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Applicant: **UNION CARBIDE CORPORATION, 270, Park Avenue, New York, N.Y. 10017 (US)**

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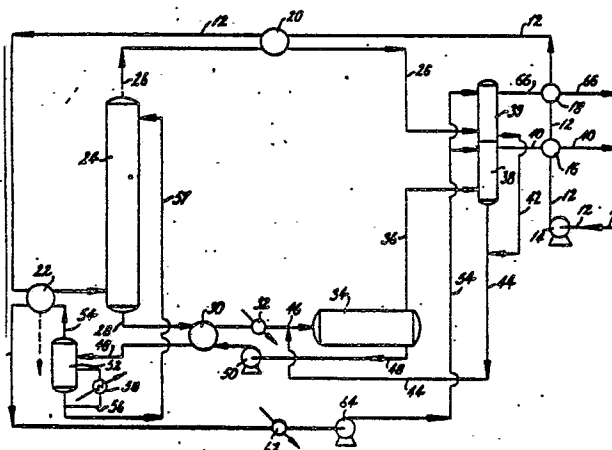
Inventor: **Forte, Paulino, 82 Homcrest Oval, Yonkers New York 10703 (US)**

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Representative: **McCall, John Douglas et al, W.P. THOMPSON & CO. Coopers Building Church Street, Liverpool L1 3AB (GB)**

Method of separating aromatic and nonaromatic hydrocarbons in mixed hydrocarbon feeds.

A process for separating aromatic and nonaromatic hydrocarbons which comprises a continuous solvent extraction - solvent decantation process. The process is particularly well-suited for a hydrocarbon feed comprising hydrocarbon mineral oils as a nonaromatic component wherein the process provides improved stability of said hydrocarbon mineral oils, normally susceptible to thermal degradation and oxidation and, further, decreases the tendency of such oils to form sludge. The process involves: (a) contacting (24) such hydrocarbon feed (10) with an aromatic selective solvent (57) to provide an aromatic-rich solvent phase (28) and a raffinate phase (26), (b) cooling (30, 32) the aromatic-rich solvent phase (28) to bring about the formation of two phases; (c) introducing the phase of the cooled aromatic-rich solvent phase (28) to a decantation zone (34) with an anti-solvent (44) for aromatic hydrocarbon in said aromatic selective solvent to provide an aromatic-rich extract phase (36) and a solvent phase (48) (d) removing anti-solvent (54) from said solvent phase (48) and recycling said solvent phase (57) to the extraction zone (24); and (e) recovering the aromatic-rich extract (40) of step (c) and the raffinate (66) of step (a).



DESCRIPTIONMETHOD OF SEPARATING AROMATIC AND NONAROMATIC HYDROCARBONS INMIXED HYDROCARBON FEEDS

This invention relates to a process for the separation of aromatic and nonaromatic hydrocarbons from a mixed hydrocarbon feed, and more particularly, to the separation of aromatic and nonaromatic hydrocarbons in high yields from a mixed aromatic, naphthenic and paraffinic hydrocarbon feed while making efficient use of process components. Further, said process significantly decreases the energy requirements necessary for the separation of aromatic and nonaromatic hydrocarbons. The process is particularly well adapted to the separation of aromatics from naphthenic/paraffinic hydrocarbons in a mixed hydrocarbon feed wherein the nonaromatic component comprises mineral oils and is especially well-suited for lubricating oils (hereinafter referred to as lube oils).

The separation of aromatic and nonaromatic hydrocarbons (generally referred to as dearomatization) from mixed hydrocarbon feeds has long been recognized as necessary for a number of varied reasons. For example, when a BTX fraction (benzene toluene and xylene) is the aromatic fraction it may be used as a raw material in the manufacture of petrochemicals, or as an additive for gasoline to increase its octane rating. Further, the nonaromatic fraction derived from these mixed feeds have varied uses as fuels, solvents and the like and, thus, are also highly desirable. Such utilities for the

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aromatic and nonaromatic fractions have resulted in the development of varied dearomatization processes with the goal being to improve the economics of these processes.

Of particular interest and difficulty is the purification of lube oils, wherein the removal of aromatic-type hydrocarbons is necessary to improve the viscosity index, thermal and oxidation stability, and color of the lube oils. The presence of aromatic-type hydrocarbons in lube oils affects the quality of these oils due to the low viscosity index, poor thermal and oxidation stability, high carbon residue, and poor color of such aromatic-type hydrocarbons. The aromatic-type hydrocarbons present in lube oils differ significantly from the BTX fraction found in higher hydrocarbon mixtures and as a result present different separation problems.

A general review of separation processes follows.

Various processes have been suggested for the separation of the aromatic and nonaromatic hydrocarbons of a mixed feed wherein the aromatic is a BTX fraction. Among these processes is a process employing an extraction column for separation of a BTX fraction which introduces a glycol solvent/water solution, BTX and reflux to a two step distillation column. BTX is then distilled to remove water and entrained glycol. A similar process has been suggested wherein two distillation columns are employed with the BTX fraction and water being distilled in the second column. In

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addition, a process using two distillation columns wherein the second column is employed to distill the BTX fraction and other components, has been suggested.

The aforementioned processes have not proven satisfactory when the separation of aromatic hydrocarbons has been from other than a BTX fraction, particularly when the process was employed for the dearomatization of lubricating oils. Therefore, a number of processes have been proposed for the dearomatization of mixed hydrocarbon feeds containing various aromatic hydrocarbons. These processes have been directed, in large part, to the choice of the extraction solvent. For example, U.S. Patent Nos. 2,400,732 and 2,402,799 disclose extraction/distillations employing a solvent containing primarily water as the extraction solvent. Numerous water based solvents have been suggested for the extraction of aromatic hydrocarbons from mixed hydrocarbon feeds but to date such extraction solvents have not proven to be satisfactory. These include water based extraction solvents such as: glycol/water wherein up to 50 percent glycol is added (U.S. Patent 2,400,802); methanol/water (U.S. Patent 3,985,644); water/non-oxygenated organic solvents (U.S. Patent 2,298,791); water/amines (U.S. Patent 2,401,852); and water/inorganic salts, acid or bases, or organic substances (U.S. Patent 2,403,485). The problems associated with employing a water-based extraction solvent are well known in the prior art.

Various processes have been suggested to help

overcome the problems associated with employing water based extraction solvents . For example, U.S. Patent 1,783,203 discloses the use of dry alcohols (C_1-C_3) for treating heavy petroleum oils. The problems relating to the flammability and toxicity of such alcohols are well known in the art. U.S. Patent 1,908,018 discloses the use of glycol ethers in a process for refining mineral oils by separating the paraffinic and naphthenic portion thereof wherein the glycol ether is mixed with the mineral oil and the mixture is cooled to provide a paraffinic layer and a naphthenic layer. U.S. Patent 2,337,732 discloses the use of ethanolamines for removing aromatics from a hydrocarbon distillate, comprising gasolines or light hydrocarbons (C_1-C_5), by an extraction-distillation process. U.S. Patent 2,295,612 discloses the use of low molecular weight polyhydric alcohols for separating aromatic mixtures to obtain resin-forming compounds. U.S. Patent 2,129,283 discloses the use of a beta, beta'-dichloro diethyl ether and 2-30% propylene glycol as the solvent for extracting naphthenic impurities from lubricating oils at temperatures from 120°F to 200°F. U.S. Patent 3,379,788 discloses the use of alkylene oxide adducts of phenyl glycidyl ether and U.S. Patent 2,834,820 discloses the use of mixed alkylene oxide adducts of ethylene or propylene oxide as solvents in dearomatization processes.

