This invention relates to a process for separating and recovering bicyclic aromatic hydrocarbons from mixtures of the same with other classes of hydrocarbons, such as hydrocarbon mixtures containing said naphthalenes and one or more of the group comprising paraffins, naphthenes, olefins and aromatics. More specifically, this invention concerns a process for recovering an extract comprising naphthalene and one or more of its homologs from a mixture of hydrocarbons containing the same and thereafter segregating the extract into specific homologs by means of a process which involves liquid-liquid phase extraction of the hydrocarbon mixture with a solvent for the naphthalene component selected from the alcohols, the alkylene glycols, and the polyalkylene glycols, recovering the hydrocarbon solute from the resulting rich solvent stream and thereafter fractionally distilling the recovered extract to separate said naphthalene and homologs.

The principal object of this invention, therefore, is to provide a process for segregating substantially pure naphthalene products, each of which consists essentially of an individual naphthalene homolog from mixtures of the same with other types of hydrocarbons, including other naphthalene homologs. Other objects of the invention concern the preparation of individual naphthalene homologs from petroleum sources in a substantially pure form containing at least 95+% of the individual naphthalenes.

In one of its embodiments this invention comprises contacting a hydrocarbon fraction boiling from about 300° to about 500° F., containing at least two homologous naphthalene hydrocarbons with a solvent for said naphthalene hydrocarbons selected from the group consisting of alcohols, an alkylene glycol, a polyalkylene glycol and ethers of said alcohol and glycols at a temperature sufficient to extract from said hydrocarbon fraction substantially all of said naphthalene hydrocarbons therefrom, providing sufficient pressure to maintain the hydrocarbon mixture and solvent in substantially liquid phase, thereby forming a rich solvent containing the naphthalene components of said hydrocarbon fraction dissolved in said solvent, contacting said rich solvent with a reflux comprising a liquid paraffinic hydrocarbon having a boiling point below the boiling point of the naphthalene hydrocarbon, separating said rich solvent from a raffinate comprising non-aromatic hydrocarbons, stripping a hydrocarbon extract from the rich solvent, separately recovering lean solvent and said hydrocarbon extract, recycling said lean solvent to said first-mentioned contacting step, and separating a naphthalene homolog from said hydrocarbon extract.

A more specific embodiment of this invention concerns a process for separating naphthalene and methyl-naphthalene from a hydrocarbon fraction boiling within the range of from about 400° to about 500° F., which comprises subjecting said petroleum fraction to countercurrent contact with an aqueous solution of diethylene glycol containing not more than about 5% by weight of water at a temperature of from about 525° to about 400° F. and at a pressure sufficient to maintain said fraction and said solution substantially in liquid phase thereby a rich solvent stream containing said naphthalene and methyl-naphthalene dissolved therein, countercurrently contacting said rich solvent stream with a reflux stream comprising a normally liquid paraffinic hydrocarbon having a boiling point less than naphthalene, thereby recovering a rich solvent stream from which the non-aromatic and alkylbenzene components boiling in the feed stock range have been displaced by contact of said rich solvent with said paraffinic hydrocarbon, reducing the pressure on said rich solvent stream at substantially isothermal conditions, withdrawing from said rich solvent residue a first vapor fraction comprising said paraffinic hydrocarbon and recycling said first fraction to contact with said rich solvent as at least a portion of said paraffinic reflux hydrocarbon, fractionally distilling a naphthalene hydrocarbon from said residue, withdrawing a bottoms comprising lean solvent, recycling said lean solvent to the first-mentioned contacting zone, said diethylene glycol solvent and thereafter fractionally distilling the naphthalene-hydrocarbon fraction to thereby segregate naphthalene from its homologs.

Another embodiment of the present invention relating to specific aspects of the present process will be referred to in greater detail in the following further description of the invention.

It has previously been known that aromatic hydrocarbons, including polycyclic aromatics, may be extracted from certain boiling range hydrocarbon fractions containing the same in admixture with paraffinic, olefinic and/or naphthenic hydrocarbons by dissolving the aromatic hydrocarbon in a solvent, such as an alcohol or glycol, but it has also been realized that the recovery of the aromatic hydrocarbon from the rich solvent stream formed by contacting the hydrocarbon fraction with the solvent does not readily release its aromatic solute by simple distillation methods, except at relatively high temperatures, at which temperatures the character of the solvent changes rapidly, tending to become highly acidic (presumably because of the adsorption of oxygen and/or the shift of oxygen atoms in the molecular composition of the alcohol or glycol solvent from hydroxyl and/or ether oxygen to carbonyl groups) and also tending to become contaminated with resins and tarry by-products. The acidic contaminants are highly corrosive at the high temperatures utilized in the extraction and/or stripping stages and the resins and tars precipitate in the equipment, necessitating frequent interruptions in the process for the removal of the resulting deposits. In effect, therefore, the use of the highly effective alcohols, alkylene glycols and polyalkylene glycols as solvents for the extraction of polycyclic aromatics which are recoverable from the rich solvent stream formed in the extractor only at relatively high temperatures makes the process unfeasible because of the tendency of the solvent to undergo deterioration into said acidic, resinos, and tarry by-products at the required high temperatures; the use of such solvents therefore impracticable because of the constant and recurring problem of cleaning the equipment in which the extraction is effected and the replacement of vital portions of the equipment corroded away by the acids developed in the solvent. As the molecular weight and boiling point of the aromatic extract increases, the required temperature of operation likewise increases and the deterioration of the solvent into acidic by-products likewise increases. In accordance with one of the provisions of the present invention, a blanket of inert gas is maintained over the surface of the glycol which would normally contact atmospheric oxygen, thereby excluding oxygen from contact with the

2,878,261
Recovery and Separation of Naphthalenes by Solvent Extraction
Donald B. Broughton, Chicago, Ill., assignor to Universal Oil Products Company, Des Plaines, Ill., a corporation of Delaware

Application November 15, 1956, Serial No. 622,488
14 Claims. (Cl. 260—674)
glycol and eliminating the deterioration of the solvent to acidic by-products which cause corrosion of the portion of the equipment coming in contact with the solvent and the deposition of resinsinous and waxy materials in the solvent reboilers and redissolution equipment. The use of the inert gas blanket in the present process is an important feature of the process, inasmuch as the deterioration of the solvent which such expedient eliminates becomes particularly significant at the high extraction temperatures attending the use of a high boiling naphthalene-containing charge stocks.

