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SEPARATION OF AROMATIC HYDROCARBON MIXTURES

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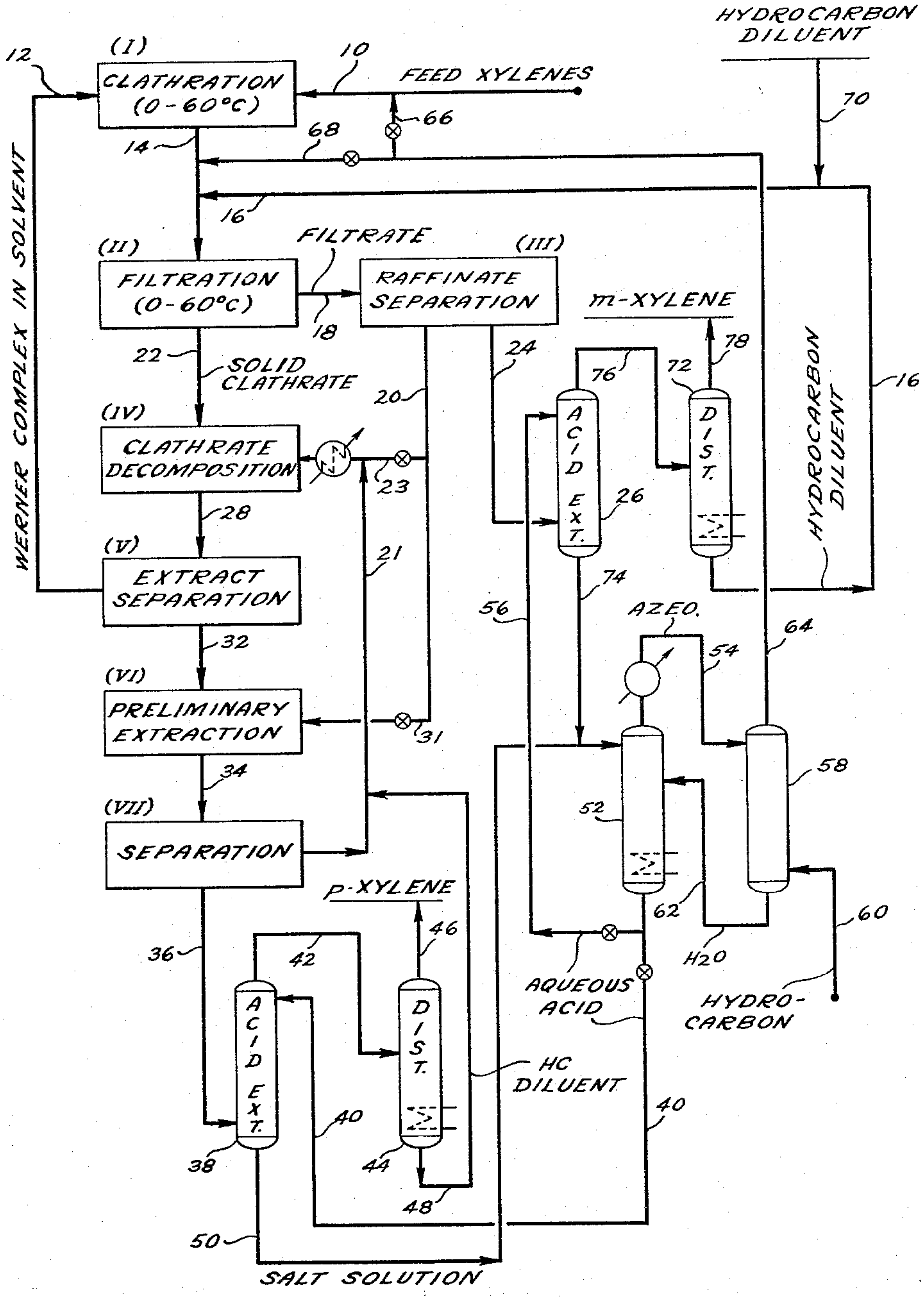

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SEPARATION OF AROMATIC HYDROCARBON MIXTURES

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This application is a continuation-in-part of application Serial No. 65,641, filed October 28, 1960, now abandoned.

This invention relates to the separation of mixtures of aromatic hydrocarbons, particularly xylene isomers, by selective clathration with Werner complexes of organic nitrogen bases and metal salts. More specifically, the clathration process involves the use of clathration solvents comprising mixtures of water and a lower aliphatic hydroxy compound, e.g. glycols, or lower alkanolamines, in which the feed mixture of aromatic hydrocarbons is relatively insoluble, and in which the Werner complex is relatively soluble at high temperatures and relatively insoluble at low temperatures. The invention is particularly concerned with methods for recovering the aromatic hydrocarbon product streams essentially free of the metal salt and organic nitrogen base components of the Werner complex.

In the clathration process of this invention as normally practiced, the aromatic hydrocarbon feed mixture is first contacted with a solution of the Werner complex in the clathration solvent at a relatively high temperature, and the mixture is then cooled to precipitate the Werner complex, which in precipitating selectively clathrates one or more components of the feedstock, e.g. para-xylene. The resulting three-phase mixture is then separated into a raffinate hydrocarbon phase, a solid clathrate phase, and a lean clathration solvent phase. The solid clathrate is thereafter redissolved in the lean clathration solvent at a relatively high temperature, thus liberating the clathrated hydrocarbon, which is separated as an immiscible liquid phase from the hot Werner complex solution. A troublesome problem in these solvent clathration processes resides in the fact that the organic nitrogen base component of the Werner complex, and to a lesser extent the metal salt component thereof, are soluble in the raffinate and extract hydrocarbon products. This problem is particularly acute in respect to the extract hydrocarbon product, since it is separated from the Werner complex solution at relatively high temperatures which favor dissociation of the Werner complex, with resultant heavy contamination of the extract hydrocarbon phase with organic nitrogen base and metal salt. Since the raffinate hydrocarbon phase is separated at relatively lower temperatures, while the Werner complex is in a solid clathrate form, there is relatively less contamination of the raffinate hydrocarbon stream.