To overcome the relatively low yields, purities and solvent recovery problems of the above processes

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several dearomatization processes have been suggested employing extraction and distillation. These include: solvent extraction-steam distillation processes (such as those disclosed in U.S. Patent Nos. 3,417,033; 3,714,034; 3,779,904; 3,788,980, 3,755,154 and 3,966,589); processes employing multiple extraction zones and azeotropic distillation (e.g. U.S. Patent 3,789,077); processes employing distillation and stripping columns (U.S. Patent Nos. 4,048,062 and 4,177,137); and multiple distillation processes (e.g. U.S. Patent 3,461,066).

Unfortunately these processes employ distillations. Further, high capital and energy costs are generally associated with employing such processes. Therefore, alternative processes have been sought whereby these problems may be minimized.

U.S. Patent No. 3,431,199 discloses a method of separating aromatic hydrocarbons from a mixed hydrocarbon feed by use of solvents comprising diethylene glycol, dipropylene glycol, sulfolane and mixtures thereof. The process is directed to the separation of light aromatics by extraction at temperatures preferably between 80° and 130°C and employs azeotropic distillation with acetone to effect separation of the aromatic hydrocarbons. The process preferably employs solvent with 2% to 8% by weight water.

U.S. Patent No. 3,551,327 discloses an extraction distillation process which employs a sulfolane-type solvent.

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U.S. Patent No. 3,985,644 discloses a method of separating naphtha into aromatic and paraffin-rich fractions with a methanol-water mixtures. The solvent is separated from the aromatic-rich phase by lowering the temperature of the mixture. As indicated therein, the solvent comprises methanol/water mixtures. These are highly toxic and flammable mixtures.

U.S. Patent No. 4,086,159 discloses a method for separating aromatic hydrocarbons from mixed hydrocarbon feeds by use of an ethoxylate alkane polyol solvent in an extraction-distillation process. The ethoxylated alkane polyol solvents high boiling point provides for the recovery of high boiling aromatics such as ethylbenzene and polysubstituted benzenes. The process necessarily requires sizable quantities of energy to carry out the energy intensive distillation steps.

U.S. Patent 4,179,362 discloses a method for separating aromatic-containing petroleum fractions into aromatic-rich and paraffinic-rich hydrocarbon streams by use of a methanol/water extraction solvent (having at least 10 volume percent water in the extraction solvent) in an extraction zone at a temperature of about 150°-450°F. The extraction employs water in the extraction step to reduce hydrocarbon solubility in the aromatic-rich extract. The extraction step is followed by further additions of water (distilled water) to the aromatic-rich extract such that the water/methanol solvent contains at least 80% water, by volume. The

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water and methanol must then be removed by flash distillation, an energy intensive process, or by some other process such as using super critical CO_2 as an extraction solvent. The use of methanol/water solvents for treating higher distillates tends to require higher process pressures and suffers from the safety constraints associated with methanol/water solvents, e.g., high flammability and high toxicity.

The above processes show the intense interest in developing a dearomatization process which lowers the cost of those processes heretofore used commercially. U.S. Patent 3,985,644 suggests one such method for achieving this goal, i.e., by reducing the use of energy-intensive steps, e.g., distillation.

Such dearomatization processes are of particular interest in the dearomatization of mineral oils, e.g., lube oils. Dearomatized lubricating oils are, generally speaking, naphthenic-and or paraffinic-type viscous materials having a low rate of viscosity change with change in temperature, i.e., relatively high viscosity index, a high degree of thermal and oxidation stability, low carbon-forming tendency, good color, and high flash points. Lubricating oil feedstocks are generally recovered as heavy distillates or bottoms from the vacuum distillation of crude oils. A crude lube oil fraction contains many different chemical components, e.g., paraffins, naphthenes, aromatics, and the like. In order to obtain refined lubricating oils of relatively good quality and high viscosity index, the

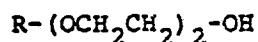
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practice has been to remove components, such as aromatic and polyaromatic compounds, which tend to lower the viscosity index of the lube oil.. The removal of these aromatic components has heretofore been carried out by processes as above-described and processes such as disclosed in U.S. Patent Nos. 2,079,885; 2,342,205; 3,600,302; 2,773,005; 3,291,728; 3,788,980; and 3,883,420.

U.S. Patent 2,079,885 discloses a process for refining hydrocarbon oils containing aromatic and non-aromatic components by counter current extraction at elevated temperatures with selective solvents such as furfural or phenol, cooling the aromatic-rich extract and oiling out the raffinate and recycling the oiled out raffinate. Unfortunately such a process results in some raffinate losses in the aromatic-rich extract.

U.S. Patent 2,342,205 discloses a solvent recovery scheme wherein aliphatic and aromatic hydrocarbons are washed with water and then distilled.

U.S. Patent 3,600,302 discloses a method of upgrading petroleum distillate fractions by extraction with a mixed solvent comprising an aromatic organic compound having a 6 membered ring containing at least one polar functional group and a diethylene glycol ether having the general formula:



U.S. Patent 2,773,005 discloses a process wherein light lubricating oils are extracted by use of phenol and water. The phenol is recovered from a second

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extract fraction wherein said extract fraction contains aromatic-type hydrocarbons and phenol (extraction solvent). Thus, the process requires regeneration of the extraction solvent by means of additional separation processes since the "second extract fraction" contains phenol (a relatively toxic compound) and aromatic-type compounds.

U.S. Patent 3,291,728 discloses a process wherein a raffinate and extract fraction from an extraction process are washed with 25 percent to 50 percent, by volume, water. The process employs the use of extraction solvent reboilers to recover solvents.

U.S. Patent 3,788,980 discloses a process for the recovery of aromatic hydrocarbons wherein a feedstock is contacted with a mixture of water and a solvent. The mixture containing aromatics is introduced to a distillation zone maintained at the boiling point of the mixture of aromatics with steam being introduced at the bottom of the distillation zone. Thus, a distillation zone is necessarily employed to remove the aromatic-type compounds.

U.S. Patent 3,883,420 discloses a process for removing aromatic hydrocarbons from an extract phase by use of a mixture of steam and a lower molecular weight paraffinic hydrocarbon (solvent). The solvent is recovered by steam stripping or by extractive distillation followed by a solvent recovery column.

There is disclosed in copending application United States Serial No. 164,039, filed June 30, 1980,

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corresponding to European Application No. A2364/U commonly assigned, a solvent extraction-solvent decantation process wherein solvent purification with mixed hydrocarbon feed or raffinate can be employed. The instant process eliminates these solvent purification steps.

