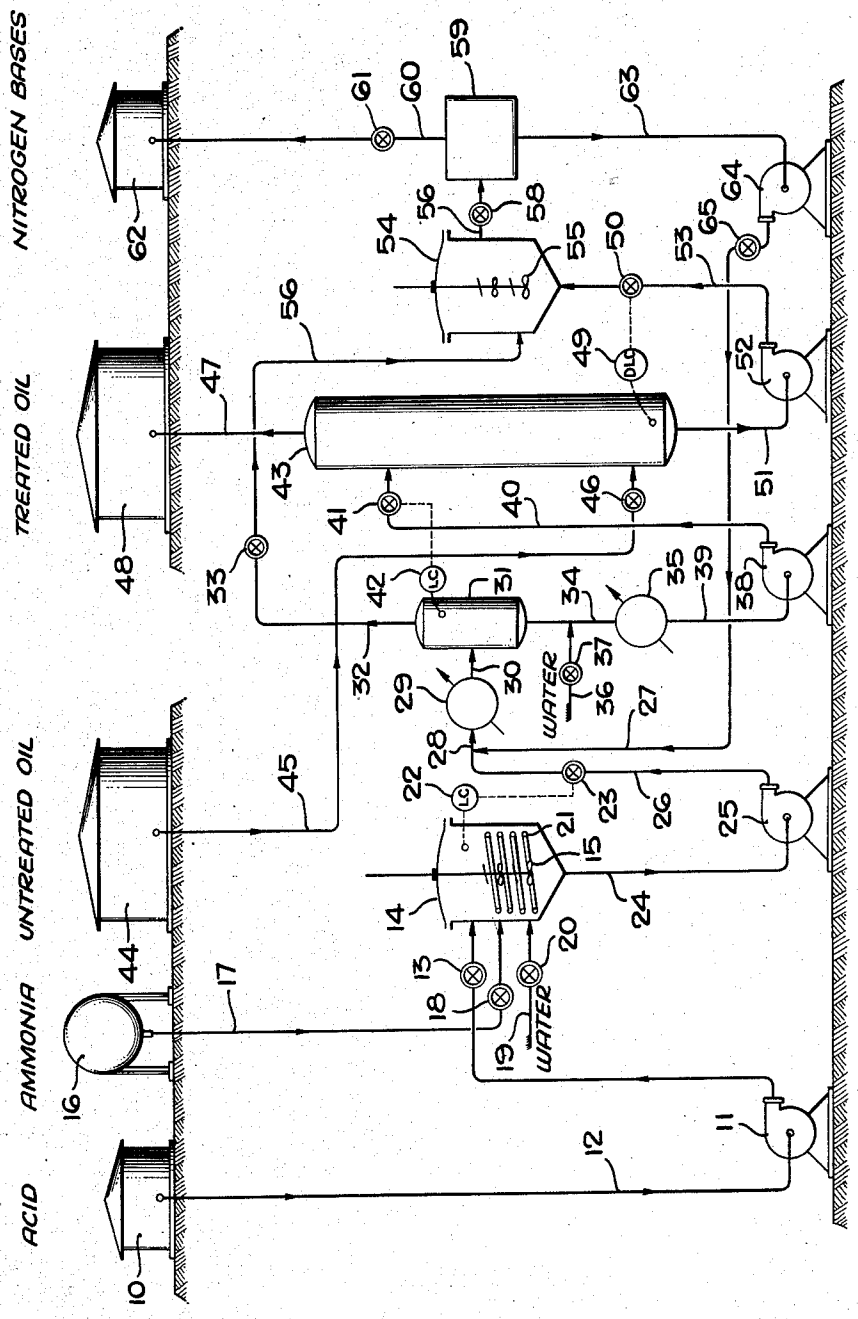
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PURIFICATION OF OILS

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PURIFICATION OF OILS

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1

This invention relates to the purification of oils by extraction and applies particularly to the removal from oil products of basically reacting constituents contained therein. This invention relates more specifically to the removal of basically reacting organic nitrogen compounds including heterocyclic mono- and polynuclear compounds known as nitrogen bases from oils such as coal tar fractions, shale oil and shale oil fractions, mineral oil fractions and oil fractions obtained during the pyrolysis of protein material such as cottonseed meal.