According to the present invention, the raffinate hydrocarbon stream is purified by a simple stripping with aqueous acid solution, and the resulting aqueous solution of organic nitrogen base salt is stripped with steam to recover an azeotrope of water and the nitrogen base, the nitrogen base then being recovered from the condensed azeotrope by extraction with a suitable hydrocarbon. It has been found, however, that this technique is impractical when used alone for purifying the extract hydrocarbon phase. As noted, this phase is more heavily contaminated with organic nitrogen base and metal salt, and direct acid stripping thereof leads to a substantial loss of metal salt in an essentially non-recoverable form, and to prohibitive expense in the azeotropic distillation step for recovering the nitrogen base from its acid salt (due to the large volume of steam required to strip the nitrogen base from its salt). To overcome this difficulty, the extract hydrocarbon phase is first subjected to a preliminary extraction step with at least a portion of the lean clathration solvent which was separated from the raffinate hydrocarbon stream. By this procedure, the bulk of the nitrogen base and nearly all of the metal salt contaminant is extracted from the extract hydrocarbon stream, and the partially purified extract hydrocarbon phase may then be subjected to stripping with aqueous acid to recover the small remaining amount of nitrogen base dissolved therein, and a negligible amount of metal salt is lost during the extraction.

In a preferred aspect of the invention, a diluent paraffinic hydrocarbon is added to the clathration mixture in the raffinate separation step, and is also present during the extract separation step, whereby both the raffinate and the extract aromatic hydrocarbons are diluted with paraffin hydrocarbon, thereby further repressing solubility of oganic nitrogen base and metal salt in the respective product streams. The paraffinic hydrocarbon is preferably one which boils sufficiently above or below the product hydrocarbon streams to be readily separated therefrom by distillation. If desired, the paraffinic hydrocarbon employed may be the same hydrocarbon used for separating the nitrogen base from its condensed water azeotrope obtained from the aqueous salt distillation step.

The process of this invention is related to that described in my U.S. Patent No. 3,049,575, but differs therefrom in certain important respects. In the process of said patent, a single, multiple purpose aqueous alkanolamine solvent is used as the clathration medium, and for stripping nitrogen base from the product streams. While this process is entirely feasible and is advantageous in some respects, it suffers from the disadvantage that the aqueous alkanolamine clathration solvent is not highly selective for stripping nitrogen base from the product hydrocarbon streams. Hence, a large number of extraction stages are required to reduce the nitrogen base content of the product streams to desired low levels of e.g. 1–10 parts per million. The process of this invention provides an optimum combination of a single-stage extraction with the clathration solvent to recover the bulk of organic nitrogen base and nearly all the metal salt from the extract hydrocarbon product stream only, followed by aqueous acid extraction to recover the small remaining amounts of nitrogen base from both of the hydrocarbon product streams.

Although it has been determined that many acids are applicable to extract the nitrogen base from the product hydrocarbon streams, it has been found that certain organic acids exhibit more of the desired properties. Among desired properties, the acid should be reasonably soluble in water, yet be relatively insoluble in hydrocarbons. The water solubility of the acid should be at least about 1%, and preferably above about 10% by weight, at 20° C. The solubility in hydrocarbons should be below 0.5% and preferably below 0.05%.

Further, the acid should exhibit good extraction properties, i.e., its salts with the nitrogen bases should also be more soluble in water than in hydrocarbons. Even though the organic acid is substantially insoluble per se in hydrocarbons, it has been found that as the degree of neutralization of the acid increases, relatively more of it becomes dissolved in the hydrocarbons, whether as free acid or as salt. This is particularly pronounced when xylene is the hydrocarbon. It is therefore preferred to employ a stoichiometric excess of acid, relative to the nitrogen base to be extracted, preferably about 1 to 3 times the stoichiometric amount required for completely neutral salts.

As the molar concentration of the acid in the aqueous solvent is increased, more nitrogen base is distributed in the resulting salt extract rather than in the raffinate hydrocarbon phase. The concentration of the acid solution should therefore be between about 0.5 and 5 molar, and preferably between about 1–3 molar.

The resultant aqueous salt extract formed by the extraction is fractionally distilled to recover as overhead between about 65–95 percent of the nitrogen base contained therein, and the aqueous acid is recovered as bottoms which is recycled to extract additional quantities of the nitrogen base. An azeotrope of water and nitrogen base is obtained as overhead when nitrogen bases boiling in the pyridine-picoline range are used.

The acidity of the acid used is also a critical operative factor. For maximum efficiency in the extraction step, maximum acidity would, of course, be desirable. But, for maximum recovery of nitrogen base during the subsequent distillation, a minimum acidity would be desirable. These two factors can be conveniently balanced against each other, and operative limits defined, by using the product of the respective dissociation constants of the acid and nitrogen base as the yardstick. It is found in general that if this product is between about 10^{-10} and 10^{-20}, an effective extraction and distillation can be effected. Preferably, the product figure should lie between about 10^{-12} and 10^{-18}. This means, of course, that stronger acids will be used in conjunction with weak bases. In the case of the picolines, suitable acids should have a dissociation constant between about 10^{-4} and 10^{-6}.

It is also desirable that the acid be relatively involatile and stable under process conditions. Its boiling point should be above the boiling point of the nitrogen base or its water azeotrope; otherwise the acid will become a contaminant in the overhead nitrogen base stream.

Organic acids found to be acceptable are the monocarboxylic acids such as acetic, propionic, n-butyric, isobutyric and n-valeric; polybasic acids having the desired properties are, by way of example, citric, oxalic, succinic, adipic, and pimelic, and blends thereof as well as many others. Hydroxy acids such as glycollic, lactic, maleic and the like may also be used. The preferred acids are the lower aliphatic polybasic and hydroxy acids containing from 2 to about 12 carbon atoms, from 2 to 6 carboxyl groups, and up to about 4 hydroxyl groups.

The condensed azeotrope of nitrogen base and water may be washed with an aliphatic or aromatic hydrocarbon, or blends thereof, in order to separate the nitrogen base from the water. The substantially water-free nitrogen base-hydrocarbon mixture is recycled to the clathration system. Although virtually any aliphatic or aromatic hydrocarbon or blends thereof are applicable for recovering the nitrogen base, it is preferred to employ all or a portion of the aromatic hydrocarbon feed to the clathration process. Alternatively, the hydrocarbon may be the paraffinic diluent to be employed in the raffinate and extract-separation steps.

The clathration solvents employed herein include in general one or more lower aliphatic hydroxy compounds in admixture with water, sufficient water being added to render the feed hydrocarbons substantially insoluble and the Werner complex relatively soluble at high temperatures and insoluble at low temperatures. Suitable lower aliphatic hydroxy compounds include for example glycols, glycol monoethers, glycerol monoethers, polyalkylene glycols, lower mono- and dialkanolamines, and the like. The preferred hydroxy compounds are the lower monoalkanolamines, and specifically monoethanolamine. Other alkanolamines which may be employed include diethanolamine, triethanolamine, 2-amino-n-butanol, 2-amino-2-methyl-1-propanol, 2-methylamino ethanol, 2-amino-2-ethyl-1,3-propanediol, 2-amino-2-methyl-1,3-propanediol, and the like. In general any lower alkanolamine containing from two to about ten carbon atoms, from one to three amino groups, and from one to three hydroxyl groups, may be employed, including primary, secondary and tertiary amines.