The process of this invention is to be distinguished from the prior art in that the instant process provides a solvent extraction-solvent decantation process that is economically advantageous, i.e., energy efficient, and overcomes problems inherent in the above-described processes.

The instant invention provides a process for the separation of aromatic and nonaromatic hydrocarbons from a mixed hydrocarbon feed in which an aromatic selective solvent, preferably relatively low molecular weight polyalkylene glycols and mixtures thereof, is employed. The process utilizes an extraction-decantation process whereby aromatic and nonaromatic hydrocarbons are recovered without or with minimal distillation to recover the aromatics such that the aromatic and nonaromatic fractions are recovered in relatively high yield using a minimum of process equipment, thereby minimizing capital investment, while providing an energy efficient process.

According to the present invention, aromatic and nonaromatic hydrocarbons in a mixed hydrocarbon feed (referred to as the "feed") are effectively separated using minimal process equipment and energy in a

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continuous solvent extraction-solvent decantation process comprising the following steps:

(a) contacting the hydrocarbon feed, at a temperature of at least about 150°C, in an extraction zone with an aromatic selective solvent to provide an aromatic-rich solvent phase containing primarily aromatic hydrocarbons and aromatic selective solvent and a raffinate phase containing primarily nonaromatic hydrocarbons;

(b) cooling the aromatic-rich solvent phase to bring about the formation of two phases;

(c) introducing said phases of the cooled aromatic-rich solvent phase to a decantation zone and introducing therewith about 0.5 to about 25.0 percent by weight of an anti-solvent for said aromatic hydrocarbons in said aromatic-rich solvent phase to provide an aromatic-rich extract phase containing primarily aromatic hydrocarbons and a solvent phase containing primarily aromatic selective solvent and anti-solvent;

(d) removing anti-solvent from said solvent phase and recycling said solvent phase to the extraction zone of step (a); and

(e) recovering as products the aromatic-rich extract of step (c) and the raffinate of step (a).

In addition, entrained and dissolved solvent may be removed from the aromatic-rich extract and raffinate by means of a water wash process.

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As noted above, there is an industrial need for an energy efficient process for the separation of aromatic and nonaromatic hydrocarbons in a mixed hydrocarbon feed, particularly in the dearomatization of crude lube oils. Naphthas, heating oils, light oils, cracked gasolines, dripolenes, lubricating oils, light paraffin distillates, heavy distillates, kerosene and the like, can contain between about 20 to 90 percent by weight aromatic-type hydrocarbons, e.g., BTX or polyaromatics. Since the individual hydrocarbon compounds which make up these hydrocarbon feed streams are well known they will not be discussed extensively, except to note that the mixed hydrocarbon feed employed herein may be any petroleum fraction containing aromatics, such as for example naphthas (virgin or cracked) kerosene, gasoline, heating oils, lubricating oils, light paraffin distillates, heavy distillates and residual oils. Preferably, the feed stream is a light paraffin distillate, heavy distillate or a lube oil fraction.

The aromatic hydrocarbons present in heavy hydrocarbon feeds, e.g., lubricating oils, generally

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include: alkylbenzenes, indanes, tetralins, indenenes, naphthalenes, fluorenes, acenaphthalenes, biphenyls, phenantrenes, anthracenes, diacenaphthalenes, pyrenes, chripenes, diaceanthracenes, benzpyrenes and other various aromatic feed components.

The solvents which are employed in the instant process have typical desirable characteristics for use in this process as follows: (a) high selectivity for the aromatic feed components at the extraction temperature; (b) high solvent capacity for the aromatic feed components at the extraction temperatures (i.e., low solvent to feed ratios); (c) low vapor pressure at the temperature of extraction to avoid the use of pressurized equipment; (d) low capacity for the aromatic feed components at the lower decantation temperature; (e) chemical and thermal stability under the process conditions; (f) adaptable to a wide range of feeds; (g) available at a reasonable cost; (h) noncorrosive to conventional metals of construction; (i) relatively low toxicity, i.e., environmentally safe; and (j) have a relatively high density such that there exists a sufficient difference between the density of the extraction solvent and the hydrocarbon (raffinate) product.

The solvents used in the instant process tend to be water-miscible organic liquids (at process temperatures) having a boiling point and decomposition temperature higher than the extraction temperature. The term "water-miscible" solvents includes those solvents

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which are completely miscible with water over a wide range of temperatures and those solvents which have a high partial miscibility with water at room temperature, since the latter are usually completely miscible at process temperatures. The solvents are generally polar and contain carbon, hydrogen and oxygen, with some exceptions.

Representative of the solvents employed in the process are the low molecular weight polyalkylene glycols and the like. Examples of the solvents employed are ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, 1,3-butylene glycol, 1,2-butylene glycol, 1,5-pentaethylene glycol, and mixtures thereof and the like. The preferred solvents are diethylene glycol, triethylene glycol, tetraethylene glycol, or mixtures thereof. The most preferred solvent is triethylene glycol.

It is believed that other solvents having the aforementioned solvent characteristics may be employed in addition to the aforementioned solvents, among these being: amines such as diethylene triamine and triethylenetetramine; alkanolamines such as monoethanolamine, diethanolamine, and triethanolamine; sulfolane; N-methyl-2-pyrrolidone; aromatic compounds such as dimethylphthalate and diphenyl ether; and halogenated compounds such as perchloroethylene, 1,1,2-trichloroethylene and 1,2,3-trichloropropane, or mixtures thereof.

The anti-solvent employed in the instant

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process is preferably water although any compound that tends to decrease the solubility of the aromatic hydrocarbon in the aromatic selective solvent may be employed. Water is the preferred anti-solvent since the energy requirements of the process are significantly minimized by removing the water by flash distillation or by stripping, thereby generating steam for use in this or other processes. Other suitable anti-solvents include ethylene glycol, glycerine, low molecular weight alcohols and the like. The concentration of the anti-solvent as determined in the decantation zone is that amount which effectively decreases the solubility of the aromatic hydrocarbon in the aromatic selective solvent as determined by the amount of aromatic hydrocarbon in the aromatic selective solvent leaving the decantation zone. The anti-solvent employed in the instant process further promotes the formation into two phases of the aromatic-rich solvent phase such that an aromatic-rich phase and solvent phase are formed. Absent the addition of anti-solvent the formation of such phases may be incomplete and unsatisfactory and, thus, commercially prohibitive. Generally the concentration of the anti-solvent present in the decantation zone is in the range of from about 0.5 to 25.0 percent by weight based on the total weight of the aromatic-rich solvent phase with the range from about 0.5 to about 15.0 percent being preferred and the range from about 5.0 to about 10.0 being most preferred. Some portion of the anti-solvent present in the decantation zone may be

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provided by anti-solvent present in the aromatic-rich solvent phase obtained from the extraction zone. The actual concentration of the anti-solvent in the decantation zone may be higher than 25.0 percent by weight depending on the selection of the hydrocarbon feed, aromatics present in the feed, aromatic selective solvent employed and the like. The aforementioned concentrations designate the total water present in the decantation zone irrespective of its source. Anti-solvent is preferably added to the aromatic-rich solvent phase prior to the decantation zone so as to provide for superior separation in the decantation zone.