Crude petroleums, especially those produced in California and South America, contain, beside hydrocarbons, small amounts of compounds of hydrogen, carbon, and nitrogen. The presence of these and other non-hydrocarbon compounds is often detrimental to the performance of the products prepared from petroleum and nearly always their elimination from their particular petroleum fraction is desirable.

The nitrogen bases present in the shale oil and fractions thereof, petroleum fractions, coal tar, and oil fractions obtained from the pyrolysis of materials containing substantial amounts of protein material, are heterocyclic mono- and polynuclear organic compounds of carbon, hydrogen, and nitrogen and are generally believed to consist largely of pyridine and quinoline and methylated derivatives thereof, although some higher alkyl and cycloalkyl derivatives thereof have been identified. It has been also shown that there are hydroaromatic bases present which include the reduced or partially reduced derivatives of pyridine and quinoline such as piperidine and decahydroquinoline and alkyl derivatives thereof, together with the higher molecular weight hydroaromatic nitrogen bases such as the pyrindacine base $C_{16}H_{25}N$. In general this nitrogen base fraction present in the oils previously mentioned contains a large number of different compounds of carbon, hydrogen and nitrogen, which compounds have not been identified. These compounds react chemically similar to the aliphatic amines, forming stable water-soluble salts with strong acids.

Nitrogen bases have been removed from oils in a variety of manners. The repeated washing of the oil with a dilute strong mineral acid, such as sulfurous acid, sulfuric, nitric and other inorganic acids or by means of the relatively strong organic acids such as acetic, chloroacetic, oxalic acid or by acidic substanes such as picric acid, etc., serve to remove from the oil a substantial portion of the nitrogen bases contained therein. It is also possible to separate nitrogen bases from a major portion of a diluting hydrocarbon oil by extraction with a solvent in which the nitrogen bases are soluble but in which a larger part of the diluting hydrocarbon oil is insoluble. Such solvents which are applicable in such extractions include aniline, furfural, isopropyl alcohol and nitrobenzene. A more important and more widely used solvent is liquid surfur dioxide which is used to extract aromatic constituents together with the nitrogen bases from an oil in the so-called Edeleanu process (United States Patent No. 911,553, issued February 2, 1909).

2

The use of dilute acids, while simple in operation, involves the handling of relatively corrosive materials and results in the conversion of the acid extraction medium to a salt when the nitrogen bases are liberated from solution. In many cases this salt which is formed is not readily reconvertible to the acid and consequently the reagent consumption is high. The liquid sulfur dioxide extraction method of the Edeleanu process requires use of low temperatures, high pressures and is more readily adaptable to the extraction of aromatics from oil fractions than to the specific preparation of nitrogen bases in concentrated form.

It has been discovered that acid ammonium or amino, or salts of strong non-volatile acids in an aqueous solution form excellent extracting solvents in a process which shows outstanding advantage over any previously used. The temperatures and pressures of operation are very moderate, the economics of the process are good, and the solvents applicable to the extraction of nitrogen bases from oil fractions by the process of my invention are not particularly corrosive and may be conveniently handled in equipment fabricated from ordinary metals of construction.

It is an object of my invention to provide a method for economical and efficient removal of basically reacting constituents from oils.

A further object of my invention is to provide a method for the purification of shale oil or

petroleum oil distillates which permits the removal of nitrogen bases therefrom.

A further object of my invention is to provide a method for the separation of a highly concentrated fraction of such nitrogen bases from shale oil, petroleum oil, coal tar oils, or pyrolysis distillates or fractions thereof.

It is a further object of my invention to provide a continuous process for the substantially complete extraction of such nitrogen bases from various oil with a minimum solvent or reagent loss.

Other objects and advantages of my invention will become apparent to those skilled in the art as the description thereof proceeds.

