, about 27% by weight of toluene, together with approximately 29% of olefins and 44% of paraffins plus naphthenes; and its specific gravity is 0.79.

In another embodiment of the invention, the selective solvent may be a mixture of methyl alcohol or methanol as the primary solvent with ethylene glycol as the secondary solvent, the most desirable proportioning being 70% of the former to 30% of the latter, by weight. This specific mixture has a specific gravity of 0.875. Here also, the mixed solvent, when introduced into the extraction system, should be as nearly anhydrous as is practicable, with a practical tolerance limit of about 1% for the moisture content. Use of this mixed solvent in accordance with the invention, in place of a mixture of dipropylene glycol and ethylene glycol, gives comparably high recovery of aromatics from suitable feed stocks, and enables production of extracts also containing the recovered aromatics at relatively high concentrations. Separation of the mixed solvent from the extract and recovery of the solvent components in proper condition for re-use in the process is somewhat less easy, however, because the low boiling point of methanol precludes simply distilling off the extracted hydrocarbons largely free from solvent, as in the case of the mixed glycols, and leaving practically all the mixed solvents as bottoms.

Thus, assuming the above-mentioned 14.5% toluene cut obtained from a cracked gasoline to be solvent treated in accordance with the invention, using the methanol-ethylene glycol solvent mixture aforesaid, separation of solvent from the toluene-rich extract is best accomplished in the following manner. The extract solution passing from the base of the column is subjected to a distilling operation whereby the methanol, together with enough of the toluene (with other extract hydrocarbons) to form the constant boiling mixture, is separated from the extract solution as an overhead distillate product. The remaining toluene and other extract hydrocarbons, and the glycol, are left as still bottoms; and they form separate liquid phases because of their very limited miscibility. The toluene-rich layer may be decanted and returned to the extraction column as reflux; while the heavier glycol layer is separately drawn off and subjected to dehydration and purification in the same manner as has already been described for the mixed glycols solvent.

The constant boiling mixture product com-

posed of methanol and toluene is washed with water to remove the methanol, yielding a solvent-free toluene-rich extract product. The water used to effect this washing may desirably have been previously used to extract the small amount of solvent (on the order of 0.02% in this instance) carried out of the extraction column by the raffinate. In order to recover and concentrate the methanol, the methanol-water solution is subjected to distillation with open steam in a suitable distilling column, in the known manner, for recovery of methanol of 99% or higher purity.

The separately recovered methanol and ethylene glycol are mixed in proper proportions to re-constitute the mixed solvent, and re-introduced into the extraction column.

As further examples of specific mixed solvents that may be employed in practicing the invention, the following are mentioned, the first solvent named in each pair being the primary solvent: isopropyl alcohol and ethylene glycol; isopropyl alcohol and propylene glycol; methyl alcohol (methanol) and propylene glycol. From experience thus far gained in actual use of the new process, however, the use of a mixture of dipropylene glycol and ethylene glycol, as hereinabove described in detail, is at present believed to enable practical realization of the benefits of the invention in greatest degree, and is accordingly regarded as the best embodiment of the invention now known to this applicant.

What is claimed is:

1. The process of extracting a valuable aromatic product from a liquid mixture of hydrocarbons that has both aromatic and non-aromatic components, which comprises intimately contacting such a hydrocarbon mixture in liquid phase with mixed primary and secondary liquid solvents comprising different aliphatic oxygenated polar carbon compounds, the primary solvent compound being at least partially miscible with said hydrocarbon mixture as a whole and selective for the aromatic component of said mixture, and being selected from that group of such compounds which consists of (1) compounds containing a single hydroxyl group in the molecule and (2) compounds containing two hydroxyl groups and at least one ether group in the molecule; while the secondary solvent compound is completely miscible with the primary but is only partially miscible, at most, with each of the components of said hydrocarbon mixture and contains at least two hydroxyl groups in the molecule, said oxygenated compounds being so proportioned in the mixed or composite solvent that a mixture of the composite solvent with the most soluble aromatic hydrocarbon to be extracted will separate into two liquid phases; separating the two liquid phases resulting from the intimate contacting of said composite solvent with said liquid mixture of hydrocarbons, namely, a raffinate phase poor in said aromatic component and comprising most of said non-aromatic component, and a solvent or extract phase rich in said aromatic component, and removing solvent from said extract phase to obtain an aromatic extract product; the extraction being performed substantially in the absence of water.