Generally, to accomplish the extraction, the ratio of aromatic-selective solvent to hydrocarbon feed in the extractor zone is in the range from about 2 to about 20 parts by weight of solvent to one part by weight of feed, the ratio from about 3 to 1 to about 15 to 1 being preferred and the ratio from about 4 to 1 to about 12 to 1 being the most preferred. The broad range may be expanded upon when nonpreferred extraction solvents are used. The optimum solvent to feed ratio depends upon whether high recovery (yield) or high purity (quality) is being emphasized, although the instant process will generally result in both high recovery and high purity.

The instant process is further characterized in that the vapor pressure at the top of the extraction zone is typically less than about 120 psig and often less than about 100 psig. This is highly advantageous

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in terms of ease of operation and the capital expenditure required for carrying out the separation process. The actual pressures in the extraction zone may be higher or lower depending on the particular hydrocarbon feed treated, the solvent employed, the selected antisolvent and its concentration, and the selected temperature at which the extraction is carried out. The pressure employed in the decantation zone is generally that pressure which is required to cause the aromatic-rich solvent phase to pass through the decantation zone. Generally a small pressure drop (pressure gradient) is observed across the decantation zone.

The temperature of the extraction zone is generally at least about 150°C and is generally in the range of from about 150°C to about 275°C, preferably in the range of from about 170°C to about 250°C and most preferably from about 200°C and about 240°C. The temperature in the extraction zone is not constant throughout and there will generally be a temperature gradient up to about 30°C or higher as between the temperature of the aromatic selective solvent introduced to the extraction zone and the temperature of the aromatic selective solvent phase exiting the extraction zone. The decantation zone is generally maintained at a temperature in the range of from about 50°C to about 200°C below the temperature of the extraction zone such that the temperature is preferably in the range of from about 25°C to about 150°C, more preferably about 25°C to about 100°C and

most preferably from about 25°C to about 70°C. The temperature employed in the decantation zone depends, in part, upon solubility of the aromatic hydrocarbon in the extraction solvent, the amount of anti-solvent present in the decantation zone and the viscosity of the selected solvent at the decantation temperature.

The equipment used in the instant processs, both for the extraction, distillation, if any, and the decantation, is of conventional design, e.g., an extraction column of the multistage reciprocating type containing a plurality of perforated plates centrally mounted on a vertical shaft driven by a motor in an oscillatory manner can be used as may columns containing pumps with settling zones and sieve trays with upcomers or downcomers, (Counter-current flow is generally utilized in the extraction column.) The separation in the decantation zone can be conducted in a decantation tank with no internal elements but preferably the decantation tank contains coalescing elements or baffles to aid in the separation. The preferred decantation zone comprises a coalescer with a porous media, such as that exemplified by Selas Corporation (Model No. LS-60P), having a depth-type coalescing element (fibrous bed coalescer element). It is understood that the "decantation zone" is a separation zone wherein phase formation occurs and wherein anti-solvent is present. The anti-solvent is preferably added prior to the decantation zone.

Heat exchangers, reservoirs, and solvent

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regenerators, if necessary, are also of conventional design as well as are the various extractors and decanters used in the various embodiments hereinafter described. The extractors employed are preferably multi-stage counter-current extractors, but can be any of the well-known types, as aforementioned.

The instant process generally provides for an overall recovery of the aromatic hydrocarbon of from about 70 to about 95 percent or better based upon the weight of aromatic in the original hydrocarbon feed and usually provides for similar recoveries for the nonaromatic hydrocarbons.

Experimental Procedure

In carrying out the examples the extraction column comprised a Karr (TM) reciprocating plate extraction column made of 2 inch (internal diameter) glass pipe, having an internal volume of about five liters and having reciprocating plates spaced two inches apart. All internal metal parts are made of No. 316 stainless steel except the reciprocating plates which were Teflon (TM). The decantation zone comprised a decantation tank with or without baffles or a glass separator (Model No. LS-60P from Selas Corporation of America) equipped with a depth-type coalescing element. A fibrous bed coalescing element is the preferred coalescing element. The tubing employed throughout was generally No. 316 stainless steel tubing having a 3/8 inch outside diameter with a 0.035 inch wall thickness.

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A water stripper was employed comprising a 4 inch (inside diameter) glass distillation column packed with stainless steel protruded metal packing (0.24 inch x 0.24 inch).

The oil content of the various phases was determined by a gas chromatograph (Hewlett-Packard Model 5750) having a 2 millimeter X 6 foot glass column packed with a 3 percent OV-101 on Chromosorb W (TM) equipped with a flame ionization detector. The water content of the various phases was determined using a Karl-Fisher automatic titrator (Model 392) and an automatic burette (Fisher Model 395).

The viscosity index (referred to as the VI) for the hydrocarbon feed and the raffinate product were initially determined by ASTM method D2270-75. The Viscosity Index for the raffinate product is a measure of the purity of the raffinate product with a higher Viscosity Index indicating a raffinate product of higher purity. The viscosity index was then determined by measurement of the refractive index of the hydrocarbon feed or raffinate product at 60°C. by correlating the viscosity index as determined by ASTM D2270-75 to the refractive index at 60°C. The values given for the viscosity index in the examples is the viscosity index as determined by measuring the refractive index at 60°C. In addition, the yield (volume % based on the total feed volume) was calculated from the refractive index at 60°C. Such yields are reported for the examples hereinafter.

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Temperatures and pressures were measured by conventional detection means.

The invention is also illustrated by the accompanying drawings, which are referred to in the Examples. In the drawings:-

Fig. 1 is a schematic flow diagram of an illustrative embodiment of the invention.

Fig. 2 is a schematic flow diagram of the process as employed in Examples 2 to 22.

Referring to Figure 1:

The mixed hydrocarbon feed is introduced at 10 through line 12 to pump 14. The feed passes through line 12 and heat exchanger 16, 18 and 20 where it is heat exchanged with aromatic-rich extract and raffinate, respectively to preheat the feed. The feed is then heat exchanged in heat exchanger 22 with steam in line 54 (steam formed by distilling the anti-solvent, i.e., water, from the solvent phase when water is the anti-solvent) prior to introduction to extraction column (zone) 24. An aromatic selective solvent, preferably having a temperature in the range of from about 150°C to about 275°C., most preferably about 200°C. to about 240°C. is introduced near the top of extraction column 24 via line 57 and percolates down column 24 removing aromatics from the hydrocarbon feed forming raffinate and an aromatic-rich solvent phase. The raffinate, containing primarily non-aromatics, exits the top of the column 24 via line 26 and in heat exchanger 20 preheats the mixed hydrocarbon feed and is cooled in turn by heat exchange with the incoming mixed hydrocarbon feed. The raffinate passes to extractor 39 where it is contacted

with water (when water is the selected anti-solvent the extraction water is water removed from the aromatic selective solvent) to recover aromatic selective solvent present in the raffinate so as to form a water phase (containing aromatic selective solvent) and a final raffinate product. A second water extraction takes place in extractor 38 wherein the aromatic-rich extract from decantation zone 34, discussed hereinafter, forms a water-phase (containing aromatic selective solvent) and a final aromatic product. The water-phases from extractors 38 and 39 contain primarily water and small amounts of aromatic selective solvent that was dissolved or entrained in the aromatic-rich extract and raffinate. The combined water-phases are recycled to decantation tank (zone) 34 via line 44, as needed, if water is the selected anti-solvent.