The operative ratios of alkanolamine in the clathration solvent may vary widely, e.g., from about 2 percent to 75 percent by weight, the remainder being water. Preferred ratios generally fall within the range of about 10 percent to 50 percent. The greater the concentration of alkanolamine in the solvent, the greater will be the solubility of Werner complex and feed mixture therein. It is preferred to use sufficient water to render the feed substantially insoluble, i.e. less than about 2%.

It has been found that the aqueous lower alkanolamine clathration solvents exhibit a large temperature coefficient of solubility for the Werner complexes employed herein. For example, when a saturated solution of Werner complex in such solvents is reduced in temperature by only about 25° to 75° C., the Werner complex is precipitated almost quantitatively. It has also been found that if the feed mixture to be separated is agitated or slurried with the Werner complex solution during precipitation from the aqueous alkanolamine solution, a remarkably efficient (in termn of specific resolution and clathration capacity) selective clathration takes place. It has also been discovered that the resulting solid clathrate may be easily and completely dissolved in the aqueous alkanolamine solution by simply raising the temperature about 25° to 75° C., thereby liberating the clathrated component and reforming the Werner complex solution for use in the clathration step. The liberated clathrated component may then be easily recovered by decantation, settling, distillation, solvent extraction or the like.

The non-clathrated component of the feed mixture (raffinate) is separated from the clathration slurry either before or after separation of the solid clathrate therefrom. Following removal of clathrate and raffinate, the aqueous alkanolamine solution, usually containing some dissolved nitrogen base and Werner complex, may then be reheated to e.g. 60–150° C., and used to dissolve the clathrate, thereby "springing" the clathrated compound (extract) and regenerating the Werner complex solution. Thus, a continuous recycle of aqueous alkanolamine and Werner complex may be maintained.

Reference is now made to the accompanying drawing which illustrates a continuous modification of the process. This modification will be described with reference to the separation of xylene isomers using aqueous monoethanolamine as the basic clathration solvent component, but it will be understood that the process is broadly applicable, with slight modifications, to the separation of other mixtures using other clathration solvents within the purview of this invention. The Werner complex employed in this modification is tetra(4-methylpyridine) nickel dithiocyanate, but other Werner complexes and components thereof may also be used. The organic acid employed to extract 4-methylpyridine from the hydrocarbon product streams is succinic acid, but a great many others are also to be considered applicable. The term nitrogen base will be used interchangeably with 4-methylpyridine, but this invention is to be considered applicable for recovering other nitrogen bases.

In clathration step (I) the feed mixture, comprising p- and m-xylene, is introduced through line **10** and a recycle solution of clathration solvent rich in Werner complex is introduced through line **12**. Clathration is effected in this step by thoroughly agitating the mixture at temperatures between about −50° and +80° C., and preferably between 0° and 40° C. It is ordinarily not feasible to employ such low temperatures as to obtain quantitatively complete precipitation of the Werner complex. This, however, is primarily a matter of preference and economics and is not a critical aspect of the invention. The initial solution of Werner complex may contain from about 10 to 60 percent by weight of Werner complex, and it is ordinarily feasible to reduce this concentration to about 0.5 to 5 percent by lowering the temperature of the solution by about 25°–75° C. The initial clathration solvent mixture may contain between about 5 percent and 80 percent by weight ethanolamine, preferably between about 10 percent and 50 percent, the remainder being water.

Upon the desired completion of clathrate formation the resulting clathrate slurry is withdrawn via line **14** and transferred to separation step II which can be a centrifuge filter, settler or any other suitable means for separating solids from liquids. It has been found desirable, however, to admix with the slurry prior to solids separation a suitable paraffin or naphthenic hydrocarbon diluent via line **16**, in order to dilute the raffinate xylene phase, thereby facilitating its separation from the adhering solid clathrate. As noted, aromatic hydrocarbons such as xylenes have some slight solvent capacity for the Werner complex components, and the addition of paraffin or naphthene hydrocarbons is found to reduce substantially the solubility of the Werner complex components in the raffinate xylene phase. Any liquid paraffin or naphthene hydrocarbons may be used for this purpose, but for additional purposes to be described hereinafter, it is preferred to use hydrocarbons boiling in the range of about 115°–230° C., heart cuts from alkylate gasolines or decane, hendecane, dodecane, tridecane, isooctane, or mixed hydrocarbon fractions boiling in this range, such as a 180° to 200° C. alkylate fraction. Suitable proportions of hydrocarbon diluent may range between about 0.5 and 10 volumes per volume of raffinate xylenes.

The liquid filtrate from separation step II consists of two liquid phases, viz., (1) a raffinate phase comprising m-xylene, diluent paraffin hydrocarbons and a small quantity of the nitrogen base compound, and (2) an aqueous solvent phase. This filtrate mixture is transferred via line **18** to step III, where stratification is allowed to take place and a phase separation is effected. The raffinate from step III, containing m-xylene, diluent and about 3–6% of 4-methylpyridine, is transferred by line **24** to a liquid/liquid acid extraction column **26**, where countercurrent extraction takes place under conventional conditions. The clathration solvent phase from step III is removed via line **20**, and utilized in subsequent steps of the process to be described hereinbelow.

The solid clathrate from step II is withdrawn via line **22** and blended with hot clathration solvent in step IV to effect declathration of the extract hydrocarbons (p-xylene) by dissolution of the Werner complex in the solvent with resultant "springing" of the p-xylene. The hot clathration solvent used in step IV is derived primarily by recycle via line **21** from separation step VII to be subsequently described. This recycle stream of clathration solvent constitutes the primary portion of the lean clathration solvent which was separated in step III and passed via line **20** to preliminary extraction step VI, followed by separation step VII, and thus includes redissolved metal salt and nitrogen base stripped from the p-xylene in step VI and VII. This preliminary extraction step VI does not ordinarily require all of the solvent separated in step III, and hence a portion thereof may be diverted directly to step IV via line **23**.