2. The process set forth in claim 1, wherein the primary solvent is selected from the group consisting of methyl alcohol, ethyl alcohol, isopropyl alcohol, dipropylene glycol, tetraethylene glycol, hexaethylene glycol, nonaethylene glycol, and "Carbowax 1500," while the secondary sol-

vent is a different solvent selected from the group consisting of ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, and propylene glycol.

3. The process of extracting a valuable aromatic product from a liquid mixture of hydrocarbons that has both aromatic and non-aromatic hydrocarbon components, which comprises intimately contacting such a hydrocarbon mixture with mixed primary and secondary solvents comprising different aliphatic alcohols, the primary solvent being at least partially miscible with said hydrocarbon mixture as a whole and selective for said aromatic component, while the secondary solvent is a dihydric alcohol that is completely miscible with the primary solvent but is only partially miscible, at most, with each of said hydrocarbon components, said alcohols being so proportioned in the mixed or composite solvent as to permit formation, at the temperature of operation, of separable liquid phases in a mixture of the composite solvent with the most soluble aromatic hydrocarbon to be extracted; separating the two phases resulting from such intimate contacting of the hydrocarbon mixture with the composite solvent, namely, a raffinate phase poor in said aromatic component and comprising most of said non-aromatic component, and a solvent or extract phase rich in said aromatic component, and removing solvent from said extract phase to obtain an aromatic extract product.

4. The process set forth in claim 3, wherein the extraction is performed within the range of ordinary moderate atmospheric temperatures and substantially in the absence of water.

5. The process set forth in claim 3, wherein the extraction is performed within a temperature range of from about 70° to 90° F., and in the substantial absence of water.

6. The process set forth in claim 3, wherein the primary solvent is selected from the group consisting of methyl alcohol, ethyl alcohol, isopropyl alcohol, dipropylene glycol, tetraethylene glycol, hexaethylene glycol, nonaethylene glycol and "Carbowax 1500," while the secondary solvent is a different solvent selected from the group consisting of ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, and propylene glycol.

7. The process set forth in claim 3, wherein both the primary solvent and the secondary solvent are glycols, and the extraction is performed within a temperature range of from about 70° to 90° F., and in the substantial absence of water.

8. The process set forth in claim 3, wherein the mixed solvent consists of dipropylene glycol and ethylene glycol.

9. The process set forth in claim 3, wherein the mixed solvent consists of approximately 65% dipropylene glycol and 35% ethylene glycol, by weight.

10. The process set forth in claim 3, wherein the mixed solvent consists of approximately 65% dipropylene glycol and 35% ethylene glycol, by weight, and the extraction is performed within a temperature range of from about 70° to 90° F., substantially in the absence of water.

11. The process set forth in claim 3, wherein the mixed solvent consists of methanol and ethylene glycol.

12. The process set forth in claim 3, wherein the mixed solvent consists of approximately 70% methanol and 30% ethylene glycol, by weight.

13. The process set forth in claim 3, wherein the mixed solvent consists of approximately 70%

methanol and 30% ethylene glycol, by weight, and is substantially free of water, and the extraction is performed within a temperature range of from about 70° to 90° F.