It should be pointed out that the terms "phase" and "product" are named after their main components, which is present in the phase in an amount of at least 50% by weight and in most cases in an amount of 80% by weight or higher. The aromatic-rich solvent phase, containing primarily aromatic selective solvent and aromatic hydrocarbons, leaves the bottom of extraction column 24 via line 28 and heat exchanger 30 where it is cooled with aromatic selective solvent in line 48. The aromatic-rich solvent phase is further cooled to promote two phase formation, if necessary, in cooler 32. Recycled aromatic selective solvent and anti-solvent, when water is the selected anti-solvent, are introduced via line 44 to decantation tank (zone) 34. Thus, the solvent contained in line 44 is returned to the process. The anti-solvent is preferably added to the aromatic-rich solvent phase prior to decantation tank (zone) 34 to further promote phase formation, e.g. at 46

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of the drawing, in the decantation zone although the anti-solvent may be added directly to decantation tank (zone) 34 if desired. The anti-solvent in the solvent/anti-solvent mixture of line 44 reduces the solubility of the aromatic hydrocarbon in the aromatic selective solvent to a degree not obtainable by simple cooling of the aromatic-rich solvent phase. The anti-solvent is present in decantation tank (zone) 34 at a concentration of from about 0.5% to about 25.0% by weight, based on the weight of aromatics and solvent in decantation tank (zone) 34, preferably from about 0.5% to 15.0% by weight and most preferably from about 5% to about 10.0% by weight. The presence of the anti-solvent decreases the solubility of the aromatic in the solvent such that typically less than about 2% weight percent aromatic and often less than about 1% weight percent, leaves decantation tank 34 via line 48.

The aromatic-rich extract phase of decantation tank (zone) 34 exits via line 36 to water-extraction column 38 where it is contacted with water (preferably water derived from the removal of water from the solvent/anti-solvent mixture) from the solvent phase of decantation tank (zone) 34. This extraction with water removes extrained and dissolved solvent from the aromatic-rich extract phase.

The solvent phase of decantation tank (zone) 34 passes via line 48 through pump 50 to heat exchanger 30 wherein it heat exchanges with hot aromatic-rich solvent of line 28 prior to introduction to distillation column

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(zone) 52. If further heating of the solvent in line 48 is desired an additional heat-exchanger (not shown) may be provided to allow heat exchange between the solvent phase of line 48 and the solvent of line 57. Such additional heat-exchanger would also serve to cool the solvent in line 57, if necessary. The use of a distillation zone in the instant embodiment is not intended to be limiting since any means for decreasing the concentration of the anti-solvent in the aromatic-selective solvent may be employed. The use of a distillation zone is preferred when the anti-solvent is water since the steam generated therein may be advantageously and economically employed in this and/or other processes (not shown).

When water is the selected anti-solvent the solvent phase in line 48 is introduced to distillation zone 52 wherein water is distilled, preferably under pressure, and removed as steam via line 54. Steam in line 54 is heat exchanged at 22 with the mixed hydrocarbon feed after which the steam may be condensed by cooler 62, and the water condensate may be employed in extractors 38 and 39. Alternatively, the steam leaving heat exchanger 22 may be advantageously employed in this or other processes (not shown). Heat exchange at 22 may result in the condensation of small amounts of aromatic selective solvent present in the steam (indicated at 22 by a dashed arrow). This solvent can be recycled to extraction column 24 by combining the solvent with the solvent from line 57 from distillation

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zone 52 (not shown). By such use of said process steam the heat input to the process may be minimized.

As above discussed alternative schemes may be substituted for that above-described for the removal of the anti-solvent, depending on the selection of the anti-solvent. The above described scheme is particularly advantageous in terms of the reduction in energy required to carry out the instant process. For example, the above-described extraction-decantation process results in a reduction in energy requirements for the dearomatization, as compared to conventional dearomatization processes, by as much as 50 percent to about 80 percent.

The total water in the system can be easily determined because the amount of water introduced at 46 to decantation tank (zone) 34 can be controlled. Allowances must be made for water losses through leakage and upsets so as to maintain the amount of water (the selected anti-solvent) present in decantation tank (zone) 34 at from about 0.5 to about 25.0 percent by weight and most preferably from about 5.0 to about 10.0 percent.

In carrying out examples 2 to 21 the process depicted in Figure 2 was employed wherein certain features discussed in reference to Figure 1 were not employed. The mixed hydrocarbon feed was introduced in line 70 from an external feed source (not shown) and was heated in heater 72. The heated feed then passed through line 74 to extraction column (zone) 76.

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Aromatic selective solvent was introduced near the top of extraction column 76 via line 104 after heating in heater 105. The aromatic selective solvent percolates the down column 76 removing aromatics from the hydrocarbon feed, forming raffinate and an aromatic rich solvent phase (hereinafter designated RS as the phase for rich-solvent). The raffinate containing primarily non-aromatics, exits the top of column 76 via line 78 and is collected as raffinate product. The viscosity index of the raffinate product is then measured by measuring the refractive index of the raffinate. at 60°C as hereinbefore discussed.

The RS phase in line 80, containing primarily aromatic selective solvent and aromatic hydrocarbons, is cooled in heat exchanger 82 (generally comprising one or more cold water heat exchanger in series) and is introduced to mixer 86. Mixer 86 may be an enlarged segment of the tubing employed to feed the contents of lines 84 and 86 to line 88 for introduction to decantation zone 90 or a conventional mixing means. Mixer 86 herein comprises a mechanical magnetic stirrer. Anti-solvent (in the instant examples water is the anti-solvent) is introduced via line 102 and the RS phase and the anti-solvent are mixed and introduced to decantation zone 90. In this embodiment the decantation zone may be a decantation tank or a fibrous bed coalescer as hereinbefore described. In addition, it may be desirable to employ a filter in line 88 (not shown), e.g., an in line cotton filter, to remove solids present in the

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phase in line 88. This is especially desirable when a fibrous bed coalescer is employed and such a filter was generally employed herein when a fibrous bed coalescer was employed. The anti-solvent may be added to decantation zone 90 directly if desired, i.e., line 102 may alternatively be introduced to decantation zone 90 although such is not preferred. As aforementioned, the addition of the anti-solvent reduces the solubility of the aromatic hydrocarbon in the aromatic selective solvent such that an aromatic-rich extract phase is formed and a solvent phase is formed containing predominantly solvent and anti-solvent (hereinafter referred to as the wet LS (lean solvent) phase).

The aromatic-rich extract phase of decantation zone 90 leaves decantation zone 90 through line 92.