Another feature of the present invention which makes the use of alcoholic and glycolic solvents feasible for extraction of naphthalene and its homologs at the required high temperatures for such solvent extractions is the introduction of a light, paraffinic hydrocarbon having a boiling point below that of the naphthalene extract into the extractor at a critical point and maintaining the light paraffin in the extract receiver vessel as a diluent of the naphthalene extract. At the required extraction temperatures, that is, at temperatures of 200°F. and higher, the rich solvent stream formed within the extraction zone and containing dissolved naphthalenes increase the solubility of other hydrocarbons (including the normally raffinate-type hydrocarbons, which in the absence of the naphthalene solute would be substantially insoluble in alcoholic and glycolic solvents) to such an extent that the entire feed stock becomes soluble in the lower portion of the extraction column, thereby rendering the entire process inoperable as a means of separating the desired naphthalene and its homologs from other types of aliphatic and aromatic hydrocarbons which accompany these naphthalenes in feed stock. By means of the present process, a countercurrently flowing reflux stream comprising a light paraffinic hydrocarbon is charged into the lower portion of the extraction column to provide a separate and distinct raffinate phase capable of extracting the non-naphthalene aromatics from the rich solvent stream and the non-naphthalene aromatics from the rich solvent stream in the lower portion of the extraction zone and thereby maintain a separate liquid hydrocarbon phase into which the raffinate hydrocarbons dissolved in the rich solvent may diffuse and which may be removed as a separate liquid phase from the top of the extraction column. In the absence of the light paraffin reflux in the bottom portion of the extraction zone, the maintenance of a separate raffinate phase in the extraction zone and the recovery of the present naphthalene products becomes inoperable.

The boiling point characteristic of the light paraffin reflux enables these hydrocarbons to be readily distilled from the naphthalene extract recovered in the stripping vessel and also enables it to be distilled as a light overhead from the rich solvent in the stripping zone without appreciably vaporizing the naphthalene solute therewith. The preferred light paraffins comprising at least a portion of the reflux charged into the extractor are the paraffins boiling from about 105°F. to about 150°F. below the boiling point of naphthalene, one of the preferred paraffins for this use being one or a mixture of C10 to C30 paraffins, such as a fraction of petroleum. In the process as herein provided, the light vapor overhead from the rich solvent stream distilled in the stripping zone, hereinafter described, is rich in the light paraffins present in the rich solvent by virtue of having displaced heavier feed stock raffinate components from the rich solvent in the preceding extraction stage. This overhead, which also contains some of the naphthalene and other aromatics particularly characteristic of the naphthalene and the alpha- and beta-methylnapthalenes which boils at approximately 465°F., although higher boiling feed stock containing the higher alkylated homologs of naphthalene, such as dimethylnapthalene isomers, ethylnapthalene and diethylnapthalene may be utilized in the present process as the source of the extraction zone, the rich overhead stream may contain one or more naphthalenes and/or homologs, but in the preferred application of the process, the feed stock is prefractionated to separate a fraction containing not more than two species within the range of boiling points for these species. Thus, a fraction boiling from the rich overhead stream containing the naphthalene and the alpha- and beta-methylnapthalene isomers and an extract product separated from such a feed stock may be fractionally distilled in the final stages of the process to separate and collect isomers and homologs of substantially 100% purity. Feed stocks which are particularly adapt for the present process are selected from the naturally occurring hydrocarbon mixtures or
naphthalene-containing mixtures which are the product or a fraction of the product of a hydrocarbon conversion process, and which boil as an azo trope normally inseparable by simple or fractional distillation means. Thus, the conversion products of hydrocarbon reforming and many other petroleum refining processes contain paraffinic, olefinic, aromatic and naphthenic hydrocarbons having a wide range of molecular weight, depending upon the boiling range of such a fraction, which, when distilled yield azotropic mixtures containing components of the same molecular weight of adjacent homologs. Illustrative of such a separation problem is the segregation of naphthalene and the alpha- and beta-methyl- and naphthalene homologs from a fraction boiling from 400°F to about 500°F, said fraction containing, in addition to said naphthalene homologs, aromatic hydrocarbons containing a total of from 5 to 7 carbon atoms in alkyl side chains attached to the benzene nucleus, as well as dodecane, various dodecane isomers, tridecane, and tri- and tetradecane isomers, as well as various alkylcyclohexanes, alkylcyclopentanes, etc. Particularly preferred sources of feedstock herein are petroleum or petroleum conversion product fractions in which the non-aromatic components are exclusively paraffinic and/or naphthenic structure.

The solvents utilized in the present process which are selectively miscible with naphthalene hydrocarbons are those which boil as an azo trope with said naphthalenes from mixtures containing the same, together with paraffinic, olefinic and naphthenic hydrocarbons are referred to herein as the mono- and dihydric alcohols and ethers. These compounds are herein specifically selected for use as solvents because of the stability of these compounds at the high temperatures required for extraction of the present hydrocarbon feed stocks which boil at temperatures above about 300°F. Typical representative alcohols utilized as solvents for the extraction of naphthalene hydrocarbons from hydrocarbon mixtures are the aliphatic alcohols containing from 1 to about 10 carbon atoms, such as methanol, ethanol, n-propanol, iso-propanol, n-butanol, sec.-butyl alcohol, tert.-butyl alcohol, amyl alcohol, isoamyl alcohol, n-hexanol, cyclohexanol, n-heptanol, n-octanol, lauryl alcohol and the various isomers thereof. The compounds herein referred to as solvents and useful as solvents in the present process include the polyhydric alcohols, such as ethylene glycol, propylene glycol, trimethylene glycol, butylene glycol, amylene glycol, glycerol, beta-methylglycerol, etc. and particularly the dihydric glycols ethers, commonly referred to as the polyhydric glycols, including, for example, diethylene glycol, (HO(CH₂CH₂OH)₂), triethylene glycol, (HO(CH₂CH₂O)₃H), tetraethylene glycol, (HO(CH₂CH₂O)₄H), dipropylene glycol, tripolypropylene glycol, and mixed ethylene glycol-propylene glycol ethers. Another class of compounds utilizable herein as solvents are the alcohol ethers of the foregoing mono- and polyhydric alcohols and polyalkylene glycols, particularly the methanol, ethanol, butanol, etc. ethers of mono- and diethylene glycol, known commercially as the “carbitols” and “cellulose” derivatives of these glycols. These materials are selectively miscible with aromatic hydrocarbons, on a comparative basis, that is, to the straight-chain and naphthenic hydrocarbons. The difference in the selectivity of the solvent for aromatic hydrocarbons and aliphatic saturated or naphthenic hydrocarbons may be enhanced by incorporating in the solvent composition certain limited amounts of water, for example, up to about 20%, and preferably up to about 5%, by weight of the composition, or even water when enhancing the selectivity between bicyclic aromatics and non-aromatic hydrocarbons, as in the present process. The solvency may also be varied by compounding the foregoing alcohols, ethers and glycols into a solvent composition, for example, by mixing diethylene glycol with dipropylene glycol in order to enhance the solvency of the composition for the hydrocarbon mixture without seriously derogating its selectivity for naphthalene hydrocarbons, the quantity of hydrocarbons dissolved by the solvent composition remaining as the proportion of glycol containing the longer alkylene groups increases. Particularly preferred solvent compositions for operation of the present process are those which contain from about 1% to about 30% by weight of dipropylene glycol, from 2% to about 5% by weight of water and the balance diethylene glycol or triethylene glycol. Also preferred for use in the extraction of naphthalene and methyl-naphthalene from hydrocarbon fractions containing the same is the solvent composition consisting of diethylene or triethylene glycol containing from 0.5% to about 10% by weight of water.