Briefly stated my invention comprises a cyclical extraction process for the removal of nitrogen bases or other basically reacting constituents from either dilute solutions or concentrates thereof in which the extraction is performed with an aqueous solvent containing an acid salt of a relatively strong base and a strong non-volatile acid. In one modification of my invention the relatively strong base is volatile and a portion thereof is evaporated from the aqueous solution containing the normal salt leaving an aqueous solution containing an acid salt. When the aqueous solution of the acid salt is contacted with an oil containing nitrogen bases, a soluble normal nitrogen base salt is formed which concentrates in the aqueous extract phase. After separating the extract from the nitrogen base-free oil raffinate phase, combination with the extract of that portion of the volatile base evaporated in the formation of the aqueous solution of the acid salt causes the nitrogen bases to be liberated from the extract by reformation of the normal salt. The free nitrogen bases may be separated as a substantially pure phase by decantation or other applicable procedure. The normal salt employed in the aqueous solution is preferably such that evaporation of a portion of the volatile base of the normal salt leaves a solution containing the acid salt which is capable of forming other normal salts with nitrogen bases or other basic constituents of an oil. When the evaporated base is recombined with the aqueous solvent containing normal salts of the nitrogen bases, basically reacting constituents are released.

More specifically I employ as the extraction solvent, an aqueous solution containing an acid salt of a strong non-volatile acid, which acid has one ionization constant of at least 1×10^{-4} and preferably between about 1×10^{-4} and about 1×10^{-2}. The cation of the acid salt may include the ammonium ion or alkyl derivatives thereof as well as hydrogen. For example, acid salts having an unneutralized acid hydrogen which are included within the previous definition include an acid salt of arsenic, phosphoric, phosphorus, pyrophosphoric, sulfuric, and the like. These acids are all strong non-volatile polybasic inorganic acids.

Although in the preferred modification of my invention the ammonium acid salts are employed, others are applicable in certain instances such as the alkyl derivatives of ammonia which are the amines, such as mono-, di-, and trimethylamine, or piperidine which is also a relatively strong base. These compounds are all low molecular weight saturated aliphatic amines which are relatively stronger bases than the nitrogen bases present in hydrocarbon oils and these compounds are volatile bases. The preferred acid salts are the acid ammonium phosphates and sulfates such as ammonium dihydrogen phosphate, ammonium bisulfate with or without free acid.

The process and apparatus of my invention may be more readily understood by reference to the accompanying drawing which comprises a schematic flow diagram of one modification of the process of my invention. In the description of that modification of my invention which is illustrated in the accompanying figure, ammonia will be used as the cation of the salt used in the extracting solution. The acid may be any of those previously named, but for purposes of illustration will be considered to be phosphoric acid.

Referring more particularly to the accompanying figure, concentrated phosphoric acid is withdrawn from tank 10 by means of pump 11 through line 12 controlled by valve 13 and is introduced into neutralization vessel 14 which is equipped with agitating means 15. Anhydrous ammonia, stored under its vapor pressure in tank 16 is withdrawn by means of line 17 controlled by valve 18 and is likewise introduced into neutralization vessel 14. Water, if desired, may be added by means of line 19 controlled by valve 20. The extraction process of my invention is recirculatory in nature and results in a substantially complete elimination of solvent or reagent loss. The amounts of acid and ammonia which are introduced into neutralization vessel 14 are quite low and serve only to make up the small amount of the salt which is lost.

The ratio of the quantities of phosphoric acid and ammonia introduced into neutralization vessel 14 is preferably controlled so as to produce a normal salt. For example, an aqueous solution of triammonium phosphate may be formed for subsequent heating and evaporation of a portion of ammonia therefrom forms an aqueous solution of an acid ammonium phosphate salt which serves as an excellent extraction solvent. Because of the fact that heat is liberated in neutralization vessel 14 during the formation of the desired salt, cooling coil 21 is provided in order to maintain the temperature control over the contents of the vessel thus permitting the effective use of the heat of neutralization generated therein in the subsequent evaporation operation.

The liquid level in vessel 14 is controlled by level controller 22 which actuates valve 23 which controls the flow through line 26. The aqueous salt solution is removed from vessel 14 by means of line 24, pump 25, line 26, controlled by valve 23 and is combined with the recirculated reformed solvent recirculated through line 27. The recirculated solvent, together with the added solvent, is introduced by means of line 28 into solvent heater 29. In solvent heater 29, the solvent is further heated to a high temperature and is introduced by means of line 30 into vapor-liquid separating drum 31 wherein the solvent is partially evaporated to form an acidic solution. A distillation tower may be employed for evaporation of the solvent. The product of evaporation, which include steam and certain amounts of the volatile cation of the salt contained therein, are removed from drum 31 by means of line 32 controlled by valve 33 and are subsequently used as more fully described hereinafter. The hot acidic solvent contained in drum 31 is removed therefrom by means of line 34, and is passed through solvent cooler 35 wherein it is cooled to a temperature which is sufficiently low to permit efficient extraction. It is sometimes desirable to add water to the acidic solvent, in which case it may be added by means of line 36 controlled by

valve 37 into line 34. The cooled solvent is removed from solvent cooler 35 by means of pump 38, line 39, line 40, controlled by valve 41 which in turn is actuated by level control 42, associated with drum 31, and is introduced into the top of extraction tower 43.