The wet LS phase of decantation zone 90 leaves the decantaion zone via line 94 and was introduced to water stripper 96 wherein some portion of the water (the selected anti-solvent herein) in the wet LS phase was removed, condensed in water condenser 98 and introduced to water accumulator 100. Water, employed as the anti-solvent, is introduced via line 102, as required to provide the desired concentration of water (anti-solvent) in decantation zone 90. Solvent exits water stripper 96 (hereinafter referred to as the dry LS (lean solvent) phase via line 104 and is introduced to extractor zone 76 after heating in heater 105 as hereinbefore discussed. The dry LS phase contains some residual water and may contain up to about 5 percent by

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weight water or higher. Typically less than about 4 percent by weight water is present in the dry LS phase. As hereinbefore discussed, a small amount of oil is present in the dry LS phase.

The following examples are provided to illustrate the invention and are not to be construed as limiting such in any way.

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EXAMPLES 1

The above-described process, according to Figure 1, is employed for the dearomatization of a crude lubricating oil feedstock having a viscosity index of about 74 (as determined by ASTM Method D2270-75). The viscosity index is a measure of the amount of aromatic hydrocarbon present in the nonaromatic hydrocarbon. The amount of aromatic hydrocarbon present in the nonaromatic hydrocarbon decreases with increasing viscosity index. Thus, a viscosity index for the raffinate product greater than 74 indicates that dearomatization has occurred.

The aromatic-selective solvent is triethylene glycol and the anti-solvent is water. The temperature in the extraction zone is about 200°C., and the temperature in the decantation zone is about 140°C. The anti-solvent is present in the decantation zone in an amount from about 5.0 percent to about 8.0 percent by weight. The solvent to feed ratio in the extraction zone is about 6 to 1.

The raffinate product has a viscosity index of about 101 with the raffinate comprising about 80 to about 85 percent by weight of the crude lubricating oil feedstock.

EXAMPLES 2-4

The process as depicted in Figure 2 was carried out according to the Experimental Procedure and the above description of Figure 2 except that the decantation zone comprised a decantation tank with baffles to improve phase separation. Table 1 sets forth the results of examples 2 to 4. The feed employed in examples 2 to 4 was an unrefined lubricating oil containing predominately C₁₅ to C₂₇ paraffin and aromatic compounds. The viscosity indexes reported in Table I for the hydrocarbon feed and raffinate product are for feed and raffinate which are not dewaxed. The raffinate product yield is based on the waxy raffinate product.

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TABLE I

Example 1

	2	3	4
VI of Feed	77	78	78
Extraction Solvent to Feed Ratio ²	4.7	4.9	4.7
Dry LS Temperature (°C) ³	206	210	ND ⁶
Decantation Zone (°C)	145	146	146
H ₂ O in dry LS (wt %)	3.41	3.51	3.17
H ₂ O in RS (wt %)	3.52	3.13	3.12
Oil in dry LS (wt %) ⁵	2.63	2.22	1.85
H ₂ in wet LS (wt %)	6.76	11.18	11.55
Oil in wet LS (wt %) ⁵	2.59	2.29	2.13
Water stripper (°C) ⁴	158	154	158.5
VI of Raffinate	91	89	95
Raffinate Yield (volume %)	ND ⁶	87	78

- 1 Example 2 did not have baffles in the decantation tank.
- 2 Volume ratio
- 3 The Dry LS temperature introduced to the extraction zone is reported.
- 4 Temperature at the bottom of the water stripper.
- 5 The oil in the wet LS and dry LS phases is mostly aromatic feed components.
- 6 Not determined.

Examples 5 to 21

Examples 5 to 21 were carried out according to the process depicted in Figure 2 and the above described Experimental Procedure. The mixed hydrocarbon feed employed in examples 5 to 21 was a lubricating oil feedstock comprising a light paraffin distillate having viscosity indexes as reported in Table II. The results of examples 5 to 21 are set forth in Table II. The viscosity indexes reported in Table II for the feed and raffinate product are for feed and raffinate product which are not dewaxed. Raffinate yield is based on the waxy raffinate product.

TABLE II
Example 1

	5	6	7	8	9	10	11	12
VI of Feed	78	77	78	78	78	77	77	78
Extraction Solvent to Feed Ratio ²	5.3	4.8	4.6	4.7	6.1	6.1	6.0	4.8
Dry LS Temperature (°C) ³	226	229	230	227	228	227	230	216
Decantation Zone (°C)	36	36	38	39	38	39	38	90
H ₂ O in dry LS (wt %)	3.15	3.29	2.78	2.50	4.01	3.32	3.90	3.70
H ₂ O in RS (wt %)	3.06	3.16	2.94	2.42	3.92	3.22	3.81	3.58
Oil in dry LS (wt %) ⁵	1.08	1.43	1.09	1.19	0.91	1.27	0.96	1.58
H ₂ O in wet LS (wt %)	7.13	8.61	5.18	7.57	8.85	8.41	8.34	11.46
Oil in wet LS (wt %) ⁵	1.26	2.06	1.23	1.37	1.24	1.21	1.09	0.96
Water stripper (°C) ⁴	157	157	161	166	151	158	152	159
VI of Raffinate	104	105	106	106	107	108	107	95
Raffinate Yield (volume %)	77	76	76	80	76	71	74	87

1 Examples 5 and 6 developed a leak in the fibrous bed coalescer.

2 Volume ratio.

3 The Dry LS phase temperature when introduced to the extraction zone is reported.

4 Temperature at the bottom of the water stripper.

5 The oil in the wet LS and dry LS phases is mostly aromatic feed components.

TABLE II (cont'd)
Example 1

	13	14	15	16	17	18	19
VI of Feed	77	80	77	77	77	77	77
Extraction Solvent to Feed Ratio ²	4.8	4.7	8.4	6.2	6.2	6.2	6.2
Dry LS Temperature (°C) ³	213	217	226	226	226	227	227
Decantation Zone (°C)	85	57	37	38	37	36	36
H ₂ O in dry LS (wt %)	3.13	2.99	3.16	3.21	3.2	4.00	4.07
H ₂ O in RS (wt %)	3.02	3.06	3.16	2.77	2.92	4.06	3.88
Oil in dry LS (wt %) ⁵	2.00	0.88	1.86	1.10	1.19	0.99	0.85
H ₂ O in wet LS (wt %)	11.43	11.25	8.35	8.43	8.16	8.95	8.94
Oil in wet LS (wt %) ⁵	2.15	0.83	1.86	1.04	1.15	0.95	0.79
Water stripper (°C) ⁴	157	158	158	159	158	151	151
VI of Raffinate	98	100	104	106	108	107	106
Raffinate Yield (volume %)	84	85	75	72	69	72	74

- 1 Examples 5 and 6 developed a leak in the fibrous bed coalescer.
- 2 Volume ratio.
- 3 The Dry LS phase temperature when introduced to the extraction zone is reported.
- 4 Temperature at the bottom of the water stripper.
- 5 The oil in the wet LS and dry LS phases is mostly aromatic feed components.

