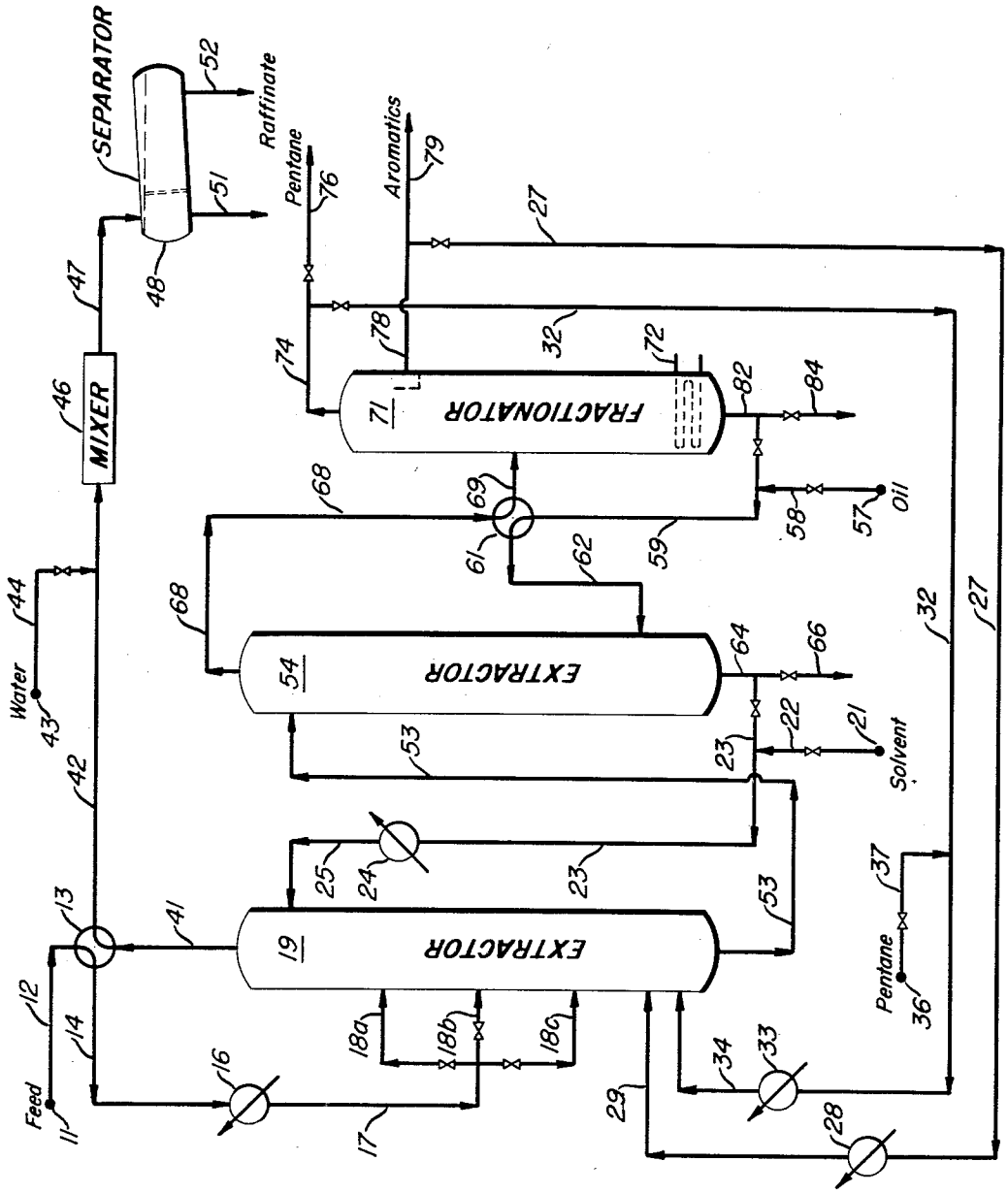
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SOLVENT RECOVERY IN SOLVENT EXTRACTION

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SOLVENT RECOVERY IN SOLVENT EXTRACTION

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This invention relates to solvent extraction of hydrocarbon mixtures. More particularly the invention relates to the recovery of the solvent from the extract phase formed in the solvent extraction of hydrocarbon mixtures.