The untreated oil to be extracted is removed from tank 44 by means of line 45 controlled by valve 46 and is introduced into the lower portion of extraction tower 43. Extraction tower 43 may conveniently comprise a packed column of suitable diameter and suitable height depending upon the type of solvent used and the type of oil to be treated. The oil rises upward through column 43 as the continuous phase and the solvent introduced into the top of tower 43 flows downwardly as the discontinuous phase, countercurrent to the rising oil. The raffinate, or treated oil from which the nitrogen bases have been substantially completely removed, is removed from the top of tower 43 by means of line 47 and is accumulated in tank 48. The solvent dissolves the nitrogen bases from the rising oil and forms soluble salts therewith which are carried downward through tower 43 with the discontinuous solvent phase. The aqueous solvent phase containing the nitrogen bases as dissolved salts and forming the extract accumulates in the bottom of tower 43 and is immiscible with the oil rising therethrough. The position of the interface between the oil or raffinate phase and the solvent or extract phase in the bottom of tower 43 is controlled by differential level controller 49 which actuates valve 50 which in turn controls the rate at which the extract is removed from tower 43 through line 51 under positive suction induced by pump 52. The extract thus removed is conducted by means of line 53 controlled by valve 50 and is introduced into neutralization vessel 54 which is equipped with agitating means 55.

In the particular modification of my invention as herein described, ammonia vapor together with steam is evaporated from vessel 31 and is removed therefrom by means of line 32 controlled by valve 33 as previously described and is introduced into neutralization vessel 54 by means of line 56. As previously described, the addition of an evaporated basic constituent to the extract obtained from contacting an oil containing nitrogen bases with an acidic solvent liberates from the extract the nitrogen bases dissolved as soluble salts therein forming two immiscible liquid phases, an oil phase containing the liberated nitrogen bases and an aqueous phase containing the solvent.

The immiscible liquid phases are removed from neutralization vessel 54 by means of line 56 controlled by valve 58 and are introduced into separator 59 where, in the particular modification being described, the oily nitrogen base phase settles to the top while the regenerated solvent phase settles to the bottom. The supernatant oil phase containing the nitrogen bases is removed from separator 59 by means of line 60 controlled by valve 61 and is introduced into tank 62 which is provided for the accumulation of separated nitrogen bases. The regenerated solvent, which is substantially completely free of nitrogen bases, is removed from separator 59 by means of line 63 and is pumped by means of pump 64 through line 27 controlled by valve 65 and is introduced into line 28 wherein it is combined with a small amount of added solvent, and is recirculated through the system.

As previously described, cations other than ammonia may be employed in the salt used in the aqueous solvent and the choice of such a cation which is most suitable for a given application in the separation of nitrogen bases from oils governs, to a large extent, the type of equipment used in separator 59 in which the extract is freed of nitrogen bases. For example, in the treating of oils having low boiling ranges, and in which are contained nitrogen bases such as pyridine and its low molecular weight homologs, the equipment necessary in separator 59 to efficiently separate the nitrogen bases from the extract obtained from the bottom of tower 43 comprises an extraction tower whereby the primary extract obtained from tower 43 may be contacted with a low molecular weight organic solvent such as for example, petroleum ether, benzene, or other applicable immiscible solvent, whereby the low molecular weight nitrogen bases may be efficiently removed. A secondary extract is thereby obtained containing the nitrogen bases which may be separated by distillation. The water soluble nitrogen bases may be removed in some cases by distillation of the primary extract.