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TABLE II (cont'd)
Example¹

	20	21
VI of Feed	77	77
Extraction Solvent to Feed Ratio ²	6.2	6.3
Dry LS Temperature (°C) ³	235	231
Decantation Zone (°C)	36	37
H ₂ O in dry LS (wt %)	4.13	3.98
H ₂ O in RS (wt %)	3.96	4.01
Oil in dry LS (wt %) ⁵	0.94	0.85
H ₂ O in wet LS (wt %)	9.08	9.32
Oil in wet LS (wt %) ⁵	1.05	0.95
Water stripper (°C) ⁴	151	151
VI of Raffinate	107	106
Raffinate Yield (volume %)	73	73

- 1 Examples 5 and 6 developed a leak in the fibrous bed coalescer.
- 2 Volume ratio.
- 3 The Dry LS phase temperature when introduced to the extraction zone is reported.
- 4 Temperature at the bottom of the water stripper.
- 5 The oil in the RS, wet LS and dry LS phases is a mixture of aromatic and monaromatic feed components.

CLAIMS

1. A process for the dearomatization of a mixed hydrocarbon feed characterised by the following steps:

(a) contacting said feed in an extraction zone at a temperature of at least about 150°C with an aromatic selective solvent to provide an aromatic-rich solvent phase containing aromatic hydrocarbons and aromatic selective solvent and a raffinate containing nonaromatic hydrocarbons;

(b) cooling said aromatic-rich solvent phase to bring about the formation of two phases;

(c) introducing said phases of the cooled aromatic-rich solvent phase to a decantation zone and introducing therewith from about 0.5 to about 25.0 percent by weight of an anti-solvent for said aromatic hydrocarbons in said aromatic selective solvent to provide an aromatic-rich extract phase containing primarily aromatic hydrocarbons and a solvent phase containing primarily aromatic selective solvent and anti-solvent;

(d) removing anti-solvent from said solvent phase and recycling said solvent phase to the extraction zone of step (a); and

(e) recovering as products the aromatic-rich extract phase of step (c) and the raffinate of step (a);

2. A process as claimed in claim 1, characterised in that the aromatic selective solvent is selected from the group consisting of polyalkylene glycols and mixtures thereof.
- 5 3. A process as claimed in claim 2, characterised in that the aromatic selective solvent is triethylene glycol.
4. A process as claimed in any one of the preceding claims characterised in that the anti-solvent in step (c) is employed in an amount from about 0.5 to about
10 15.0 percent by weight.
5. A process as claimed in claim 4, characterised in that the anti-solvent in step (c) is employed in an amount from about 5.0 to about 10.0 percent by weight.
6. A process as claimed in any one of the preceding
15 claims, characterised in that the anti-solvent is water.
7. A process as claimed in any one of the preceding claims, characterised in that the temperature in the extraction zone is from about 150°C to about 275°C.
8. A process as claimed in claim 7, characterised in
20 that the temperature in the extraction zone is from about 170°C to about 250°C.
9. A process as claimed in claim 8, characterised in that the temperature of the extraction zone is from about 200°C to about 240°C.
- 25 10. A process as claimed in any one of the preceding claims, characterised in that the temperature in the decantation zone is from about 25°C. to about 150°C.
11. A process as claimed in claim 10, characterised in that the temperature in the decantation zone is
30 to about 100°C.
12. A process as claimed in claim 11, characterised in that the temperature in the decantation is from about from about 25°C to about 100°C.

13. A process as claimed in any one of the preceding claims, characterised in that the ratio of solvent to feed in the extraction zone of step (a) is in the range of about 4 to about 12 parts by weight of solvent to one part by weight of feed.

14. A process as claimed in any one of the preceding claims, characterised in that it includes the additional step of separately contacting the raffinate and aromatic-rich extract of step (e) with water to form two water phases containing primarily water and aromatic selective solvent.

15. A process as claimed in claim 14, characterised in that it includes the additional step of recovering the aromatic selective solvent of the water phases and recycling said solvent to step (c).

16. A process as claimed in any one of the preceding claims for the dearomatization of a mixed hydrocarbon feed comprising a lubricating oil fraction which is characterised by the following steps:

(a) contacting said feed at a temperature of from about 150°C to about 275°C in an extraction zone with triethylene glycol to provide an aromatic-rich solvent phase containing primarily aromatic hydrocarbons and triethylene glycol and a raffinate containing primarily nonaromatic hydrocarbons;

(b) cooling said aromatic-rich solvent phase to bring about the formation of two phases;

(c) introducing said phases of the cooled aromatic-rich solvent phase to a decantation zone at a temperature of from about 25°C to about 70°C and introducing therewith from about 0.5 to about 25.0 percent by weight water to provide an aromatic-rich extract phase containing primarily aromatic hydrocarbons and a solvent phase containing primarily triethylene glycol

and water;

(d) distilling water from the triethylene glycol;

(e) recycling the triethylene glycol of step

5 (d) to step (a);

(f) separately contacting the raffinate of step (a) and the aromatic-rich extract of step (c) with water to form two water phases containing primarily water and triethylene glycol;

10 (g) combining the water phases of step (f);

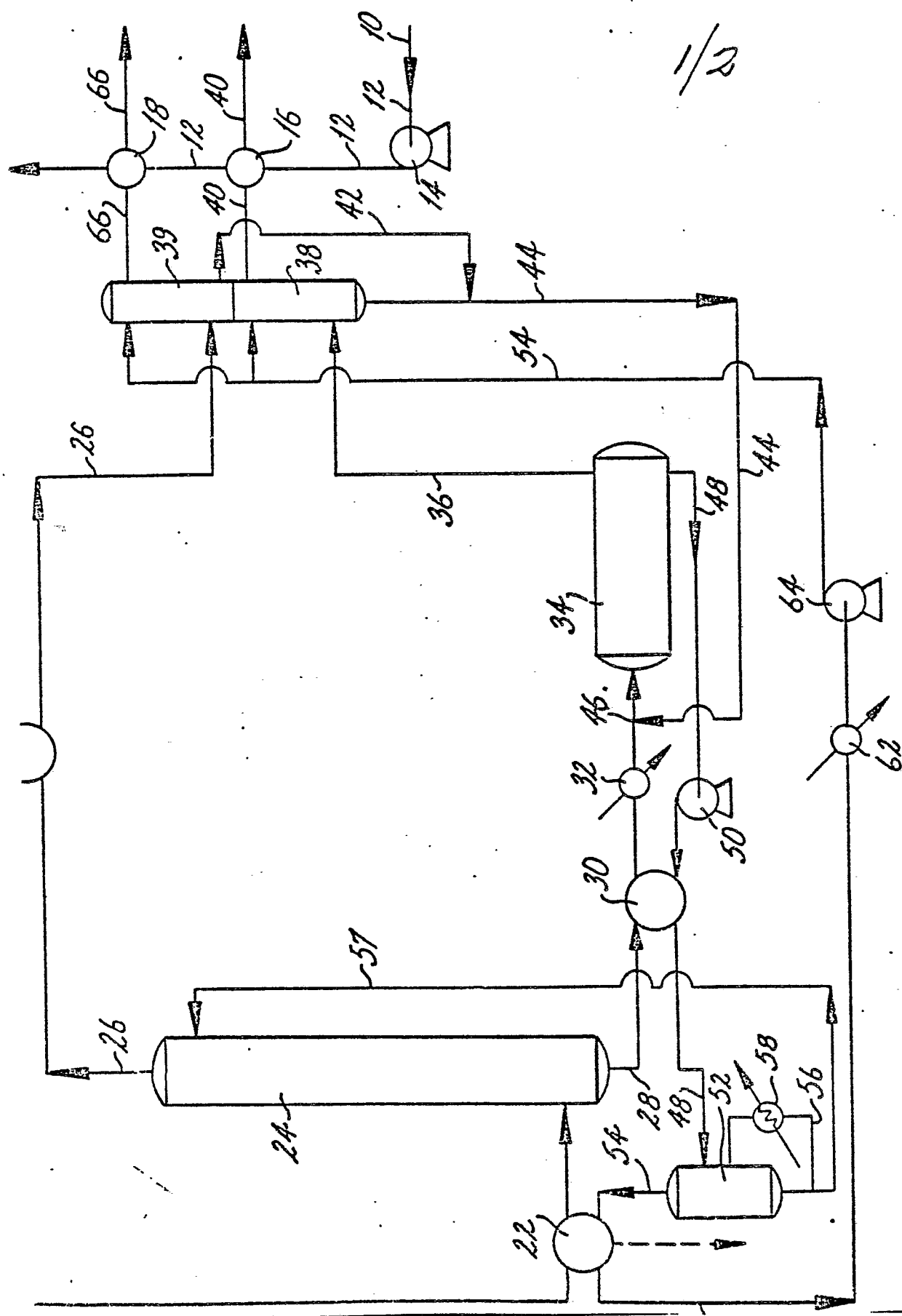
(h) recycling at least a portion of the combined water phase of step (g) to step (c); and