Hydrocarbons naturally occur as mixtures of the various classes of hydrocarbons, namely, paraffinic, olefinic, naphthenic and aromatic. Usually the mixture contains slight amounts of compounds containing oxygen and/or sulfur. These mixtures have been separated into more or less pure classes of compounds by means of selective solvents such as phenol, liquid SO_2, glycols, liquid propane, alcohols, etc.,Generally the solvent is recovered from solution with the extract hydrocarbons by evaporation and/or distillation. The usefulness of certain of the well known solvents is seriously limited by relatively low decomposition temperatures.

Recently certain of the glycols have been used in commercial processes for the recovery of aromatic hydrocarbons from petroleum naphthas in spite of the relatively low decomposition temperature of these glycols. The incipient decomposition temperature of diethylene glycol is 327° F. and of triethylene glycol is 403° F. In this process operation at decomposition temperature is avoided by the use of a solution of glycol and water, which solution has a boiling point markedly lower than the boiling point of the glycol itself.

Another well known method for avoiding operation at the decomposition temperature of glycols takes advantage of the relatively low miscibility of aromatic hydrocarbons and glycols at ordinary atmospheric temperatures. In this process a solution of polyethylene glycol and water is used to extract aromatic hydrocarbons from petroleum naphtha at temperatures between about 200° and 300° F., the solvent-aromatic hydrocarbon phase is separated and the aromatic hydrocarbons forced out of solution in the solvent by cooling the extract phase to about 100° F. Obviously this method is uneconomic in regard to heat consumption.

An object of this invention is the separation of hydrocarbon mixtures by treatment thereof with a glycol solvent. Another object is the recovery of glycol solvent from a solution of glycol and hydrocarbons under conditions avoiding thermal decomposition of said solvent. A particular object is the recovery of glycol solvent for reuse in the extraction process without lowering the temperature of the solvent-hydrocarbon solution appreciably below the temperature of the solvent-feed contacting zone. A more particular object is the recovery of glycol solvent by a liquid-liquid extraction operation utilizing a liquid hydrocarbon oil to remove extract hydrocarbons from the glycol-hydrocarbon solution and thereby regenerate the glycol solvent. A preferred object is a combination process wherein a petroleum naphtha which contains aromatic hydrocarbons is extracted with a polyethylene glycol to obtain an extract phase, and the glycol is regenerated for reuse in the process by contacting the extract phase with a liquid hydrocarbon oil that is essentially immiscible in the glycol and is miscible with the extract hydrocarbons and recovering the extract hydrocarbons from solution in said oil by distillation. Other objects will become apparent in the course of the detailed description of the invention.

It has been found that glycol suitable for reuse in a solvent extraction step can be obtained from a glycol-hydrocarbon solution by contacting said solution with a liquid hydrocarbon oil which is essentially immiscible in said solvent and is miscible with the extract hydrocarbons in an amount sufficient to remove essentially completely the extract hydrocarbons from the glycol-hydrocarbon solution. Preferably the liquid hydrocarbon oil has a boiling range markedly different from the boiling range of the extract hydrocarbons in order that the extract hydrocarbons may be readily separated therefrom by distillation.

The feed to the process of this invention consists of a mixture of hydrocarbons from at least two of the broad classes, paraffinic, naphthenic, olefinic and aromatic, such as naturally occur in petroleum or the products from hydrocarbon conversion processes. A preferred feed consists of petroleum naphthas containing large amounts of aromatic hydrocarbons, e. g., catalytically cracked naphthas and the naphtha boiling range material from catalytic reforming in the presence of hydrogen. Examples of these stocks are hydroformate and platformate. The process is also applicable to the separation of olefins and diolefins as in the separation of butadiene from admixture with butanes and butenes or to the separation of styrenes from ethylbenzene and xylenes. Other feeds which may be charged to this process are kerosenes, heater oils, gas oils and lube oil distillates. In general the process is applicable to any feed which is susceptible to separation by treatment with a glycol solvent.