In another possible modification of my invention, ammonia or added basic constituents such as the low molecular weight amines and similar compounds previously mentioned, may be dispensed with and the basically reacting nitrogen bases may themselves be used in place of the volatile cation. In carrying out this modification of my invention, the solvent initially used comprises a dilute acid solution capable of dissolving the nitrogen bases contained in the untreated oil. The extract formed may be heated to separate therefrom a portion of the nitrogen bases which may then be separated from the regenerated solvent most conveniently by heating and subsequent decantation, or by further extraction. The regenerated solvent thus obtained is not completely free from dissolved nitrogen bases and is recirculated from separator 59 through line 63 under positive suction induced by pump 64, through line 27 to heater 29 where it is further heated to a temperature which is sufficiently high to substantially completely evaporate the remaining nitrogen base contained therein. Subsequent cycles of this modification of the process conform substantially to that described except that in this modification the nitrogen base rather than the ammonia is the cation of the salt used in the extracting solvent.

The following examples will serve to more clearly illustrate my invention:

Example I

A gas-oil fraction prepared from oil shale by high temperature oil shale eduction and subsequent fractional distillation has the following characteristics:

Boiling range, 425° to 560° F.
Gravity, 32.2° A. P. I.
Nitrogen bases, 7.7 volume per cent

The nitrogen bases contained in this gas-oil fraction comprise the substituted quinoline type of nitrogen compound. This gas-oil fraction is treated at atmospheric pressure at a temperature of about 100° F. with an aqueous solution of 25 weight per cent ammonium bisulphate (NH_4HSO_4) in a packed tower. The raffinate rises through the tower as a continuous oil phase and is removed containing less than 0.2 volume per cent nitrogen bases. The extract is removed from the bottom of the tower and heated to a

temperature between about 200° F. and 300° F. causing thereby a substantially complete separation from the extract of the nitrogen bases as a separate oil layer. The two phases are separated by means of decantation and the solvent phase, containing a small amount of dissolved nitrogen base, is cooled and returned as fresh solvent to the extraction tower.

Example II

The shale oil gasoline prepared from the same shale oil source as the gas-oil described in Example I has the following properties:

Boiling range, 280° to 405° F.
Gravity, 46.8° A. P. I.
Nitrogen bases, 3.2 volume per cent

The nitrogen bases present in this gasoline appear to be alkylated pyridines and because the lower molecular weight alkylated pyridines are soluble in water and aqueous extraction solutions, they must be separated in a different manner from the nitrogen bases present in the gas-oil fraction.

A 15 weight per cent solution of triammonium phosphate is heated and water and ammonia are evaporated leaving an acid solution of ammonium dihydrogen phosphate and phosphoric acid. This acid salt solution is cooled to 100° F. and used to extract the shale oil gasoline in a packed tower. A raffinate is produced from the top of the tower which contains less than 0.2 volume per cent nitrogen bases. An extract containing the nitrogen bases as the normal ammonium nitrogen base phosphate salts is removed from the tower bottom. The extract is contacted with the previously evaporated ammonia and water reforming the normal triammonium phosphate salt and substantially completely liberating the nitrogen bases. The normal salt solution containing free nitrogen bases partly in solution is extracted in a secondary extraction tower with a low boiling hydrocarbon solvent thereby separating the nitrogen bases as a secondary extract. The secondary raffinate consisting of the reformed normal salt solution, is returned to the evaporation apparatus for evaporation of ammonia and conversion to the acid salt. The secondary extract consisting of the nitrogen bases in a low boiling hydrocarbon solution is distilled to effect a complete separation.

Example III

The gas-oil fraction described in Example I was treated as follows with an ammonium phosphate extracting solution. The extracting solvent utilized comprises a 25 weight per cent solution of triammonium phosphate. This extraction solution is heated and sufficient quantities of ammonia and water vapor are evaporated so that the composition of the salt in the solvent approximates that of the ammonium dihydrogen phosphate solution as in Example II with excess phosphoric acid. This acidic solvent is used as the extracting solution in an extraction tower wherein it countercurrently contacts the gas-oil fraction and produces a raffinate containing less than 0.15 volume per cent nitrogen bases and an extract which contains the nitrogen bases as normal ammonium nitrogen base phosphate salts. The extract is removed from the extraction tower and combined with the ammonia evaporated from the original triammonium phosphate solution causing the substantially complete separation of the nitrogen bases into an oily phase. The oily phase containing the separated substituted quinolines and heavier nitrogen bases is separated by decantation from the reformed aqueous solution of triammonium phosphate which contains a small amount of combined nitrogen base. The reformed solution is recycled to the evaporation apparatus for reuse in the extraction tower.