(i) recovering the aromatic-rich extract and raffinate of step (f).

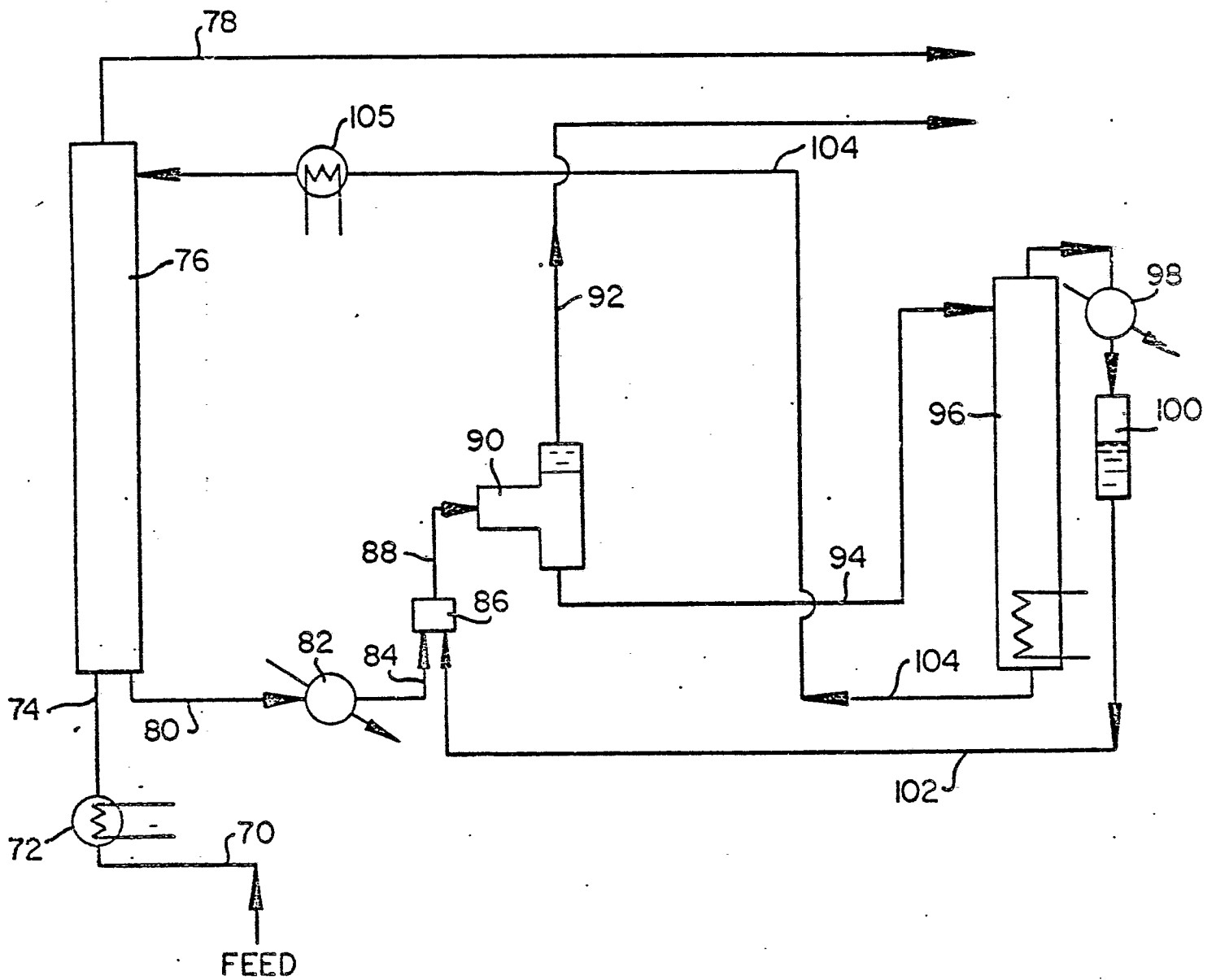
15 17. A process as claimed in any one of the preceding claims, characterised in that less than about two percent by weight aromatic hydrocarbon is present in the solvent phase of step (c).

20 18. Product of a process as claimed in any one of the preceding claims.

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EUROPEAN SEARCH REPORT

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Application number

EP 81 30 2928

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.3)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	<u>US - A - 2 698 831 (F. TEYKL)</u> * Column 2, lines 7-34; column 3, lines 19-47; column 4, lines 1-23; claims 1-6 *	1,4,6, 10-12	C 10 G 21/02 21/28
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	<u>GB - A - 865 698 (SHELL)</u> * Page 2, lines 3-114; page 3, lines 25-83; claims 1-14; figure *	1,2	
	--		
	<u>US - A - 2 754 249 (H.C. MYERS)</u> * Column 2, lines 6-46; column 3, lines 7-35; column 3, line 71 - column 4, line 49; column 6, line 2 - column 7, line 17; claims 1,2; figure 2 *	1,4-6, 10-12, 16	C 10 G 21/00 21/02 21/28
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	<u>US - A - 2 261 287 (C.L. REED)</u> * Page 1, left-hand column, line 46 - page 2, left-hand column, line 38; claims 1,2; figure *	1,4-6, 10-12	
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D	<u>US - A - 2 400 802 (G.B. ARNOLD)</u> * Page 1, left-hand column, line 42 - page 2, right-hand column, line 48; claims 1-6 *	1-3,7- 13	CATEGORY OF CITED DOCUMENTS X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
DA	<u>US - A - 3 291 728 (A.A. BOYUM)</u>		
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The present search report has been drawn up for all claims			&: member of the same patent family, corresponding document
Place of search The Hague		Date of completion of the search 13-10-1981	Examiner LO CONTE