The selective solvents utilized in this process are broadly known as glycols, i. e., the dihydric alcohols. Particularly desirable solvents are the polyglycols, i. e., polymeric glycols containing ether linkages. The halogen and the other derivatives of glycols are also suitable solvents for this process. Particular examples of the solvents are ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, ethylene glycol monomethyl ether, ethylene glycol diethyl ether, propylene glycol monoethyl ether. The preferred solvents are the polyethylene glycols.

The solvent power of these glycols improves at elevated temperatures. Therefore, normally a selective solvent extraction process using glycol solvent operates at temperatures between about 100° F. and the incipient thermal decomposition temperature of the particular glycol. More usually the contacting zone is maintained at a temperature between about 200° and 300° F. It is to be understood that certain of the polyglycols are solids at ordinary temperatures and the temperature maintained in the process must be at least high enough to maintain these particular glycols in the liquid state. Furthermore, the process is a liquid-liquid operation and sufficient pressure must be maintained on the system to keep the solvent, the feed and the hydrocarbon oil in the liquid state.

It has been found that the glycol solvent can be recovered for reuse in the process by contacting the glycol-hydrocarbon solution, i. e., extract phase, with a liquid hydrocarbon oil which is essentially immiscible with the glycol and is miscible, or substantially so, with the extract hydrocarbons. Sufficient hydrocarbon oil should be used to remove essentially completely the extract hydrocarbons from the glycol. The use of smaller amounts of hydrocarbon oil results in circulation of extract hydrocarbons in the system and a decrease in overall yield of the desired extract hydrocarbons. Since the extract hydrocarbons are usually the desired product of the process, it is preferred that the liquid hydrocarbon oil be readily

separable from these extract hydrocarbons; preferably the liquid hydrocarbon oil boils in a range appreciably different from the boiling range of the extract hydrocarbons—thereby the hydrocarbon oil and the extract hydrocarbons are readily separable by distillation.

The solubility of paraffinic hydrocarbons in glycols is extremely low. Naphthenic hydrocarbons are also only very slightly soluble in glycols. These hydrocarbons are essentially completely miscible with virtually all hydrocarbons for which glycols have appreciable solvent power. The most suitable liquid hydrocarbon oil for the glycol recovery step of this process consists substantially of paraffinic hydrocarbons, naphthenic hydrocarbons and mixtures thereof. The liquid hydrocarbon oil may have a boiling range either lower than or higher than the boiling range of the extract hydrocarbons. It is preferred to use a hydrocarbon oil having a higher boiling range.

Suitable hydrocarbon oils may be obtained either from special crudes or more usually by the refining of distillates from ordinary crudes. Examples of suitable hydrocarbon oils are: The highly refined product obtained by acid treating or liquid SO_2 extraction of kerosene distillates. The white oils, i. e., either technical grade or white mineral grade oils, meeting the U. S. Pharmacopoeia standards obtained by very heavy acid treating of various distillates. Lubricating oils obtained by selective solvent extraction of distillates from paraffinic and naphthenic-type crudes. Paraffin waxes are particularly suitable when operating at temperatures appreciably above the melting point of the wax.

When the feed to the process consists of a mixture of olefins and diolefins the diolefins may be recovered from the extract phase by contacting the extract phase with a liquid hydrocarbon oil consisting either of olefins or paraffins or naphthenes. That is, a liquid hydrocarbon oil essentially immiscible in the glycol solvent under the conditions of contacting of the oil and the extract phase.

The preferred liquid hydrocarbon oil is paraffinic or naphthenic or mixture thereof which boils appreciably above the boiling point of the extract hydrocarbons.

The annexed drawing which is made a part of this specification shows an illustrative embodiment of the process of this invention. It is to be understood that many items of equipment and details of operation are omitted where these can be readily supplied by those skilled in this art.