14. The process of extracting a valuable aromatic product from a liquid mixture of hydrocarbons that has both aromatic and non-aromatic components, which comprises intimately contacting such a hydrocarbon mixture in liquid phase with mixed primary and secondary liquid solvents comprising different aliphatic oxygenated polar carbon compounds, the primary solvent compound being at least partially miscible with said hydrocarbon mixture as a whole and selective for the aromatic component of said mixture, and being selected from that group of such compounds which consists of (1) compounds containing a single hydroxyl group in the molecule and (2) compounds containing two hydroxyl groups and at least one ether group in the molecule; while the secondary solvent compound is completely miscible with the primary but is only partially miscible, at most, with each of the components of said hydrocarbon mixture and contains at least two hydroxyl groups in the molecule, said oxygenated compounds being so proportioned in the mixed or composite solvent that a mixture of the composite solvent with the most soluble aromatic hydrocarbon to be extracted will separate into two liquid phases; separating the two liquid phases resulting from the intimate contacting of said composite solvent with said liquid mixture of hydrocarbons, namely, a raffinate phase poor in said aromatic component and comprising most of said non-aromatic component, and a solvent or extract phase rich in said aromatic component; then intimately contacting such aromatic-rich extract phase with a more concentrated aromatic extract product derived from a later stage of the process, thereby producing an extract phase richer in said aromatic component and poorer in said non-aromatic component, and removing solvent from such enriched extract phase to obtain an aromatic extract product practically free of solvent; the extracting and enriching operations being performed substantially in the absence of water.

15. The process set forth in claim 14, wherein the primary solvent is selected from the group consisting of methyl alcohol, ethyl alcohol, isopropyl alcohol, dipropylene glycol, tetraethylene glycol, hexaethylene glycol, nonaethylene glycol, and "Carbowax 1500," while the secondary solvent is a different solvent selected from the group consisting of ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, and propylene glycol.

16. The process of extracting a valuable aromatic product from a liquid mixture of hydrocarbons that has both aromatic and non-aromatic hydrocarbon components, which comprises intimately contacting such a hydrocarbon mixture with mixed primary and secondary solvents comprising different aliphatic alcohols, the primary solvent being at least partially miscible with said hydrocarbon mixture as a whole and selective for said aromatic component, while the secondary solvent is a dihydric alcohol that is completely miscible with the primary solvent but is only partially miscible, at most, with each of said hydrocarbon components, said alcohols being so proportioned in the mixed solvent as to permit formation, at the temperature of operation, of separable liquid phases in a mixture of the composite solvent with the most soluble aromatic component.

matic hydrocarbon to be extracted; separating the two phases resulting from such intimate contacting of the hydrocarbon mixture with the composite solvent, namely, a raffinate phase poor in said aromatic component and comprising most of said non-aromatic component, and a solvent or extract phase rich in said aromatic component; then intimately contacting such aromatic-rich extract phase with a more concentrated aromatic extract product derived from a later stage of the process, thereby producing an extract phase richer in said aromatic component and poorer in said non-aromatic component, and removing solvent from such enriched extract phase to obtain an aromatic extract product practically free of solvent.

17. The process set forth in claim 16, wherein the extracting and enriching operations are performed within the range of ordinary moderate atmospheric temperatures, and the mixed solvent is substantially free of water.

18. The process set forth in claim 16, wherein the extraction and enriching operations are performed within a temperature range of from about 70° to 90° F., and in the substantial absence of water.

19. The process set forth in claim 16, wherein the primary solvent is selected from the group consisting of methyl alcohol, ethyl alcohol, isopropyl alcohol, dipropylene glycol, tetraethylene glycol, hexaethylene glycol, nonaethylene glycol and "Carbowax 1500," while the secondary solvent is a different solvent selected from the group consisting of ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, and propylene glycol.

20. The process set forth in claim 16, wherein both the primary solvent and the secondary solvent are glycols, and the extraction is performed within a temperature range of from about 70 to 90° F., in the substantial absence of water.

21. The process set forth in claim 16, wherein the mixed solvent consists of dipropylene glycol and ethylene glycol.

22. The process set forth in claim 16, wherein the mixed solvent consists of approximately 65% dipropylene glycol and 35% ethylene glycol, by weight.

23. The process set forth in claim 16, wherein the mixed solvent consists of approximately 65% dipropylene glycol and 35% ethylene glycol, by weight, and the extracting and enriching operations are performed within a temperature range of from about 70° to 90° F., in the substantial absence of water.