Since the clathration solvent introduced into step IV is at a temperature about 25° to 75° C., higher than the clathration temperature in step I, the solid clathrate rapidly becomes dissolved, thus liberating the clathrated xylene phase and forming a clathration solvent rich in Werner complex. The resulting two-phase liquid mixture is then passed via line **28** to extract-separation step V. One phase, the rich clathration solvent mixed with the Werner complex, is withdrawn therefrom and recycled via line **12** to clathration step I. The other phase, or extract xylene phase, containing p-xylene, hydrocarbon diluent, substantial quantities of 4-methyl pyridine as well as metal salt from the Werner complex, is withdrawn via line **32** and introduced into preliminary extraction step VI, where it is subjected to solvent extraction at a temperature of e.g. 20–50° C. with lean clathration solvent introduced via line **31**. By virtue of this preliminary extraction step, the metal content of the extract p-xylene is reduced to below about 10 p.p.m. (from an initial concentration generally in the range of about 20–50 p.p.m.), and the nitrogen-base contents is reduced to levels in the range of about 2–10% by weight (from an initial concentration in the range of about 10–20 weight-percent). This is ordinarily accomplished in a single stage by simple agitating in a suitable mixing vessel the extract p-xylene phase and the lean solvent phase.

The two-phase mixture from preliminary extraction step VI is then transferred via line **34** to phase separation step VIII, wherein clathration solvent is separated and recycled via line **21** to step IV as previously described, and the p-xylene extract phase is taken off via line **36** and sent to acid extraction column **38**, which may be a conventional packed column for countercurrent solvent extraction.

The procedure for extracting nitrogen base from the p-xylene extract phase in column **38** is identical to that for extracting the nitrogen base from the m-xylene raffinate phase. Hence, the succeeding description of acid extraction in column **38** will also apply to the procedure employed in extraction column **26**.

The object of the acid extraction is to remove the nitrogen base from the extract phase in order to recover the same, and at the same time provide a pure p-xylene product. These objects may be realized by washing the p-xylene extract phase with a 1.5 molar aqueous succinic acid solution introduced into the extractor **38** via line **40**, and absorption by the acid of the nitrogen base is effectively accomplished in an economical 3-stage extractor, such being the strong affinity of the acid solution for the nitrogen base. The extraction is normally carried out at temperatures in the range of about 20–50° C. The purified p-xylene phase, substantially free of nitrogen-base and nickel is removed overhead via line **42** and transferred to distillation column **44**. Purified p-xylene product is withdrawn overhead from column **44** via line **46**, while the aliphatic diluent is recovered as bottoms via line **48** and recycled to clathrate decomposition step IV via line **21**, where it acts as a diluent for the p-xylene recovered from the clathrate, and effectively inhibits solubility of nitrogen base and metal salt in the recovered p-xylene.

The aqueous salt extract from extraction column **38** is transferred via line **50** to azeotropic distillation column **52**, where the salt is thermally decomposed and 4-methyl pyridine is recovered overhead as a water azeotrope via line **54**. For maximum operating efficiency, the aqueous salt extract should be added at the top of the distillation column just below the head, with no reflux being employed. Changing the feed location, however, affects the results only to a relatively small degree.

In distillation column **52**, the well-known salt-acid-base equilibrium is involved:

$$\text{Salt} \rightleftarrows \text{Acid} + \text{Base}$$

The free base in equilibrium with the salt is volatilized as its water azeotrope. Of course, as 4-methylpyridine removal proceeds, the relative concentration of acid builds up until finally a state is reached ("pinch" effect) that requires massive amounts of boilup to remove additional amounts of 4-methylpyridine. To overcome this tendency, it is desirable to increase the degree of dissociation of the salt. This is accomplished by increasing the temperature. It has been determined that the increase in 4-methylpyridine volatility with increasing temperature is quite pronounced. Thus, at 98° C. and 753 mm. of mercury the overhead from the distillation is about 12.17 percent 4-methylpyridine. Under this condition, only about 75% of the 4-methylpyridine can be recovered economically. But, by increasing the temperature to 150° C. by increasing the pressure, the overhead then contains about 20% 4-methylpyridine. This is a 65 percent increase in the volatility of 4-methylpyridine. Therefore, at 150° C. about 93 percent of the entering 4-methylpyridine may be recovered. This recovery level regenerates the acid solution with sufficient completeness that virtually all of the 4-methylpyridine may then be recovered from the clathration product streams in a 3-stage extraction. Therefore the preferred distillation temperature is between about 35°–300° C. and preferably between 100°–175° C.

The bottoms from distillation column **52** is aqueous succinic acid which is recycled in part to extraction column **38** via line **40**, and in part to acid extraction column **26** via line **56**. The overhead azeotrope of water and 4-methylpyridine is condensed and transferred via line **54** to countercurrent extraction column **58**, where it is scrubbed with a hydrocarbon solvent, preferably all or a portion of the xylene feed mixture, which is introduced via line **60**. Extracting a nitrogen base such as 4-methylpyridine from water with an aliphatic or aromatic hydrocarbon has been found to be remarkably efficient. The 4-methylpyridine shows a decided and distinct affinity for the hydrocarbon, and in many cases a single stage extraction may be utilized, thus eliminating the need for a countercurrent extraction column. The stripped aqueous phase from column **58** is withdrawn as bottoms via line **62** and returned to distillation column **52**. The nitrogen base-hydrocarbon extract from column **58** is withdrawn overhead via line **64**, and, if the hydrocarbon solvent employed is the feed mixture of xylenes, is sent directly to clathration step I via lines **66** and **10**. However, if paraffinic hydrocarbon solvents are employed, it is preferred to divert all or a portion of the paraffinic diluent in line **16** to line **60**, and the resulting hydrocarbon extract in line **64** is recycled to line **14** via line **68**. Additional paraffinic hydrocarbon makeup diluent may be added via line **70**.

The m-xylene raffinate recovered via line **24** from step III is treated in acid extraction column **26** and distillation column **72**, in a manner identical to the recovery of p-xylene in columns **38** and **44**. Aqueous nitrogen base salt extract from column **26** is transferred via line **74** to azeotropic column **52** where it is treated in conjunction with the salt extract from column **38**. The m-xylene diluent mixture recovered from extraction column **26** is transferred to distillation column **72** via line **76**, from which pure m-xylene is recovered overhead via line **78**, and high-boiling diluent as bottoms via lines **16**, which is recycled to step II as previously described.

The Werner-type complexes employed herein are made up of at least three components. The fundamental unit is a water-soluble salt of a metal having an atomic number above 12 which is capable of forming coordinate complexes of the Werner-type. This includes primarily the metals of groups IB, IIB, IVB, VIIB, and VIII of the Periodic Table, such for example as iron, cobalt, nickel, copper, zinc, cadmium, silver, manganese, chromium, mercury and molybdenum. Aluminum may also be used in some instances. The preferred metals are those of atomic number 25 to 28 inclusive, i.e., manganese, iron, cobalt and nickel.

The anion of the metal salt may comprise any acid-forming negative radical, the salts of which will form relatively water-insoluble Werner complexes with heterocyclic nitrogen bases. The preferred anions are polyatomic monovalent anions, such as thiocyanate, isothiocyanate, azide, cyanate, isocyanate and cyanide. Other operable anions include formate, acetate, propionate, and the like.