In the drawing the feed is a hydroformate naphtha obtained from the cracking of a virgin heavy naphtha over a cobalt molybdena catalyst in the presence of hydrogen. This hydroformate has an ASTM end point of about 385° F. and contains benzene, toluene, ethylbenzene and xylene as the aromatic hydrocarbon constituents. Substantially no olefinic hydrocarbons are present in this feed.

Feed from source **11** is passed through line **12** through heat exchanger **13** wherein the temperature is raised by indirect contact with hot raffinate phase. From exchanger **13** the feed is passed by way of line **14** through heat exchanger **16**, line **17** and manifold **18***a*, **18***b*, **18***c* into extractor **19**. In heat exchanger **16** the feed is raised to about the temperature of operation of extractor **19**.

In this embodiment the feed is introduced at about the vertical mid-point of extractor **19** by way of valved line **18***b*. However, the feed may be introduced at various points along the height of extractor **19** as illustrated by lines **18***a*, **18***b* and **18***c*. The type of feed and operating conditions will determine the exact point of feed inlet into extractor **19**.

Extractor **19** is a vertical tower equipped to provide intimate contact of two immiscible liquids of different densities. Extractor **19** may be filled with conventional tower packing such as Raschig rings, Berl saddles, spheres, or may be provided with contacting trays such as bubble trays or perforated plates.

Extractor **19** is operated at an elevated temperature appreciably lower than the incipient decomposition temperature of the triethylene glycol solvent used herein. In this embodiment extractor **19** operated at a temperature of 275° F. Although extractor **19** may in some cases be operated with a temperature gradient over the height of the vessel, in this embodiment a substantially constant temperature is maintained throughout the vessel.

In some cases it is desirable to operate with a glycol-water solution as the selective solvent, e. g., a solution of diethylene glycol containing between about 5 and 10 volume percent of water. In this embodiment an essentially anhydrous triethylene glycol solvent is used.

The amount of solvent used per volume of feed is dependent upon the type of feed, the type of glycol and operating conditions in extractor **19**. In general the amount of solvent used may be between about 1 and 25 volumes per volume of feed, preferably between about 5 and 15 volumes. In this embodiment 8 volumes of triethylene glycol are used per volume of feed.

In order to improve the selectivity of extraction a reflux stream of aromatic hydrocarbons is introduced near the bottom of extractor **19** by way of valved line **27**, heat exchanger **28** and line **29**. The aromatic hydrocarcarbons used as reflux have the same composition as the aromatic hydrocarbon product. The amount of reflux used will vary with the degree of selectivity desired on a particular piece of equipment. In general it will be between about 2 and 10 volumes per volume of aromatic hydrocarbon extracted from the feed, i. e., product aromatic hydrocarbon; herein the ratio of reflux to product is 6:1.

Although the selectivity of the glycol solvent is very good, some non-aromatic hydrocarbons are extracted from the feed. These non-aromatic hydrocarbons boil in the range of the aromatic hydrocarbons and cannot be separated by fractional distillation. In order to improve the purity of the aromatic hydrocarbon product, it is desirable to remove these close boiling non-aromatic hydrocarbons. This is accomplished in this embodiment by introducing a wash oil into extractor **19** just above the extract phase outlet. The wash oil should be a hydrocarbon that is easily separable from the product aromatic hydrocarbons by distillation. In this embodiment pentane is used as the wash oil. Pentane is introduced into extractor **19** by way of line **32**, heat exchanger **33** and line **34**. Makeup, or fresh, pentane may be introduced from source **36** into line **32** by way of valved line **37**. In this embodiment the amount of pentane introduced into extractor **19** is about 1 volume per volume of aromatic hydrocarbon product. Of course this amount may be varied in accordance with the requirements of any particular operation.

A raffinate phase consisting of substantially dearomatized feed naphtha and some occluded and dissolved solvent is withdrawn from the top of extractor **19** by way of line **41**. This hot raffinate phase is passed through heat exchanger **13** where it raises the temperature of fresh feed, thereby saving heat. The cooled raffinate phase is passed from heat exchanger **13** into line **42** where it is contacted with water from source **43** and line **44**. The water-raffinate phase stream is intimately agitated in mixer **46** for a time sufficient for the water to dissolve the solvent present in the raffinate phase. The amount of water used must be at least enough to form a separate aqueous phase. In this illustration about 5 volume percent of water based on raffinate phase is used. A countercurrent tower may be used to contact the water and raffinate phase and thereby lessen the water usage.