24. The process set forth in claim 16, wherein the mixed solvent consists of methanol and ethylene glycol.

25. The process set forth in claim 16, wherein the mixed solvent consists of approximately 70% methanol and 30% ethylene glycol, by weight.

26. The process set forth in claim 16, wherein the mixed solvent consists of approximately 70% methanol and 30% ethylene glycol, by weight, and the extracting and enriching operations are performed within a temperature range of from about 70° to 90° F., in the substantial absence of water.

27. The process set forth in claim 1, further characterized by the fact that the extraction is effected by continuous countercurrent contacting of a solvent phase with a hydrocarbon phase.

28. The process set forth in claim 1, further characterized by the fact that the extraction is effected by continuous countercurrent contacting

of a continuous solvent phase with a disperse hydrocarbon phase.

29. The process set forth in claim 2, further characterized by the fact that the extraction is effected by continuous countercurrent contacting of a solvent phase with a hydrocarbon phase.

30. The process set forth in claim 3, further characterized by the fact that the extraction is effected by continuous countercurrent contacting of a solvent phase with a hydrocarbon phase.

31. The process set forth in claim 3, wherein the primary solvent is selected from the group consisting of methyl alcohol, ethyl alcohol, isopropyl alcohol, dipropylene glycol, tetraethylene glycol, hexaethylene glycol, nonaethylene glycol and "Carbowax 1500," while the secondary solvent is a different solvent selected from the group consisting of ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, and propylene glycol; the extraction being effected within a temperature range of from about 60° to 100° F. and in the substantial absence of water, by continuous countercurrent contacting of a solvent phase with a hydrocarbon phase.

32. The process set forth in claim 3, wherein the mixed solvent consists of dipropylene glycol and ethylene glycol, the extraction being effected by continuous countercurrent contacting of a solvent phase with a hydrocarbon phase.

33. The process set forth in claim 3, wherein the mixed solvent consists of approximately 65% dipropylene glycol and 35% ethylene glycol, by weight, and the extraction is performed within a temperature range of from about 70° to 90° F., substantially in the absence of water, the extraction being effected by continuous countercurrent contacting of a continuous solvent phase with a disperse hydrocarbon phase.

34. The process set forth in claim 14, further characterized by the fact that the extracting and enriching operations are effected by continuous countercurrent contacting of the solvent phase and the hydrocarbon phase.

35. The process set forth in claim 14, further characterized by the fact that the extracting and enriching operations are effected by continuous countercurrent contacting of the solvent in continuous phase with hydrocarbon feed in disperse phase.

36. The process set forth in claim 14, further characterized by the fact that the extracting and enriching operations are effected by continuous countercurrent contacting of the solvent phase and the hydrocarbon phase.

37. The process set forth in claim 16, further characterized by the fact that the extracting and enriching operations are effected by continuous countercurrent contacting of the solvent phase and the hydrocarbon phase.

38. The process set forth in claim 16, wherein the primary solvent is selected from the group consisting of methyl alcohol, ethyl alcohol, isopropyl alcohol, dipropylene glycol, tetraethylene glycol, hexaethylene glycol, nonaethylene glycol and "Carbowax 1500," while the secondary solvent is a different solvent selected from the group consisting of ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, and propylene glycol; the extracting and enriching operations being effected within a range of from about 60° to 100° F. and in the substantial absence of water, by continuous countercurrent contacting of the solvent phase and the hydrocarbon phase.

39. The process set forth in claim 16, wherein

23

the mixed solvent consists of dipropylene glycol and ethylene glycol, the extracting and enriching operations being effected by continuous countercurrent contacting of the solvent phase and the hydrocarbon phase.

40. The process set forth in claim 16, wherein the mixed solvent consists of approximately 65% dipropylene glycol and 35% ethylene glycol, by weight, and the extracting and enriching operations are performed within a temperature range of from about 70° to 90° F., in the substantial absence of water, the extracting and enriching operations being effected by continuous countercurrent contacting of the solvent in continuous phase with hydrocarbon feed in disperse phase.