The methods of my invention as herein disclosed for the removal of nitrogen bases in particular and other basically reacting compounds in general from oils apply equally well to the dilute solutions of such basically reacting materials or concentrates thereof and the use of dilute solutions in the examples or the mode of preparation or the source of the oil containing such nitrogen bases must not be taken as limiting my invention. As previously stated in this specification, phosphoric acid, sulfuric acid, arsenic acid and other non-volatile acids which have ionization constants within the limits previously set forth are applicable to the oil purification processes herein disclosed, and my invention is not to be limited to the particular acids used in the examples or in the description. Similarly, the specific concentrations of salts indicated in the examples of applicable solvents are only illustrative of the process of my invention and salt concentrations of from as low as 1% to 2% by weight to as high or higher than about 40% by weight are applicable depending upon the salt used, the temperature of operation, and the type of oil being treated. Although an operating pressure was not indicated in the description of my invention, it is most convenient to carry out the process at pressures substantially equal to atmospheric pressure although in some instances it is advisable to utilize elevated pressures such as when solvents of low boiling range are employed in the secondary extraction indicated, or other particular cases.

Having described and illustrated my invention for the removal of basically reacting constituents from oils by extraction with aqueous solutions of acid salts and realizing that many modifications thereof may occur to those skilled in the art without departing from the spirit and scope of my invention,

I claim:

1. A continuous process for the separation of nitrogen bases from hydrocarbon oil solutions thereof which comprises combining a volatile base selected from the class of volatile bases consisting of ammonia and the mono-, di- and trimethyl amines and a strong non-volatile polybasic inorganic acid in the presence of water to form an aqueous solution of the normal salt of said volatile base and said non-volatile acid, heating said aqueous solution and evaporating thereby a portion of said volatile base to form an aqueous solution of an acid salt of said volatile base and said non-volatile acid, contacting said hydrocarbon oil solution of nitrogen bases with said aqueous solution of said acid salt to form a hydrocarbon oil raffinate and an extract containing said nitrogen bases as normal nitrogen base salts, separating said raffinate from said extract, combining said extract with the evaporated portion of said volatile base thereby reforming in solution said normal salt and liberating said nitrogen bases, removing the liberated nitrogen bases and returning the solution of normal salt for reuse in the process.

2. A continuous process for the separation of nitrogen bases from hydrocarbon oil solutions thereof which comprises combining ammonia with a strong non-volatile acid having one ionization constant which is at least 1×10^{-4} in the presence of water to form an aqueous solution of the normal ammonium salt of said non-volatile acid, heating said aqueous solution of said normal ammonium salt and evaporating thereby a portion of said ammonia to form an aqueous solution of an acid ammonium salt of said non-volatile acid, contacting said hydrocarbon oil solution of nitrogen bases with said aqueous solution of said acid ammonium salt to form an extract containing said nitrogen bases as normal ammonium nitrogen base salts of said non-volatile acid and a raffinate which is substantially completely free of said nitrogen bases, separating said extract from said raffinate, combining said extract with the ammonia evaporated in the formation of said aqueous solution of said acid ammonium salt thereby reforming said aqueous solution of said normal ammonium salts and simultaneously liberating said nitrogen bases from said normal ammonium nitrogen base salts in said extract, separating the liberated nitrogen bases in substantially pure form from the reformed aqueous solution of said normal ammonium salts, and returning said solution of normal salts for reuse in the process.

3. A continuous process for the separation of nitrogen bases from hydrocarbon oil solutions thereof which comprises combining ammonia with sulfuric acid in the presence of water to form an aqueous solution containing less than about 40 weight per cent of diammonium sulfate, heating said aqueous solution and evaporating therefrom a portion of said ammonia to form an aqueous solution containing ammonium bisulfate together with free sulfuric acid, contacting said hydrocarbon oil solution of said nitrogen bases with said acid ammonium bisulfate solution to form an extract containing said nitrogen bases as the normal ammonium nitrogen base sulfate salts thereof and a raffinate which is substantially completely free of nitrogen bases, separating said raffinate from said extract, combining said extract with the ammonia evaporated in the formation of said acid ammonium bisulfate solution thereby liberating from said extract said nitrogen bases as an insoluble phase and simultaneously reforming said aqueous solution containing said diammonium sulfate, separating by decantation the liberated nitrogen bases in substantially pure form, and returning the reformed aqueous solution of diammonium sulfate for reuse in the process.