The contents of mixer **46** are passed by way of line **47** into separator **48**. In separator **48** the aqueous phase of water and solvent separated from the raffinate hydrocarbons and is withdrawn by way of line **51**. Raffinate hydrocarbons are withdrawn from separator **48** by way of line **52** and are passed to storage not shown.

Under some conditions of operation an essentially glycol-free raffinate can be obtained by simple settling of

the raffinate phase at ordinary atmospheric temperatures. Water washing is used to recover the glycol solvent in this embodiment in order to minimize losses of solvent. The aqueous solution may be stripped of water by various methods well known to the art and then returned to the process. When operating with a glycol-water solvent the glycol-water solution may be returned directly to the process in order to provide makeup water to the system.

Extract phase is withdrawn from the bottom of extractor **19** by way of line **53** and is passed into an upper portion of extractor **54**. Extractor **54** is a vessel similar to construction to vessel **19**. Makeup liquid hydrocarbon oil from source **57** is passed by way of valved line **58** into valved line **59** where it meets a circulating stream of liquid hydrocarbon oil. The oil in line **59** is passed through heat exchanger **61** and through line **62** into a lower portion of extractor **54**. In heat exchanger **61** the liquid hydrocarbon oil is dropped to the temperature of operation of extractor **54** which is about that of extractor **19**, i. e., about 275° F. Normally the temperature in extractor **54** will be a few degrees lower than that of extractor **19** because of unavoidable heat losses.

The liquid hydrocarbon oil used in this embodiment is a solvent-extracted heavy kerosene essentially free of aromatic hydrocarbons. This kerosene boils between about 450° and 575° F. The amount of kerosene used is dependent upon the type of aromatic hydrocarbons present in extractor **54**, the type of solvent used and operating conditions in extractor **54**. The amount of oil used may be between about 1 and 25 volumes of oil per volume of aromatic hydrocarbons present in the extract phase introduced into extractor **54**. In this embodiment 9 volumes of kerosene are used per volume of aromatic hydrocarbons.

A second raffinate phase is withdrawn from extractor **54** by way of line **64**. This second raffinate phase consists of regenerated triethylene glycol solvent and contains only a trace amount of hydrocarbon material. The regenerated solvent is recycled to extractor **19** by way of valved line **23**, heat exchanger **24** and line **25**, or the solvent may be withdrawn from the system by way of valved line **66**.

A second extract phase is withdrawn from extractor **54** by way of line **68**. This second extract phase consists essentially of kerosene, aromatic hydrocarbons, pentane and trace amounts of solvent. The extract phase in line **68** is passed through heat exchanger **61** and line **69** into fractionator **71**.

Fractionator **71** is provided with reboiler **72**. Fractionator **71** shows schematically the distillative separation of the second extract phase into a pentane fraction, an aromatic hydrocarbon fraction and a bottoms fraction. A pentane fraction is taken overhead from fractionator **71** by way of line **74** and is recycled to extractor **19** by way of valved line **32**, heat exchanger **33** and line **34**, or pentane may be removed from the system by way of valved line **76**.

In this embodiment all of the aromatic hydrocarbons present in the second extract phase are shown as being removed by way of a side-draw-off from fractionator **71**. This aromatic hydrocarbon fraction is withdrawn by way of line **78**. The requisite amount needed for reflux in extractor **19** is withdrawn and is passed by way of line **27**, heat exchanger **28** and line **29** to extractor **19**. The product aromatic hydrocarbons are passed by way of line **79** to storage and further processing not shown.

The product aromatic hydrocarbons may be separated by distillation into a benzene fraction, a toluene fraction and a C_8 aromatic hydrocarbon fraction. Nitration grade materials may be obtained either by acid treating each fraction or by vapor phase clay treating.