41. The process of extracting a valuable aromatic product from a mineral oil distillate containing a substantial percentage of aromatics, which comprises continuously feeding said distillate into an extraction column at an intermediate level, and at the same time continuously introducing into said column at a suitably higher level a mixed solvent consisting of dipropylene glycol and ethylene glycol in proportions, by weight, within the range of from 25%-80% dipropylene glycol to 75%-20% ethylene glycol, in such manner that the resultant solvent and hydrocarbon phases travel countercurrently in intimate mutual contact, leading away a solvent-poor raffinate of low aromatic content from the column at a level above that of solvent introduction, continuously introducing into the column at a level substantially below that of feed introduction a liquid reflux richer in aromatics than the solvent phase at the feed level, withdrawing extract solution enriched in aromatics from the column at a level below the reflux inlet, while maintaining a separation interface between the two phases at a predetermined constant level in the column by properly coordinating the rates at which the several liquids enter and leave the column, utilizing a part of said extract solution, after at least partial separation of solvent therefrom, to supply the reflux aforesaid, and separating solvent from the remainder to obtain a concentrated aromatic extract product.

42. The process set forth in claim 41, wherein the mixed solvent consists, approximately, of 65% dipropylene glycol and 35% ethylene glycol and is employed in continuous phase, while the mineral oil distillate constituting the feed is in disperse phase, and the constant-level separation interface is maintained at a level between that of solvent introduction and that of raffinate withdrawal.

43. The process set forth in claim 41 which further includes separating most of the solvent for re-use by distilling overhead from the withdrawn extract solution under reduced pressure substantially all the extracted matter and water contained therein, together with a small proportion of the solvent, leaving the mixed glycols solvent as a virtually water-free residuum.

44. The process set forth in claim 41, which further includes separating most of the solvent for re-use by distilling overhead from the withdrawn extract solution under reduced pressure substantially all the extracted matter and water contained therein, together with a small proportion of the solvent, leaving the mixed glycols solvent as a virtually water-free residuum; and which further includes separating high-boiling impurities from at least a portion of said mixed glycols residuum, before re-use, by subjecting it to reduced pressure distillation wherein the gly-

24

cols are distilled overhead, leaving said impurities as a residuum.

45. The process set forth in claim 41, wherein the mixed solvent consists, approximately, of 65% dipropylene glycol and 35% ethylene glycol and is employed in continuous phase, while the mineral oil distillate constituting the feed is in disperse phase, and the constant-level separation interface is maintained at a level between that of solvent introduction and that of raffinate withdrawal; which further includes separating most of the solvent for re-use by distilling overhead from the withdrawn extract solution under reduced pressure substantially all the extracted matter and water contained therein, together with a small proportion of the solvent, leaving the mixed glycols solvent as a virtually water-free residuum, and separating high-boiling impurities from at least a portion of said mixed glycols residuum, before re-use, by subjecting it to reduced pressure distillation wherein the glycols are distilled overhead, leaving said impurities as a residuum.

46. The process set forth in claim 41, which further includes separating most of the solvent for re-use by distilling overhead from the withdrawn extract solution under reduced pressure substantially all the extracted matter and water contained therein, together with a small proportion of the solvent, leaving the mixed glycols solvent as a virtually water-free residuum; and which further includes separating high-boiling impurities from at least a portion of said mixed glycols residuum, before re-use, by subjecting it to reduced pressure distillation wherein the glycols are distilled overhead, leaving said impurities as a residuum, water-washing the raffinate to separate therefrom for re-use the small amount of solvent contained therein, and then subjecting the resultant aqueous solvent to a suitable dehydrating treatment for removal of water therefrom.

47. The process set forth in claim 41, which further includes separating most of the solvent for re-use by distilling overhead from the withdrawn extract solution under reduced pressure substantially all the extracted matter and water contained therein, together with a small proportion of the solvent, leaving the mixed glycols solvent as a virtually water-free residuum; and which further includes separating high-boiling impurities from at least a portion of said mixed glycols residuum, before re-use, by subjecting it to reduced pressure distillation wherein the glycols are distilled overhead, leaving said impurities as a residuum, water-washing the raffinate to separate therefrom for re-use the small amount of solvent contained therein, and then subjecting the resultant aqueous solvent to a suitable dehydrating treatment for removal of water therefrom; water-washing the overhead distillate separated from the extract solution, and dehydrating the aqueous solvent thus recovered.