The second major component of the Werner complexes consists of one or more organic nitrogen base or bases, which are bound to the central metal atom through coordinate bonds. The operative complexes are mainly of the tetra- and hexa-coordinate types, wherein the metal atom is coordinated with four or six atoms of basic nitrogen. The nitrogen base should be selected so as to give a maximum selective absorption for the particular compound which is to be absorbed into the crystal lattice of the complex. For example, if it is desired to absorb p-xylene, a very suitable nitrogen base is 4-methylpyridine. Not all nitrogen bases are equally effective in forming complexes which will absorb the desired component. For example, the 3-methylpyridine complex with nickel thiocyanate is not as effective as the 4-methylpyridine complex for absorbing para-xylene, presumably because of the steric effects of the 3-methyl group. However, the 3-methylpyridine complex may be used advantageously for absorbing other compounds. The nitrogen bases should therefore be selected by a judicious combination of theoretical reasoning and actual testing of the complexes with the particular mixture to be separated.

In general, any organic nitrogen base may be employed which is sufficiently basic to form coordinate complexes with the above-described salts. This includes monocyclic and polycyclic compounds wherein at least one of the heterocycles contains from one to three hetero-N atoms, benzylamines, α-lower alkyl benzylamines and the like. In over-all size, the nitrogen base may contain from three to about thirty carbon atoms, preferably from four to fifteen. Interfering functional groups such as —COOH should be absent, but other more neutral, relatively non-coordinating functional groups may be present such as halogen, hydroxyl, nitro, alkoxy, aryloxy, amino, cyano, carboalkoxy, alkanoyl, acetyl, etc. Examples of suitable bases include pyridine, substituted pyridines, piperidines, substituted piperidines, and the like.

A particularly preferred class of heterocyclic bases are the resonance-stabilized bases which contain one to three, but preferably one, hetero-N atoms. Suitable examples are pyridine, the picolines, pteridine, triazole, quinoline, the quinaldines, isoquinoline, pyrimidine, pyrazine, pyridazine, and substituted derivatives of such compounds. Of this preferred class, a subgroup which is particularly versatile and useful comprises the substituted pyridines, and especially the 4-substituted, the 3-substituted, and the 3,4-disubstituted pyridines. These compounds form relatively stable Werner complexes capable of selectively forming clathrates stable at room temperatures with a wide variety of aromatic compounds. Suitable substituted pyridines comprise the following:

4-methyl pyridine
4-ethyl pyridine
4-n-propyl pyridine
4-isopropyl pyridine
4-n-butyl pyridine
4-vinyl pyridine
4-chloro pyridine
4-hydroxy pyridine
4-hydroxymethyl pyridine
4-methoxy pyridine
4-amino pyridine
methyl isonicotinate
4-cyano pyridine
4-acetyl pyridine
4-chloromethyl pyridine
3-methyl pyridine
3-ethyl pyridine
3-isopropyl pyridine
3-vinyl pyridine
3-chloro pyridine
3-hydroxy pyridine
3-methoxy pyridine
3-acetyl pyridine

3-cyano pyridine
ethyl nicotinate
3,4-dimethyl pyridine
3,4-diethyl pyridine
3-methyl, 4-ethyl pyridine
4-methyl, 3-ethyl pyridine
4-methyl, 3-cyano pyridine
4-acetyl, 3-methyl pyridine
4-methoxy, 3-ethyl pyridine
isoquinoline

Many other similar examples could be cited, as will be apparent to those skilled in the art, and the complexes may include only one such base, or a mixture of two or more may be employed, in which case a mixed complex may be formed.

The preferred Werner complexes of monovalent anion salts of this invention may be designated by the following general formula:

$$[A_nX\cdot Z_y]$$

wherein X is the metal atom as above defined, Z is the heterocyclic nitrogen base, A is the anion as above defined, *y* is a number from 2 to 6, and *n* is a number from 1 to 3.

Examples of suitable complexes which may be employed are as follows:

$[\mathrm{Ni}\ (\gamma\text{-picoline})_4(\mathrm{SCN})_2]$
$[\mathrm{Co}\ (\gamma\text{-picoline})_4(\mathrm{SCN})_2]$
$[\mathrm{Co}\ (\text{pyridine})_4(\mathrm{OCN})_2]$
$[\mathrm{Fe}\ (\gamma\text{-picoline})_4(\mathrm{SCN})_2]$
$[\mathrm{Co}\ (\gamma\text{-picoline})_4(\mathrm{CN})_2]$
$[\mathrm{Ni}\ (\text{4-methylpyridine})_4(\mathrm{NNN})_2]$
$[\mathrm{Ni}\ (\text{4-n-propylpyridine})_4(\mathrm{SCN})_2]$
$[\mathrm{Ni}\ (\text{isoquinoline})_4(\mathrm{SCN})_2]$
$[\mathrm{Ni}\ (\text{4-ethylpyridine})_4(\mathrm{SCN})_2]$
$[\mathrm{Mn}\ (\text{4-methylpyridine})_4(\mathrm{SCN})_2]$
$[\mathrm{Mn}\ (\text{isoquinoline})_4(\mathrm{SCN})_2]$

Obviously many other complexes similar to the above could be employed, not all of which would give optimum separation of all mixtures, but which should be selected to meet the specific peculiarities of the mixture concerned.

The amount of complex to be employed, relative to the feed mixture, depends upon its specific capacity for absorbing the particular feed component concerned, and also upon the proportion of that component present in the original mixture, as well as upon the temperature of clathration. The complexes are found in general to be capable of absorbing between about 5% to 70% by weight of absorbable compounds. Optimum efficiency may require that more or less than this "stoichiometric" amount of complex be employed, depending upon its relative capacity for other components in the mixture to be resolved. In general, the amount of complex to be employed may vary between about 0.25 and 20 parts by weight per part of the feed component to be clathrated. Smaller proportions of complex will generally yield a purer extract, while the larger proportions result in more complete recovery of absorbable components from the feed mixture.

A wide variety of feed mixtures may be resolved by the methods described herein. These methods are operative for separating substantially any mixture of hydrocarbons wherein the components differ in molecular configuration, and wherein at least one component is substantially aromatic or cyclic in character. By "substantially aromatic" is meant that at least about 20% of the carbon atoms in the molecules to be clathrated are present as digits of an aromatic ring. Any remaining carbon atoms may be present as saturated or unsaturated aliphatic side-chains, or saturated or unsaturated non-aromatic ring systems. Such compounds may contain a total of from 4 to 60 carbon atoms, preferably from 6 to 20.