The relationship between solubility, volatility and selectivity of various aromatic hydrocarbons present in a typical feed stock utilizable in the present process, for example, a fraction boiling from about 400°F to about 500°F of a hydroreformed gas oil fraction, based on a solvent composition containing 98.2% diethylene glycol and 1.8% water, is illustrated by the data in the following table, these data being based on an extraction temperature of 375°F and on the basis of the hydroreformed charge stock containing about 20% naphthalene and about 26% alpha- and beta-methylnaphthalenes by weight, as a typical feed stock, and at the above values as typical of the operating temperature and composition of solvent. It is to be emphasized, however, that such data are merely exemplary of typical conditions, the volatility and solvency relationships for the indicated aromatics being within the same range for other glycol solvents and the relative differences in these properties being of the same order of magnitude, regardless of the identity of the glycol or of the extraction conditions.

### TABLE 1

<table>
<thead>
<tr>
<th>Hydrocarbon Component to be Extracted</th>
<th>R. P. F. in °F., Normal</th>
<th>Rel. Volat. in Absence of Solvent #2</th>
<th>Rel. Volat. in Presence of Solvent #2</th>
<th>Rel. Solv. in Extraction Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>472</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>methyl-methylnaphthalene</td>
<td>472</td>
<td>0.720</td>
<td>0.869</td>
<td>0.869</td>
</tr>
<tr>
<td>p-methyl-methylnaphthalene</td>
<td>472</td>
<td>0.500</td>
<td>0.690</td>
<td>0.690</td>
</tr>
<tr>
<td>Monoalkyl Aromatic:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6-Carbon atoms in alkyls</td>
<td>555</td>
<td>1.150</td>
<td>2.49</td>
<td>1.90</td>
</tr>
<tr>
<td>6-Carbon atoms in alkyls</td>
<td>559</td>
<td>0.500</td>
<td>1.30</td>
<td>1.30</td>
</tr>
<tr>
<td>7-Carbon atoms in alkyls</td>
<td>505</td>
<td>0.327</td>
<td>0.90</td>
<td>0.90</td>
</tr>
</tbody>
</table>

These data indicate the feasibility of a solvent extraction process for separating naphthalene and methyl-naphthalene from a mixture of hydrocarbons containing them as well as the C₆, C₇ and C₈ mono- and polyalkyl monocyclic aromatic hydrocarbons and aliphatic paraffins.

It will be noted from the above data that all of the aromatics present in the petroleum naphtha, the naphthalenes are most soluble in the glycol solvent, being, on an average, more than twice as soluble as the alkylbenzenes having boiling points in the same boiling range as the naphthalenes. This solubility relationship permits substantially complete recovery of the indicated naphthalenes in substantially pure form, free of monocyclic aromatic impurities, particularly in view of the boiling points of most aromatics when dissolved in the rich solvent (i.e., the relatively lesser volatility of the naphthalene hydrocarbons in the presence of the solvent than the monocyclic aromatics). The effect of the latter factor is to enable complete vaporization of the monocyclic aromatics present in the rich solvent stream formed in the extraction column from the rich solvent by taking...
overhead from the rich solvent stripper a first vapor fraction relatively richer in said monomeric aromatics (these being the lowest boiling aromatics in the presence of all the aromatics dissolved in the rich solvent), continuing the rich solvent stripping until the rich solvent is free of monomers, and thereafter (but only after freeing the rich solvent of dissolved monomers) vaporizing into a separate stripper side-cut fraction the remaining naphthalenes in a high state of purity. Any naphthalenes removed from the rich solvent into the vapor overhead fraction of the stripper are recovered therefrom when the vapor overhead is recycled as a reflux stream to the lower portion of the extraction zone. The naphthalenes thus refluxed into the extraction zone and contacted with the rich solvent stream just prior to its removal from the extraction into the stripping zone also serve to displace non-aromatic and monomeric alkylnaphthalene-type feed stock hydrocarbons from the rich solvent by virtue of the selective solubility of said naphthalenes in the solvent, these naphthalene-type components thereby being displaced into the raffinate stream removed from the top of the extraction pressure of from about 10 to about 150 pounds per square inch, preferably within the range of from about 10 to about 150 pounds per square inch, depending upon the extraction temperature of the process flow and any additional quantities required to replace solvent losses are charged into line 7 through line 8 in amounts controlled by valve 9. As the liquid phase solvent descends through the rising stream of hydrocarbons introduced through line 5, it selectively extracts from the rich solvent stream essentially all the aromatic components present in the feed stock. Thus, as the hydrocarbon phase flows upwardly through the column it becomes progressively leaner in bicyclic aromatic components, although richer in less preferentially dissolved alkylnaphthalenes, the ultimate hydrocarbon residue removed from the top of the extraction zone through line 10, herein referred to as "raffinate," consisting almost exclusively of non-aromatic and alkylnaphthalene hydrocarbons present in the initial feed stock and introduced by way of the reflux stream. The raffinate is separately treated, as hereinafter more fully described.