48. The process set forth in claim 41, which further includes separating most of the solvent for re-use by distilling overhead from the withdrawn extract solution under reduced pressure substantially all the extracted matter and water contained therein, together with a small proportion of the solvent, leaving the mixed glycols solvent as a virtually water-free residuum; and which further includes separating high-boiling impurities from at least a portion of said mixed glycols residuum, before re-use, by subjecting it to reduced pressure distillation wherein the

glycols are distilled overhead, leaving said impurities as a residuum, water-washing the raffinate to separate therefrom for re-use the small amount of solvent contained therein, and then subjecting the resultant aqueous solvent to a suitable dehydrating treatment for removal of water therefrom; water-washing the overhead distillate separated from the extract solution, dehydrating the aqueous solvent thus recovered, the water previously used in washing solvent from the raffinate being employed in washing said overhead distillate.

49. The process of extracting a valuable aromatic product from a mineral oil distillate containing a substantial percentage of aromatics, which comprises continuously feeding said distillate into an extraction column at an intermediate level, and at the same time continuously introducing into said column at a suitably higher level a substantially water-free mixture of primary and secondary liquid solvents comprising different aliphatic oxygenated polar carbon compounds; the primary solvent compound being at least partially miscible with said mineral oil distillate as a whole and selective for the aromatic content thereof, and being selected from that group of such compounds which consists of (1) compounds containing a single hydroxyl group in the molecule and (2) compounds containing two hydroxyl groups and at least one ether group in the molecule; while the secondary solvent is completely miscible with the primary but is only partially miscible, at most, with each of the components of said distillate and contains at least two hydroxyl groups in the molecule; said oxygenated compounds being so proportioned in the mixed or composite solvent that a mixture of the composite solvent with the most soluble aromatic hydrocarbon to be extracted will separate into two liquid phases; causing the resultant solvent and hydrocarbon phases to travel a substantial distance countercurrently in intimate mutual contact, and leading away a solvent-poor raffinate of low aromatic content from the column at a level above that of solvent introduction; continuously introducing into the column at a level substantially below that of feed introduction a liquid

reflux richer in aromatics than the solvent phase at the feed level, and withdrawing extract solution enriched in aromatics from the column at a level below the reflux inlet, while maintaining a separation interface between the two phases in the column by properly coordinating the rates at which the several liquids enter and leave the column; utilizing a part of said extract solution, after at least partial separation of solvent therefrom, to supply the reflux aforesaid, and separating solvent from the remainder to obtain a concentrated aromatic extract product.

50. The process set forth in claim 49, wherein the mixture of primary and secondary liquid solvents comprises different aliphatic alcohols, the secondary solvent being a dihydric alcohol.

51. The process set forth in claim 49, wherein both the primary solvent and the secondary solvent are glycols.

ALLEN S. SMITH.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,056,830	Coleman et al. -----	Oct. 6, 1926
2,081,719	Van Dijck -----	May 25, 1937
2,091,078	McKittrick et al. ---	Aug. 24, 1937
2,101,643	Engelke -----	Dec. 7, 1937
2,215,915	Cope et al. -----	Sept. 24, 1940
2,241,430	Snow -----	May 13, 1941
2,243,873	Lyman -----	June 3, 1941
2,246,297	Duncan et al. -----	June 17, 1941
2,302,383	Stratford et al. -----	Nov. 17, 1942

FOREIGN PATENTS

Number	Country	Date
96,701	Hungary -----	Oct. 1, 1929
336,945	Great Britain -----	Oct. 20, 1930
439,674	Great Britain -----	Dec. 11, 1935
456,958	Great Britain -----	Nov. 18, 1936

OTHER REFERENCES

Petroleum Review and Mining News, Oct. 17, 1903, page 310. (Article by Kharitchkoff.)