Examples of mixtures which may be separated herein include the following, but these examples are by no means exhaustive.

o-xylene m-xylene	prehnitene durene
p-xylene ethylbenzene	durene isodurene
o-xylene p-xylene	prehnitene isodurene
m-xylene p-xylene	cyclohexane benzene
o-ethyl toluene p-ethyl toluene	methyl-cyclohexane toluene
o-ethyl toluene m-ethyl toluene	benzene n-heptane
mesitylene pseudocumene	benzene 2,3-dimethyl pentane
cumene mesitylene	methyl cyclopentane benzene
cumene pseudocumene	picene chrysene
p-cymene p-diethylbenzene	picene 1,2,5,6-dibenzenthracene
m-cymene mesitylene	cyclohexane methyl cyclopentane

The following examples are cited to illustrate more concretely the results obtaintable in the practice of this process, but are not to be construed as limiting in scope.

Examples 1 and 2 serve to illustrate that aqueous solutions of organic acids are exceptionally effective to extract 4-methylpyridine from hydrocarbon streams.

EXAMPLE 1

To a separatory funnel was added 50 ml. of an aqueous solution containing 2.5 grams of dissolved succinic acid, 2 ml. of 4-methylpyridine and 50 ml. of hydrocarbon (25% xylene-75% isooctane). After equilibration, the phases were separated and the 4-methylpyridine content determined in each by titration.

Phase	Vol. (ml.)	Grams, 4-methyl-pyridine
Hydrocarbon	50	0.00161
Aqueous	52	0.0394

In this example the distribution of 4-methylpyridine was 24.5–1 in favor of the aqueous solution.

EXAMPLE 2

To a separatory funnel was added 48 ml. water, 2.0 ml. of acetic acid, 2.0 ml. of 4-methylpyridine and 50 ml. of hydrocarbon mixture (25% xylene-75% isooctane). After equilibration the phases were separated and the 4-methylpyridine content determined in each by titration. The results are shown below:

Phase	Vol. (ml.)	Grams, 4-methyl-pyridine
Hydrocarbon	50	0.00258
Aqueous	52	0.0379

This example shows the distribution of 4-methylpyridine is 14.8–1 in favor of the aqueous solution.

Example 1, contrasted with Example 2, further illustrates that a dibasic organic acid is more effective in extracting 4-methylpyridine from hydrocarbon streams than monocarboxylic acids.

EXAMPLE 3

In order to demonstrate the effect of acid concentration on the efficiency of extraction of a nitrogen base from a hydrocarbon stream the following tabulated data is provided showing the equilibrium distribution prevailing in a one-stage extraction:

Aqueous Succinic Acid Concentration	Pounds of Nitrogen Base [1]/Pound of Acid Solution	Pounds of Nitrogen Base/Pound of Hydrocarbon [2]
0.5 molar	.070	.010
Do	.080	.015
Do	.085	.020
Do	.100	.030
1.27 molar	.110	.010
Do	.140	.020
Do	.150	.025
Do	.160	.030
1.6 molar	.140	.010
Do	.150	.013
Do	.170	.020
Do	.190	.028

[1] 4-methylpyridine.

[2] 75% isoctane, 25% xylenes.

From the data presented it can be seen that aqueous succinic acid possesses a strong affinity for 4-methylpyridine.

Also, it may be seen that the extraction of the nitrogen base from a hydrocarbon stream is a function of the concentration of the acid. The greater the concentration of the acid, the smaller the volume of acid required.

EXAMPLE 4

In order to demonstrate that 4-methylpyridine can be distilled from aqueous acid solutions, prepared synthetic mixtures were distilled through a short glass-helix packed column.

A small distillation column was charged with a mixture containing 100 ml. of water, 5 ml. (0.083 mole) of acetic acid and 7 ml. (0.071 mole) of 4-methylpyridine. The mixture was distilled very rapidly until a total of 22 ml. of overhead product was collected. An aliquot of the overhead was titrated and found to be 18.1 weight percent 4-methylpyridine. The overhead contained 60 percent of the 4-methylpyridine charged to the still.

EXAMPLE 5

Another distillation was performed in the same column employed in Example 4, using 150 ml. of water containing 7.5 grams (0.063 mole) of succinic acid, and 7 ml. (0.071 mole) of 4-methylpyridine. Again, the mixture was distilled rapidly and a total of 27 ml. of product collected. An aliquot of the overhead was titrated and found to be 12.4 weight-percent 4-methylpyridine. The overhead contained 50.7 percent of the 4-methylpyridine charged to the still.

EXAMPLE 6

In order to demonstrate that a major portion and a commercially practical quantity of 4-methylpyridine can be distilled from aqueous succinic acid solutions, a synthetic mixture was prepared containing: 119 ml. of water, 12.7 grams (0.107 mole) succinic acid and 10.1 grams (0.115 mole) of 4-methylpyridine. It will be noted that only one of the carboxyl groups of succinic acid was completely neutralized in this mixture and the mixture was distinctly acid to litmus paper. Nevertheless, on distillation 4-methylpyridine was taken overhead. The distillation was performed in the same column used in Examples 4 and 5 under similar conditions. The results are shown below:

Cut No.	Vol. (ml.)	Wt. Percent 4-methylpryidine	Wt. Percent of 4-methylpyridine Charged
1	12	22.0	26.0
2	17.	9.5	41.9
3	15	9.1	65.2
4	11	10.0 (some reflux used)	76.0
5	22.5	3.3	83.3

The above data shows that up to about 76% of the 4-methylpyridine can be recovered efficiently, but that after this point is reached, the amount of 4-methylpyridine in the overhead decreases rapidly, and a large boil-up is required to effect further recovery.

Although 75 percent removal of 4-methylpyridine from aqueous hydrogen-4-methylpyridinium succinate solution is sufficient for commercial operation it is desirable to increase 4-methylpyridine recovery in order to increase the efficiency and capacity of the aqueous succinic acid solvent for the extraction step. It has been determined as previously stated that increases in temperature increase the relative volatility of 4-methylpyridine whereas decreases in temperature decrease the volatility. These conditions are reflected in Example 7.

EXAMPLE 7

The changes in 4-methylpyridine volatility with changes in reflux temperature may be demonstrated in the following way: A 1.5 molar solution of hydrogen 4-methylpyridinium succinate was charged to an Othmer equilibrium still and the mixture distilled until phase equilibrium was attained at a specific temperature and pressure. The experiment was then repeated with a fresh sample of feed at a different temperature and pressure. In each experiment after phase equilibrium was attained the 4-methylpyridine content in the vapor was measured. The data obtained as well as that extrapolated is shown in the following table.