Although the glycol solvent selectively extracts the naphthalene components of the feed stock, including its homologues, the solvent nevertheless dissolves to a certain limited extent the alkylnaphthalenes and non-aromatic paraffin, olefin and/or naphthenic constituents also present in the feed stock, the non-aromatic content of the solute present in the rich solvent stream is in such an amount to contaminate the final product with an impurity (from the standpoint of being a contaminant of the desired naphthalenes) boiling at approximately the same temperature as the desired aromatics. For the purpose of removing the latter, small amounts of impurities from the rich solvent stream prior to the stripping stage, a countercurrently flowing reflux stream comprising relatively volatile paraffins (i.e., boiling at a temperature below the initial boiling point of the feed stock) is contacted with the rich solvent stream for the purpose of displacing the feed stock non-aromatic impurities from the rich solvent with paraffins which may be subsequently easily separated from the rich solvent and/or the aromatic extract as a separate and distinct fraction. As heretofore indicated, the reflux stream comprises one or more paraffinic hydrocarbons (such as a light fraction of a paraffinic gasoline) boiling below the initial boiling point of the feed stock (preferably at a temperature from about 50° to about 150° F. below the feed stock initial boiling point). In the process utilizing, for example, a feed stock boiling from about 400° to about 500° F., a suitable reflux stream may comprise a fraction of a saturated gasoline or a naphthene boiling from 10° to about 150° F. below the initial boiling point of the feed stock such as methylcyclohexane, dimethylocyclohexane, etc. This reflux stream which is made up largely of the light vapor overhead from the rich solvent stripping column, as hereinafter described, is introduced into extraction zone 6 in the lower portion thereof, preferably contacting the rich solvent just prior to the removal of the latter from the bottom of the column, the reflux hydrocarbon thereafter flowing upwardly in countercurrent relationship to the descending rich solvent in substantially liquid hydrocarbon phase in excess of that which replaces the feed stock raffinate solute of the rich solvent joining the raffinate components of the feed stock which leave the extraction column through line 10. In such countercurrent contact between the extract reflux and rich extract streams, the raffinate-type alkylnaphthalenes and non-aromatic hydrocarbons at approximately the same temperature as the desired aromatic product are displaced from the rich solvent and their place taken by the reflux hydrocarbon which may subsequently be readily separated from the aromatic extract product by simple distillation. In the illustration of the process shown in the accompanying drawings the reflux hydrocarbon is charged into extractor 6.
through line 11 in amounts controlled by valve 12, the reflux hydrocarbons being derived from the aforementioned recycle stream supplied through line 13 connecting with reflux charge line 11. Any additional reflux hydrocarbon required to replace losses and to supply the initial charge of reflux is charged into the process flow through line 14 in amounts controlled by valve 15. This stream is mixing with line 11.

The reflux stream charged into column 6 through line 11 is composed predominantly of the aforementioned light hydrocarbon overhead of the rich solvent stripper, and also the light paraffin component recovered from the raffinate stream of column 6, as hereinafter described. As a consequence of recycling the stripper overhead, this stream contains, in addition to the light paraffins, a substantial proportion of the most volatile aromatics extracted from the feed stock. These aromatics are redissolved in the solvent by virtue of the recycle of overhead to the lower portion of extraction vessel 6 as a reflux stream and 31 with the solvent stream in said zone 6. That portion of the paraffin recruited herein as reflux have a boiling point substantially below the boiling point of the feed stock, a convenient method of separation comprises fractionally distilling the same from the raffinate stream, although other methods of separation by means known to the art may also be employed. For the purpose of fractionally distilling the raffinate, a latter stream is conveyed by means of pump 16 through line 10 in amounts controlled by valve 17 into line 18, through heater 19 and line 20 into raffinate still 21, which is generally in the form of a suitably packed or bubble cap, and having a temperature heated to a temperature above the boiling point of the paraffin component in heater 19 flashes upon entering column 21, the flashed vapors being taken overhead through line 22, liquefied in condenser 23 to a condensate stream removed from condenser 23 through line 24, valve 25, and drained into receiver 26. A portion of the liquid condensate comprising the desired light paraffin reflux hydrocarbon is recycled to the upper section of fractionating column 21, that portion being withdrawn from receiver 26 through line 27, diverted into line 28 in amounts controlled by valve 29 and discharged through line 31 onto an upper plate of column 21 for use as said distillation reflux. The remaining portion of the condensate in receiver 26, comprising said light paraffin overhead of column 21 is discharged in controlled amounts, determined by valve 32, into light paraffin reflux recycle line 11. The high boiling bottoms or residue of the raffinate from which the recycle reflux has been removed as overhead is reboiled by removal from the bottom of distillation column 21 through line 33, circulated through reboiler heater 34, and the resulting vaporized portion of the bottoms returned into column 21 through line 35. The raffinate residue comprising the alkylbenzene and paraffinic non-extracted portion of the feed stock is removed from reboiler 34 through line 36 and valve 37 for discharge from the process flow. The non-extracted residue of the feed stock may be withdrawn from the process flow for further conversion into aromatic components by additional reforming or permanently withdrawn from the process, as desired.