4. A continuous process for the separation of nitrogen bases from hydrocarbon oil solutions thereof which comprises combining ammonia with phosphoric acid in the presence of water to form an aqueous solution containing less than about 40 weight per cent of triammonium phosphate dissolved therein, heating said aqueous solution and evaporating ammonia therefrom thereby forming an aqueous solution containing ammonium dihydrogen phosphate together with free phosphoric acid, contacting said hydrocarbon oil solution of nitrogen bases with said last-named aqueous solution to form a raffinate substantially completely free of nitrogen bases and an extract containing said nitrogen bases as the normal ammonium nitrogen base phosphate salts thereof, separating said extract from said raffinate, combining said extract with said ammonia evaporated in the formation of said last-named aqueous solution thereby liberating said nitrogen bases from said extract and simultaneously reforming said aqueous solution containing said triammonium phosphate dissolved therein, fractionating said solution of liberated nitrogen bases and reformed aqueous triammonium phosphate solution, separating thereby a first fraction containing said nitrogen bases in substantially pure form and a second fraction containing regenerated triammonium phosphate solution, and returning said second fraction for reuse in the process.

5. A continuous process for the separation of nitrogen bases from hydrocarbon oil which comprises heating an aqueous solution of a normal salt of a strong non-volatile polybasic inorganic acid and a volatile base selected from the class consisting of ammonia and the mono-, di- and trimethyl amines thereby evaporating a portion of said volatile base to form an aqueous solution of an acid salt of said non-volatile acid and said volatile base, contacting said hydrocarbon oil containing nitrogen base with said last-named aqueous solution to form a hydrocarbon oil raffinate substantially free from nitrogen bases and an extract containing said nitrogen bases as normal nitrogen base-volatile base salts, separating said raffinate from said extract, combining said extract with the evaporated portion of said volatile base thereby reforming said normal salt and liberating said nitrogen bases, removing the liberated nitrogen bases and returning the solution of normal salt for reuse in the process.

6. A continuous process for the separation of nitrogen bases from hydrocarbon oil which comprises heating an aqueous solution containing less than about 40 weight per cent of diammonium sulfate and evaporating therefrom a portion of said ammonia to form an aqueous solution containing ammonium bisulfate together with free sulfuric acid, contacting said hydrocarbon oil containing nitrogen bases with said acid ammonium bisulfate solution to form an extract containing nitrogen bases in the form of normal ammonium nitrogen base sulfate salts and a hydrocarbon oil raffinate which is substantially free of nitrogen bases, separating said raffinate from said extract, combining said extract from the ammonia evaporated in the formation of said acid ammonium bisulfate solution thereby liberating from said extract said nitrogen bases and simultaneously reforming an aqueous solution of diammonium sulfate, separating the liberated nitrogen bases in substantially pure form and returning the reformed aqueous solution of diammonium sulfate for reuse in the process.

7. A continuous process for the separation of nitrogen bases from hydrocarbon oil which comprises heating an aqueous solution containing less than about 40 weight per cent of triammonium phosphate and evaporating ammonia therefrom, thereby forming an aqueous solution containing ammonium dihydrogen phosphate, contacting said hydrocarbon oil containing nitrogen bases with said last-named aqueous solution to form a raffinate substantially free of nitrogen bases and an extract containing said nitrogen bases in the form of the normal ammonium nitrogen base phosphate salts thereof, separating said extract from said raffinate, combining said extract with the ammonia evaporated in the formation of said last-named aqueous solution thereby liberating said nitrogen bases from said extract and simultaneously reforming said aqueous solution of tri-

ammonium phosphate, separating the nitrogen bases from the aqueous solution of triammonium phosphate and returning the triammonium phosphate solution for reuse in the process.

8. A process according to claim 1 in which said volatile base is monomethyl amine and said strong non-volatile acid has one ionization constant which is at least 1×10^{-4}.

9. A process according to claim 1 in which said volatile base is dimethyl amine and said strong non-volatile acid has one ionization constant which is at least 1×10^{-4}.

10. A process according to claim 1 in which said volatile base is trimethyl amine and said strong non-volatile acid has one ionization constant which is at least 1×10^{-4}.

ART C. McKINNIS.

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