Volatility of 4-methylpyridine vs. reflux temperature

Vapor Temp., ° C.	Pressure, mm. Hg	4-methylpyridine Content in Vapor (Wt. Percent)
150.0	2,586	20.10
125.0	1,293	15.60
100.0	760	12.18
98.0	753	12.16
79.5	353	10.17
63.8	178	8.17
49.0	93	6.37

The above data show that the volatility of 4-methylpyridine from aqueous hydrogen 4-methylpyridinium succinate increases with increasing temperature, or pressure. Therefore, in order to enhance the recovery of 4-methylpyridine, elevated temperatures should be employed, entailing superatmospheric pressures.

EXAMPLE 8

The 4-methylpyridine is recovered from the distillation as the 4-methylpyridine-water azeotrope. In order to recycle the 4-methylpyridine to the process it should be relatively anhydrous. In the clathration process, relatively large quantities of a paraffinic or naphthenic hydrocarbon may be used as a diluent, and this material is available for extracting 4-methylpyridine. In order to test the feasibility of this scheme, several equilibrium distribution experiments were conducted on the system:

water, isooctane and 4-methylpyridine. These experiments were made at 65° C. and the data are shown below:

Materials Added, ml. (25° C.)			Products (65° C.)				D*
			H_2O Phase		i-Octane Phase		
H_2O	i-Octane	4-methylpyridine	Vol. (ml.)	g. 4-MP/g. H_2O	Vol. (ml.)	g. 4-MP/g. i-octane	
25	50	10	28.5	0.14	56.5	0.183	1.31
25	50	5	26.5	0.0496	54.5	0.1076	2.17
25	50	2	26.0	0.0182	51.0	0.044	2.42

D*=Distribution Coeff.=grams 4-methylpyridine/gram i-octane/grams 4-methylpyridine/gram H_2O.

These data show that at 65° C. the distribution of 4-methylpyridine decidedly favors isooctane, and that one extraction stage is suitable for recovering most of the 4-methylpyridine for recycle to the clathration process.

EXAMPLE 9

Run No. 1: To a 300 ml. 3-necked flask equipped with a stirrer, condenser and thermometer is added 40 g. of $Ni(4\text{-methylpyridine})_4(SCN)_2$, 40 ml. of ethanolamine and 120 ml. of water. The mixture is heated and stirred until solution is complete (92° C.). To the hot solution is added 23 ml. of feed xylenes and the mixture is cooled to 25° C. in a water bath, resulting in precipitation of solid clathrate. After stirring at 25° C. for 10 minutes, 40 ml. of isooctane is added and, after an additional 2 minutes of stirring, the mixture is filtered. The filtrate consists of two liquid phases: a clear and colorless raffinate hydrocarbon phase and a blue aqueous solvent phase. The phases are separated, and the solid clathrate is redissolved in the aqueous solvent phase at 92° C., liberating the extract xylenes. Analysis of the respective xylene phases gives results tabulated in Table I.

The results of three other runs conducted in a manner analogous to the above, but using somewhat different solvent ratios and compositions, are also given in Table 1:

TABLE 1

Run No.	Volume Percent MEA[1] in Solvent	Weight Ratio, Solvent: Werner Complex	Sol'n. Temp.,[3] ° C.	Feed	Isomer Distribution				Recovery[2]	
					Para 14.8	Meta 81.2	Ortho 0.6	Et. Bz 3.4	Para	Meta
1	25	4.0	92	Extract xylenes	47.2	47.0	0.3	5.5	92.6	16.5
				Reject xylenes	0.9	96.4	0.5	2.2	7.4	83.5
2	33	3.0	83	Extract xylenes	48.3	46.1	0.3	5.4	92.9	18.9
				Reject xylenes	1.2	95.6	0.6	2.6	7.1	81.1
3	40	3.0	73	Extract xylenes	49.4	45.2	0.2	5.2	93.8	18.1
				Reject xylenes	1.2	95.9	0.5	2.4	6.2	81.9
4	45	3.0	64	Extract xylenes	52.3	42.5	0.2	5.0	90.1	17.4
				Reject xylenes	1.5	95.2	0.5	2.8	9.9	82.6

[1] MEA=monoethanolamine.

[2] Vol. percent isomer charged recovered in that phase.

[3] Temperature required to dissolve the clathrate in the solvent portion employed.

EXAMPLE 10

This example illustrates the degree of contamination of product m-xylene and p-xylene streams produced as described in Example 9, with 4-methylpyridine and nickel. It also demonstrates that the p-xylene stream is much more heavily contaminated than the m-xylene stream, and that a single-stage preliminary extraction with the aqueous clathration solvent gives a marked reduction in contamination. It further illustrates the desirable effect of the paraffinic hydrocarbon diluent in repressing solubility of 4-methylpyridine and nickel in the product streams. The preliminary extraction in each case consisted of contacting approximately six volumes of the MEA-water clathration solvent with one volume of the p-xylene-diluent stream at room temperatures. The results were as follows:

TABLE 2

Product Stream	Ratio Xylene to Aliphatic Hydrocarbon (By Volume)	Weight Percent 4-methylpyridine	Nickel Concentration (p.p.m.)
M-xylene	49:51	7.9	25.0
P-xylene (before contacting with MEA-water solvent)	17:83	14.9	>50
P-xylene (after contacting with MEA-water solvent)	17:83	5.3	<2
M-xylene	32:68	6.5	5.3
P-xylene (before contacting with MEA-water solvent)	19:81	16.6	>50
P-xylene (after contacting with MEA-water solvent)	19:81	6.3	<2
M-xylene	23:77	5.0	<2
P-xylene (before contacting with MEA-water solvent)	16:84	15.6	>40
P-xylene (after contacting with MEA-water solvent)	16:84	5.3	<2

It will be observed that a single-stage extraction in all cases reduced the nickel concentration of the p-xylene stream from initial levels above 40–50 p.p.m. to less than 2 p.p.m. The 4-methylpyridine content of the p-xylene streams was also reduced to levels comparable to that of the m-xylene streams.

If these p-xylene streams were sent directly to the acid extraction step, prohibitive amounts of nickel would be lost to the acid solution, and the azeotropic distillation procedure for recovering 4-methylpyridine from its salt solution would require a prohibitively large amount of steam.

EXAMPLE 11

This example illustrates the large temperature coefficient of solubility of the aqueous alkanolamine solvents for Werner complexes. The solubility of nickel tetra(4-methylpyridine)dithiocyanate in the 40% ethanolamine-

60% water solvent, was determined at various temperatures, with the following results:

TABLE 3

Temperature, ° C.:	Solubility of Werner complex, gms./100 gms. solvent
0	1.6
15	3.3
25	5.3
35	8.0
73	33.2

Thus, when using a clathration temperature of 0° C. and a solution temperature of 73° C., over 95% of the Werner complex can be precipitated during clathration, and all of the resulting clathrate can be redissolved at 73° C.