and from which the feed stock raffinate components have been displaced by countercurrent contact with the light paraffin-containing reflux stream 11. A portion of the extraction vessel 6 is withdrawn from column 6 through line 38 in amounts controlled by valve 39 and transferred by means of pump 40 into line 41 which conveys the rich solvent into the upper, flashing section of extract stripper column 42. Stripping zone 42 is in the form of a distillation column having a flash section in the upper portion and a fractional distillation section in the lower portion, the two sections being divided by a side-to-side pan sealed into the upper portion of the column from the distillation section below it, as illustrated by interior pan 43 in column 42. The pressure maintained in the flashing section above pan 43 is somewhat less than the pressure on the rich solvent stream flowing into stripping vessel 42, such that upon entering column 42 onto pan 43, the most volatile solute components in the rich solvent, that is, the light paraffin components, immediately flash from the rich solvent by virtue of the sensible heat content of the rich solvent, thereby providing substantially isothermal stripping of the solute from the rich solvent. Also present in the light vapors, because of their significant (although substantially lower) vapor pressures at the temperature of the rich solvent are water vapor, substantially all of the monocyclic aromatic components in the extract, a smaller portion of the naphthalene components extracted by the solvent and a still smaller proportion of the solvent component which has the lowest vapor pressure. This relationship in the volatilities of the solute components is shown in the data of Table 1, particularly the data relating to the relative volatilities of the various aromatic hydrocarbon feed stock components in the presence of the solvent, the data indicating that the alkylbenzenes are, on an average, the most readily vaporized components of the rich solvent, naphthalene, which is the most volatile bicyclic aromatic in the presence of the solvent also constitutes a substantially proportion of the vapor removed from stripper 42, the methylsulfane solvents constituting the least prevalent component. It is evident, therefore, that all of the monocyclic aromatics will vaporize from the rich solvent prior to any substantial vaporization or the naphthalenes or, at least, constitute a major aromatic hydrocarbon component of the overhead vapor. These are removed from column 42 through light vapor overhead line 44, passing through valve 45 into condenser 46 wherein they are condensed into a liquid condensate which are transferred by line 47 into strip overhead vapor line 48 wherein the phase of greatest density, comprising aqueous solvent, settles and is removed from an upper hydrocarbon layer in vessel 48. The non-vaporized portion of the rich solvent stream accumulating on side-to-side pan 43 is removed from the primary flashing section of column 42 at a reduced pressure (relative to the extraction pressure) through line 49 and valve 50 and discharged at a substantially lower pressure than the pressure maintained in the primary flashing section of column 42 onto a lower tray of column 42, the vapor released isothermally from the rich solvent stream at said lower pressure being removed from the latter secondary flash zone through line 51 and valve 52 and discharged into overhead vapor line 44. The secondary flash vapors thus recovered from column 42 comprise the remaining reflux paraffins contained in the rich solvent, additional steam vaporized from the rich solvent and an additional quantity of aromatic solute present in the rich solvent stream. The secondary flash section may be further-sealed from the lower distillation section of the column to provide multiple flash zones, if desired. In general, the pressure reduction from the extraction zone to the primary flash section is preferably a major drop in pressure (say, one half to three quarters of the pressure differential between the extraction pressure and the distillation pressure in column 42) the remaining one half to one
third in the pressure drop taking place in the secondary and subsequent flash sections, if desired. The primary flash vapors join the primary flash vapors in line 44, being liquefied in condenser 46 with the primary overhead flash vapors and thereafter accumulate in receiver vessel 48 with the primary vapor overhead. The combined hydrocarbons of the primary and secondary flash zones which separate as an upper layer in receiver vessel 48, and which also consist of light paraffin reflux, as well as the aromatic hydrocarbons vaporized in part from the rich solvent steam are transferred as reflux stream by means of pump 53 from receiver vessel 48 through line 54 and valve 55 into line 13 for recycle into the lower portion of extraction vessel 6 through line 11, as previously described, the light paraffins and aromatics stripped from the rich solvent in vessel 42 being returned to extractor 6 for recovery of the naphthalene hydrocarbons contained in the light vapor overhead and for displacement of feed stock raffinate components in the rich solvent stream, as previously described. Since the aromatics in the stream are redissolved in the rich solvent by recycle as a portion of the reflux stream into extraction zone 6, a gradual build-up of monocyclic aromatics in the recycle into excessively large quantities of total recycle would result unless a portion of this stream were continuously removed from the process 58 by means of valve 13c. For this purpose a bleed line 13a containing valve 13b, is provided as a draw-off line from recycle line 13 to remove that portion of the extract representing the alkyl benzene components of the reflux recycle redissolving in the rich solvent.

The lower aqueous phase accumulating in receiver vessel 48 which contains a small proportion of the mono- or polyhydric alcohol solvent component vaporized from the rich solvent stream in the flashing sections of stripping vessel 42, accumulates in settling leg 56 of receiver 48 as a heavy liquid layer and is continuously drained therefrom through line 57 in amounts controlled by valve 58, into line 59 for reconstituting the aqueous component of the solvent composition prior to recycling the lean solvent to extraction vessel 6 and to provide stripping steam in the reboiling section of column 42. Any additional water required for replacement of water loss by reconstitution of the lean solvent composition to its desired water content may be introduced into the process flow from storage line 60 in amounts controlled by valve 61. The water thus added to the solvent is desirably introduced into the reboiling section of column 42 in the lower portion of the column, the water thus producing steam in reboiler 62 which is charged into the lower portion of column 42 as the stripping agent to remove the last traces of aromatic solute from the rich solvent residue in the lower portion of the column.

The rich solvent stream, as it descends through the distillation section of stripper 42, is progressively stripped by means of the aforementioned steam introduced into the reboiling section of the column to substantially completely remove the non-aromatic and alkyl benzene components of the hydrocarbon solute present in the rich solvent, these hydrocarbons being withdrawn together with the stripping stream and vaporized organic solvent (such as glycol), through line 51, as aforesaid. A higher boiling side-cut fraction comprising the desired naphthalene products of this invention is withdrawn from column 42, together with stripping steam and vaporized solvent, through line 63, liquefied in condenser 64 to form a liquid condensate which is drained by means of line 65 and through valve 66 into side-cut receiver 67. The liquid phase collecting in the receiver separates into a hydrocarbon phase and an aqueous, dilute solvent phase containing a greater proportion of the glycol solvent component than the overhead in receiver 48 because of the substantially higher temperature of vapor withdrawal of this side-cut fraction.

The hydrocarbon phase in receiver vessel 67 is made up exclusively of naphthalene and its homologs which are normally solid melting at relatively high temperatures and which have a density greater than water. Except for the special provision herein of a paraflin diluent of the naphthalene phase present in receiver vessel 67, the hydrocarbons distilled from the rich solvent and collecting in receiver 67 would form a crystalline mass of solid hydrocarbons in receiver 67. Such a solid phase hydrocarbon would ordinarily be difficult to handle in the presence of the less dense aqueous phase also present in the receiver vessel. In accordance with the present process a volatile paraflin hydrocarbon diluent of low density is continuously maintained within receiver vessel 67 to disperse and distribute the naphthalenes and homologues in solution in the paraflin diluent as a liquid layer, reducing the density of the hydrocarbon phase thereby below the specific gravity of water and maintaining the hydrocarbon phase as an upper liquid layer in the receiver vessel. For this purpose it is preferred that the amount of light paraflin, such as the aforementioned octane fraction, maintained within the receiver vessel 67 be sufficient to provide at least 0.1 volume of light paraflin per volume of naphthalene distillate and preferably from about 1 to 10 to about 10 to 1 volumes per volume of paraflin. The paraflin diluent is supplied to receiver vessel 67 through line 68 by means of pump 69, from paraflin storage vessel 70, the paraflin diluent being supplied from a previously recovered upper layer in a subsequent distillation, as hereinafter more fully described. The lower aqueous phase distilled from the rich solvent in column 42 separating as a lower aqueous layer collects in the dense liquid leg 69 of the receiver vessel and is advantageously decanted thereto. By continuous withdrawal through line 70 which connects with line 57 for recycle to the reboiling section of column 42 through line 59, into reboiler 62 to thereby form the stripping steam supplied to column 42. The lower aqueous phase also contains all of the organic solvent (e.g., such as glycol) distilled from the rich solvent as the side cut fraction; by recycling the lower aqueous phase into column 42, the water thus returned not only provides steam per stripping solute from the rich solvent, but the organic solvent contained therein is returned to the process flow for recycle in the system. The diluted naphthalene layer accumulating above the aqueous phase in receiver 67 and containing the light paraflin diluent is continuously removed therefrom through line 71 and valve 72 into extract fractionator 73. The naphthalene contained in the extractate from the light paraflin diluent. The heat required to vaporize the light paraflin diluent is supplied thereto by reboiler 74, the bottoms from column 73 being withdrawn therefrom through line 75 and valve 76 into reboiler 74 from which the resulting heated bottoms and light paraflin diluent are returned to the column through line 77 and valve 78 for further vaporization of paraflin diluent therefrom. The vapors of light paraflin are taken overhead from column 73 through line 79, liquefied in condenser 80 and the resulting condensate drained into receiver 81 from which it is transferred through line 82 by means of pumps 83 into line 68 and valve 84 for recycle into extract receiver vessel 67. It will thus be noted that the light paraflin diluent which serves to maintain the naphthalene extract collected in receiver vessel 67 in liquid phase is continuously supplied thereto in a closed circuit, being recycled to the extract receiver vessel from the overhead of extract fractionator 73 and returned continuously repeat the cycle to extract fractionator 73 from which it is again vaporized and recycled to extract receiver 67.