The bottoms fraction from fractionator **71** consists essentially of kerosene. This bottoms fraction is withdrawn by way of line **82** and is recycled to extractor **54** by way of valved line **59**, heat exchanger **61** and line **62**. In heat exchanger **61** the hot recycle oil is reduced in temperature to about 275° F. by indirect contact with the second extract phase from line **68**. The bottoms from fractionator **71** may be withdrawn from the system by way of valved line **84**.

The following example is cited to illustrate the results obtainable by this invention:

An extract phase was prepared by dissolving benzene in triethylene glycol. The synthetic extract phase consisted of 80 volume percent of triethylene glycol and 20 volume percent of benzene. Triethylene glycol was selected for this illustration because of its greater solvent power for benzene at the temperature to be used in the test.

The liquid hydrocarbon oil used in this test was an acid-treated kerosene. This kerosene is characterized below. The presence of about 9 volume percent of aromatic hydrocarbons is particularly pointed out:

ASTM distillation, ° F.:	
IBP	512
10% rec	553
20%	562
30%	568
40%	570
50%	574
60%	580
70%	584
80%	590
90%	596
FBP	614
Refractive Index, n_D^{25}	1.4554
Specific gravity, 60° F	0.8303
Bromine number	0.42
Total aromatics by sulfonation, vol. %	8.9

The extract phase was contacted countercurrently with the oil in a York-Scheibel extraction tower which provided about 40 mechanical stages. The extract phase was charged near the top of the extractor at a rate of 200 ml. per minute. The oil was charged near the bottom of the extractor at a rate of 300 ml. per minute. Thus 7.5 volumes of oil were used per volume of benzene present in the extract phase. The extractor was maintained at a uniform temperature of 275° F.

The benzene-oil phase was withdrawn from the top of the tower and was distilled. The distillation column was 8 inches in diameter and contained 12 feet of one-half inch Berl saddles. A reflux ratio of 10:1 was used. Stripping steam was introduced into the column because the maximum attainable bottoms temperature was only 347° F. The oil completely freed of benzene was recovered as a bottoms product from the distillation operation. A benzene product containing no oil was recovered from the top of the column.

The glycol phase removed from the bottom of the extractor was carefully fractionated and found to contain only 0.6 volume percent of hydrocarbon material. Analysis of this hydrocarbon material indicated that about 20 volume percent consisted of aromatic hydrocarbons boiling above benzene—apparently derived from the aromatic hydrocarbon constituents of the kerosene. This regenerated triethylene glycol can be used as a selective solvent with essentially no impairment of extraction efficiency.

A separate test was made on the solvent power of a kerosene-benzene solution for triethylene glycol. A kerosene-benzene solution containing 40 volume percent of benzene was contacted with triethylene glycol at 275° F. It was found that the kerosene-benzene solution did not dissolve a measurable amount of the triethylene glycol.

Thus having described the invention, what is claimed is:

1. An aromatic hydrocarbon recovery process which comprises (1) contacting a liquid petroleum naphtha containing appreciable amounts of aromatic hydrocarbons with liquid triethylene glycol solvent under conditions to

form extract and raffinate phases, (2) separating an extract phase comprising solvent and aromatic hydrocarbons from a raffinate phase, (3) contacting said extract phase with a kerosene essentially free of aromatic hydrocarbons under conditions to form a second raffinate phase consisting essentially of triethylene glycol solvent and a second extract phase consisting essentially of aromatic hydrocarbons and kerosene, (4) separating said second raffinate phase from said second extract phase and recycling said second raffinate phase to the naphtha contacting zone (1), (5) recovering aromatic hydrocarbons by distillation from said second extract phase and (6) recycling the recovered kerosene to the extract phase contacting zone (3), wherein said naphtha contacting zone and said extract phase contacting zone are operated at substantially the same temperature.

2. The process of claim 1 wherein the volume ratio of kerosene to aromatic hydrocarbon present in said extract phase charged to said extract phase contacting zone (3) is about 8.

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