In the event that the xylene feed stream were substituted for the isooctane in Example 8, even more favorable results would be obtained due to the increased solubility of 4-methylpyridine in xylenes. Indeed, 4-methylpyridine removal by xylene is so efficient that extraction may be accomplished in a single extraction stage if desired.

The foregoing disclosure of this invention is not to be considered as limiting since many variations may be made by those skilled in the art without departing from the scope or spirit of the following claims.

I claim:

1. A clathration process for resolving a feed mixture of aromatic hydrocarbons, which comprises:

(1) contacting said feed mixture with a Werner complex of an organic nitrogen base coordinated with a salt of a metal of atomic number 25–28, said contacting being carried out in a clathration solvent comprising water and a lower aliphatic hydroxy compound at a temperature between about −50° and +80° C., to effect selective clathration of one feed component with said Werner complex;

(2) separating the resulting mixture, still at a temperature between about −50° and +80° C., into a solid clathrate phase, a feed-raffinate hydrocarbon phase which is relatively lightly contaminated with dissolved metal salt and organic nitrogen base components of said Werner complex, and a lean clathration solvent phase;

(3) dissolving said solid clathrate phase in the extract phase of lean clathration solvent derived from the preliminary extraction step (5) defined hereinbelow, at a temperature which is between about 25° and 75° C. higher than the clathration temperature employed in step (1), whereby a declathrated feed-extract hydrocarbon phase is formed which is relatively heavily contaminated with dissolved metal salt and organic nitrogen base components of said Werner complex;

(4) separating said feed-extract hydrocarbon phase from the remaining rich clathration solvent phase containing redissolved Werner complex;

(5) recycling said rich clathration solvent phase to step (1);

(6) subjecting said feed-extract hydrocarbon phase to a single-stage preliminary extraction with at least a portion of said lean clathration solvent from step (2), thereby forming a partially decontaminated feed-extract hydrocarbon phase having a major portion of metal salt and organic nitrogen base components removed therefrom and an extract phase of lean clathration solvent which is recycled to step (3) as previously described;

(7) extracting said feed-raffinate hydrocarbon phase from step (2) with an aqueous organic acid solution to remove organic nitrogen base therefrom, and recovering a purified feed-raffinate hydrocarbon phase and a first extract-salt phase; and

(8) separately extracting said partially decontaminated feed-extract hydrocarbon phase from step (6) with an aqueous organic acid solution to substantially remove remaining organic nitrogen base therefrom, and recovering a purified feed-extract hydrocarbon phase and a second extract-salt phase.

2. A process as defined in claim 1 including the additional steps of:

(9) combining said first and second extract salt phases from steps (7) and (8) and distilling the mixture to produce an overhead azeotrope of organic nitrogen base and water, and a bottoms of aqueous acid;

(10) recycling said bottoms of aqueous acid to steps (7) and (8);

(11) condensing and extracting said nitrogen base-water azeotrope with a hydrocarbon to produce an aqueous raffinate which is recycled to step (9), and an extract phase of hydrocarbon and organic nitrogen base which is recycled to one of steps (1) and (2).

3. A process as defined in claim 1 wherein a paraffinic hydrocarbon diluent is added to steps (2) and (3) to reduce the solubility of organic nitrogen base in said feed-raffinate hydrocarbon phase and in said feed-extract hydrocarbon phase.

4. A process as defined in claim 1 wherein said feed mixture comprises xylene isomers.

5. A process as defined in claim 1 wherein said organic acid is a dibasic acid.

6. A process as defined in claim 1 wherein said organic acid is selected from the group consisting of succinic acid, adipic acid, pimelic acid and oxalic acid.

7. A process as defined in claim 1 wherein said clathration solvent comprises water and a lower alkanolamine.

8. A clathration process for resolving a feed mixture of xylene isomers which comprises:

(1) contacting said feed mixture with a Werner complex of a picoline base coordinated with a salt of a metal of atomic number 25–28, said contacting being carried out in a clathration solvent comprising water and a lower alkanolamine at a temperature between about 0° and 40° C., to effect selective clathration of one xylene isomer with said Werner complex;

(2) separating the resulting mixture, still at a temperature between about 0° and 40° C., into a solid clathrate phase, a xylene-raffinate phase which is relatively lightly contaminated with dissolved metal salt and picoline base components of said Werner complex, and a lean clathration solvent phase;

(3) dissolving said solid clathrate phase in the extract phase of lean clathration solvent derived from the preliminary extraction step (5) defined hereinbelow, at a temperature which is between about 25° and 75° C. higher than the clathration temperature employed in step (1), whereby a declathrated xylene-extract phase is formed which is relatively heavily contaminated with dissolved metal salt and picoline base components of said Werner complex;

(4) separating said xylene-extract phase from the remaining rich clathration solvent phase containing redissolved Werner complex;

(5) recycling said rich clathration solvent phase to step (1);

(6) subjecting said xylene-extract phase to a single-stage preliminary extraction with at least a portion of said lean clathration solvent from step (2), thereby forming a partially decontaminated xylene-extract phase containing less than about 10 p.p.m. of the metal component of said Werner complex, and an extract phase of lean clathration solvent which is recycled to step (3) as previously described;

(7) extracting said xylene-raffinate phase from step (2) with an aqueous organic acid solution to remove picoline base therefrom, and recovering a purified

xylene-raffinate phase and a first extract-salt phase; and

(8) separately extracting said partially decontaminated xylene-extract phase from step (6) with an aqueous organic acid solution to remove organic nitrogen base therefrom, and recovering a purified xylene-extract phase and a second extract-salt phase.

9. A process as defined in claim **8** wherein a paraffinic hydrocarbon diluent is added to steps (2) and (3) to reduce the solubility of picoline base in said xylene-raffinate phase and in said xylene-extract phase.

10. A process as defined in claim **8** wherein said organic acid is a dibasic acid.

11. A process as defined in claim **8** wherein said organic acid is selected from the group consisting of succinic acid, adipic acid, pimelic acid and oxalic acid.

12. A process as defined in claim **8** including the additional steps of:

(9) combining said first and second extract salt phases from steps (7) and (8) and distilling the mixture to produce an overhead azeotrope of picoline base and water, and a bottoms of aqueous acid;

(10) recycling said bottoms of aqueous acid to steps (7) and (8);

(11) condensing and extracting said picoline base-water azeotrope with a hydrocarbon to produce an aqueous raffinate which is recycled to step (9), and an extract phase of hydrocarbon and picoline base which is recycled to one of steps (1) and (2).

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