The bottoms from column 73 comprising the naphthalene extract from which the greater proportion of the glycol solvent component has been distilled and comprising a mixture of naphthalene and its homologues initially present in the feed stock is withdrawn from reboiler 74 through line 85 by means
of pump 86, transferred via line 87 through valve 88 into naphthalene separation column 89 for fractionation of the mixed naphthalene and homologues into separate components. The heat supplied for distillation and fractionation of the naphthalene mixture is supplied through reboiler 90, the bottoms from column 89 being withdrawn through line 91, valve 92, heater and reboiler 90 and the resulting vapors and heated liquid being returned to the column through line 93 and valve 94. The most volatile vapors fractionated in column 89 are removed as an overhead vapor from the column through line 95, condensed to a liquid condensate in cooler 96 and recovered as liquid in receiver vessel 97. This condensate which consists exclusively of naphthalenes in the naphthalene extract component of greatest volatility is essentially pure naphthalene, free of its higher homologues by virtue of the fractionation in column 89 and control of the overhead vapor temperature. This product may be withdrawn from receiver 97 through line 98 and valve 99 into storage or for other disposition as a substantially pure naphthalene product. Preferably, however, at least a portion of the naphthalene condensate is returned as reflux to naphthalene distillation column 89 by withdrawing from line 98 at least a portion of the condensate through line 100, by means of pump 101, which discharges the naphthalene condensate to reflux return line 102. This reflux is desirably returned in limited amounts, controlled by valve 103, to the upper plate of fractionating column 89 to provide thereby the desired degree of fractionation in the column.

The bottoms from the naphthalene column are transferred by means of pump 104 from reboiler 94 through line 105 and valve 106 into line 107 which conveys the bottoms of column 89 into methylnaphthalene separation column 108. The methylnaphthalene in the bottoms is a mixture of its alpha and beta isomers, which are distilled overhead from column 108 through line 109 into cooler 110 which operates at a temperature sufficiently below the boiling point, but above the melting point of the distillate to liquify the methylnaphthalene. The resulting liquid condensate is withdrawn from cooler 110 into receiver 111 from which methylnaphthalene may be withdrawn as part of the product through line 112 and valve 113. At least a portion of the methylnaphthalene condensate in receiver vessel 111 is preferably refluxed to the uppermost plate in column 108 by withdrawing a portion of the condensate from line 112 and transferring the same by means of pump 114 through line 115 and valve 116 to cool in cooler 110 to a temperature indicated by fractionation introduced into the liquid bottoms of column 108, withdrawn therefrom through line 117, by means of reboiler 118, the heated bottoms being recycled back to column 108 through line 119. The net bottoms make, comprising higher boiling homologues of naphthalene, such as dimethylnaphthalene, etc. are removed from the process flow through line 120 and valve 121 for further processing, as desired.

The solvent residue from which substantially all of the volatile hydrocarbon components have been removed by vacuumization and stripping in extract stripper 42 is withdrawn from column 122 with high bottoms residue through line 122 and valve 123, a major portion thereof being recycled to the lean solvent inlet of extract vessel 6, in an amount determined by valve 124, being transferred by means of pump 125 through heater 126 into lean solvent recycle line 7 which supplies the lean solvent into the upper portion of countercurrent extract vessel 6, as previously described. Heat exchanger 126 may be provided to either cool the high temperature bottoms of extract stripper 42 to the desired extraction temperature, or, in the event that the solvent residue in the lean solvent of stripper 42 is at a temperature below the desired extraction temperature, heat exchanger 126 may be a heater for raising the temperature of the lean solvent to the desired extraction temperature. In general, however, vaporization of the solute from the rich solvent is effected predominantly by pressure reduction, thereby providing substantially isothermal stripping of the rich solvent stream. The lean solvent leaving the bottom of the stripper for recycle to extraction column 6 is usually at approximately the desired extraction temperature and may be heated to column 6 without heating or cooling. Pump 125 also increases the pressure on the lean solvent recycle to the operating pressure maintained in extractor 6, as previously described, thus restoring the pressure differential between extraction zone 6 and the primary flash zone of extract stripper 42.

In the preferred operation of column 42 at least a portion of the solvent residue accumulating in the lower section of the column is separately reboiled in order to generate steam which supplies the stripping agent for recovery of the aromatic solute from the rich solvent in column 42. For this purpose a portion of the lean solvent residue from line 122 is withdrawn therefrom through line 127 in an amount determined by valve 128, mixed with recycle water supplied through line 59 by connection of line 59 with line 127, and reboiled in heater 62. The steam and hot solvent residue thus produced leave reboiler 62 through line 129 for discharge into the stripping section of column 42, as heretofore indicated. The steam thus charged into the lower section of the column constitutes the solvent to its desired selected composition for use as a lean solvent in extraction column 6, steam distills the aromatic extract from the rich solvent, and reduces the boiling point of the rich solvent. For the purpose of maintaining the solvent composition at its desired water content, samples of the lean solvent may be withdrawn from line 122 for analysis and adjustment in water content to the preferred selected composition for extraction purposes in column 6.

One of the preferred means of maintaining the glycol solvent component in its unaltered form, that is, as a glycol of the same identity as the component of the solvent composition initially charged into the process and to avoid the development of acidic and resinous or tarry by-products in the composition, comprises maintaining a blanket of an inert gas over the glycol vaporized from the rich solvent in stripping column 42 and returned to the process by recycle of the lower aqueous phases in the various receiver vessels attached to overhead and side cut lines from column 42. By this means, oxygen which unavoidably leaks into the receiving vessels and ordinarily absorbed by the glycol solvent is excluded from the system, thereby eliminating the major cause of glycol deterioration in an extraction process utilizing glycol solvents. A suitable means for maintaining such a blanket of inert gas over the aqueous layers in the receiver vessels comprises introducing the inert gas, such as nitrogen, carbon monoxide, etc. into one end of each of the receivers and withdrawing the inert gas from the other end. Thus, in overhead receiver vessel 48, the inert gas is admitted into the receiver through line 128 and valve 129, the gas flowing across the vessel, completely covering the liquid contents of the receiver and excluding air therefrom, being withdrawn from the vessel through line 130 and valve 131. In order to blanket the aqueous solvent in side cut receiver vessel 67 an inert gas inlet line 132 containing valve 133 may be connected to receiver 67 and the gas vented, after passing through the receiver, through line 134 and valve 135.

This invention is further illustrated with respect to several of its embodiments in the following example, the charge stock, process conditions, solvent and other operating factors recited therein, however, not being intended to limit the scope of the invention necessarily in accordance with the values for these factors specified in the example.

The hydrocarbon charge stock was prepared by fractionally distilling the conversion product of the so-called...
Platforming process to separate a gasoline boiling range cut from the Platformate having an end boiling point of 400° F. The bottoms which represents that portion of the Platformate product boiling above about 400° F. containing approximately 3.5% of the total Platformate product and consists almost exclusively of aromatic hydrocarbons, including 20% by weight of naphthalene and 26% by weight of methyl-naphthalene, the remaining aromatic components comprising benzene hydrocarbons of 11, 12 and 13 carbon atoms per molecule, the carbon atoms being present in one or more alkyl side chains attached to the benzene nucleus. The original Platformate from which the bottoms cut boiling above 400° F. was separated as still residue was prepared in a prior Platforming process by passing a mixture of a straight-run gasoline fraction having an end boiling point of 400° F. and hydrogen (utilizing a hydrogen to hydrocarbon mole ratio of 9:1) at 550° F. and at a pressure of 500 pounds per square inch over a Platforming catalyst comprised of a platinum supported on an alumina-halogen composite.

The residue of the Platformed product was separated by fractionally distilling the Platforming effluent, taking overhead the aforementioned gasoline boiling range fraction having an end boiling point of 400° F. from the bottoms residue and the latter utilized as feed stock.

The above bottoms fraction, consisting almost entirely of aromatic components, is a relatively difficult feed stock from which to separate its naphthalene and methyl-naphthalene components, because of its highly aromatic character, dissolving substantially in its entirety in the usual solvent compositions selective for aromatic hydrocarbons without producing a separable raffinate in which the undesired components of the fraction are concentrated. In accordance with the present process, separation of an aromatic concentrate by solvent extraction is effected by charging a low molecular weight paraffinic reflux stream into the extraction zone with the selective solvent and the feed stock, the light paraffins diluting the aromatic-rich feed, reducing its viscosity, its density, and its total miscibility with the solvent and enabling the production of a naphthalene product of substantially 100% purity.

The above feed stock is charged at a temperature of 375° F., at a rate of 1000 barrels per day and at a pressure of 100 pounds per square inch on the thirtieth tray of a countercurrent solvent extraction column containing sixty decks. A solvent composition consisting of 98.2% by weight of diethylene glycol and 1.8% by weight of water at a temperature of 380° F. and at the aforementioned pressure, is charged into the top of the solvent extraction zone at a rate of 6500 barrels per day. A reflux hydrocarbon stream derived in part from an overhead stream of the stripping column utilized to separate the hydrocarbon solute from the rich solvent stream formed in the extraction zone and in part from the light paraffin fraction recovered from the raffinate stream of the extraction zone is charged at a rate of 1760 barrels per day into the bottom of the extraction column. Analysis of this reflux stream indicates that it is made up of approximately 850 barrels per day of octanes, approximately 690 barrels per day of naphthalenes, and the remainder comprises monocyclic aromatic hydrocarbons stripped from the rich solvent stream in the subsequent stripping zone. A raffinate stream comprising the non-extracted components of the combined feed and reflux streams is removed from the top of the extraction column at a rate of 1100 barrels per day, the raffinate retaining only a very small proportion of the naphthalene hydrocarbons present in the original feed stock and substantially all of the monocyclic aromatics contained in the feed. The raffinate was diverted, after being washed with a stream of water to thereby recover the glycol therefrom, into a raffinate fractionator wherein the octane components is distilled therefrom and the latter recycled to the reflux line leading into the bottom of the extraction zone.

The rich solvent stream formed in the extraction column, at a temperature of 347° F. and at the extractor pressure of approximately 4000 pounds per square inch, is removed from the bottom of the extraction zone, heated to a temperature of 370° F. and charged into the top of a flash stripping column wherein the pressure is reduced in three stages to atmospheric pressure. In the first stage the pressure is reduced to approximately 50 pounds per square inch in a refluxing flash column, light vapor overhead from the top plate of the stripping column which is separated from the lower plates by a side-to-side pan sealed circumferentially on the inside of the stripping column. The overhead vapor at 370° F. is flashed off at a rate of approximately 675 barrels per day being thereafter blended with the octane overhead from the raffinate fractionator and the combined stream recycled as reflux to the bottom of the extractor.

The overhead vapor also contains a portion of the desired naphthalene and methyl-naphthalene as well as most of the monocyclic aromatics extracted from the original feed stock. The raffinate stream, which in turn comprises hydrocarbons containing monocyclic aromatics in the reflux stream, a portion of the overhead from the stripping column, amounting to the net monocyclic aromatic component charged into the system as feed stock and not removed from the process in the raffinate (about 8 barrels per day) is charged into the receiver vessel attached to the overhead vapor condenser, the aqueous solvent being separately removed by decantation from the upper layer reflux hydrocarbons, combined with other aqueous glycol condensates, and charged into the rebolbing section of the stripping column.

The rich solvent residue is continuously drained from the primary stage flashing section into a secondary flash section wherein the pressure is reduced from 50 pounds per square inch to 5 pounds per square inch, the resulting secondary flash vapor being taken off at 370° F. at a rate of approximately 1450 liquid barrels per day, of which 750 barrels per day represent hydrocarbons comprising predominantly aromatic components, together with the remaining octanes present in the rich solvent and approximately 700 barrels per day of aqueous glycol. The vapors are condensed by cooling to form a two-layer liquid. The aqueous glycol condensate in the receiver vessel is attached to the secondary flash condenser, the glycol layer being drained from the receiver, mixed with the overhead aqueous glycol and charged into the stripper reboiler to provide stripping steam for the column. The hydrocarbon portion of the secondary flash overhead is combined with the hydrocarbon portion of the primary flash overhead and recycled as reflux to the extraction column. The rich solvent residue thereafter flows into the stripping section of the column wherein the pressure on the rich solvent is reduced to atmospheric. A resulting side-cut fraction is recovered from the stripping zone at a temperature of 374° F., the vapors comprising a mixture of aqueous glycol and the hydrocarbon portion comprising predominantly naphthalene and methyl-naphthalene extract. These vapors are cooled sufficiently to form a liquid condensate which is drained into a receiver vessel. The aqueous glycol liquid layer is drained from the bottom of the receiver, mixed with the aforementioned aqueous glycol layers, and charged into the rebolbing section of the stripping column to provide stripping steam. A light liquid paraffin stream comprising the octane fraction (overhead) recovered from the subsequent extract column is charged into the extract fractionator in the amount of 222 barrels per day is charged into the extract receiver in order to maintain
the naphthalene components of the side-cut fraction in liquid phase and to reduce the density of the naphthalene sufficient to contain the hydrocarbon distillate of the extract in liquid phase and to allow said extract to distil into the stripping column, consisting essentially of a gas-fired heater into which the stripped solvent bottoms is charged and heated to a temperature of 380° F. and into which the aqueous solvent phases of the various receiving vessels heretofore referred to are charged in order to generate steam supplied to the lower portion of the stripping column for vaporization of the aromatic solute from the rich solvent residue. A lean solvent stream containing approximately 1.8% water is continuously removed from the reboiler at a rate of 6500 barrels per day and pumped into the top of the extraction vessel for use as selective solvent therein. The bottoms of the extract fractionator from which the octane reflux has been removed for recycle to the extract receiver is removed from the extract fractionator at a temperature of 450° F. and at a rate of 405 barrels per day into a naphthalene fractionating column from which 184 barrels per day of naphthalene of 99.9% purity is taken overhead at a temperature of 424° F. The product crystallizes readily, the crystals melting at 80.2° C. The bottoms fraction from the naphthalene column, at a temperature of 480° F. is charged into a methylphthalein column from which an overhead fraction (B. P. 468° F.) in an amount of 215 barrels per day is recovered. This fraction contains both the alpha- and beta-methylphthalenic isomers and contains approximately 1% by weight of monocyclic aromatics. A bottoms fraction is recovered from the methylphthalein column, at a temperature of 510° F. in an amount representing approximately 4 barrels per day. This residue contains monocyclic aromatic hydrocarbons having about 13 carbon atoms per molecule, as well as a small proportion of alkyl naphthalenes of higher molecular weight than methylphthalenes.

In the above process nitrogen was charged into the overhead receivers and side cut receiver in order to blanket the surface of the aqueous glycol phase with an inert gas and thereby prevent absorption of oxygen by the glycol. For this purpose, nitrogen was bled into the receivers at a rate of 100 ft³ per hour, being removed from the opposite ends of each of the receiver vessels. In this manner the glycol was maintained in an unaltered condition for long periods of use, the glycol replacement rate being less than 1.5 barrels per day on the above plant.

Prior to use of the above nitrogen blanket on the aqueous glycol phase, however, the receiver vessels permitted sufficient leakage of air into the unit to rapidly deteriorate the glycol. It was observed that as operation of the unit continued beyond the first day on stream, the pH of the glycol decreased rapidly, caused rapid corrosion of the steel equipment, formation of tar and loss of glycol from the unit at a rate of more than 60 barrels per day. Glycol deterioration became so rapid that an auxiliary glycol still was required to continuously distill a slip stream of the solvent for removal of tar and degradation products.

I claim as my invention:

1. A process for recovering a naphthalene hydrocarbon from a mixture containing naphthalene and benzene hydrocarbons which comprises subjecting said mixture to countercurrent contact with an aqueous solution of solvent in which said naphthalene hydrocarbon is selectively soluble and selected from the group consisting of an aliphatic alcohol containing up to 10 carbon atoms, an alkylene glycol, a polyalkylene glycol, and a glycol ether, at a temperature of from about 200° F. to about 450° F. and at a pressure sufficient to maintain the mixture in sub-

5. The process of claim 1 further characterized in that said solvent is isopropylene glycol containing from 0.5 to about 10% by weight of water.

6. The process of claim 1 further characterized in that said solvent is triethylene glycol containing from 0.5 to about 10% by weight of water.

7. The process of claim 1 further characterized in that said mixture boils from about 300° to about 500° F.

8. The process of claim 1 further characterized in that said first-mentioned contacting step is effected at a temperature of from about 300° to about 400° F.

9. The process of claim 8 further characterized in that said extract stripping step is effected by reducing the pressure on said rich solvent.

10. The process of claim 1 further characterized in that the lowest boiling overhead fraction from said extract stripping step is recovered separately from a naphthalene-rich fraction stripped from said rich solvent and said vapor overhead fraction, in admixture with said paraffin reflux hydrocarbon is recycled to said contacting step.

11. The process of claim 10 further characterized in that said naphthalene-rich fraction separately collected in said stripping step is continuously mixed with a light, normally liquid paraffinic diluent in an amount of said diluent sufficient to completely dissolve the naphthalene-rich fraction and maintain said fraction in liquid phase.

12. The process of claim 11 further characterized in that the diluent-naphthalene-rich mixture is continuously distilled and the separated light paraffin hydrocarbon continuously recycled to form said diluent-aromatic rich mixture.

13. A process for recovering naphthalene and methyl-

14. A process for recovering naphthalene and methyl-pthalenic naphthalene from a hydrocarbon fraction boiling from about 400° to about 500° F. and containing alkyllbenzenes of 11 to 13 carbon atoms which comprises contacting said fraction at a temperature of from about 300° to about 400° F. and at superatmospheric pressure with a solvent selectively miscible with aromatic hydrocarbons comprising diethylene glycol containing from 0.5 to about 10% by weight of water to form thereby a rich solvent and a raffinate, countercurrently contacting said rich solvent with a light paraffin reflux hydrocarbon to thereby displace from said rich solvent said alkyllbenzenes, distilling said raffinate and recovering a recycle fraction of said light paraffin reflux, reducing the pressure on said rich solvent to thereby flash overhead from the rich solvent residue a light hydrocarbon fraction, combining said light hydrocarbon fraction with said light paraffin reflux re-
cycle, distilling the rich solvent residue to recover a naphthalene-methyl-naphthalene extract substantially free of non-naphthalene contaminants, and distilling said extract into a naphthalene product and a separately recovered methyl-naphthalene product.

14. The process of claim 13 further characterized in that said light paraffin reflux is the octane to decane fraction of a gasoline boiling range material.