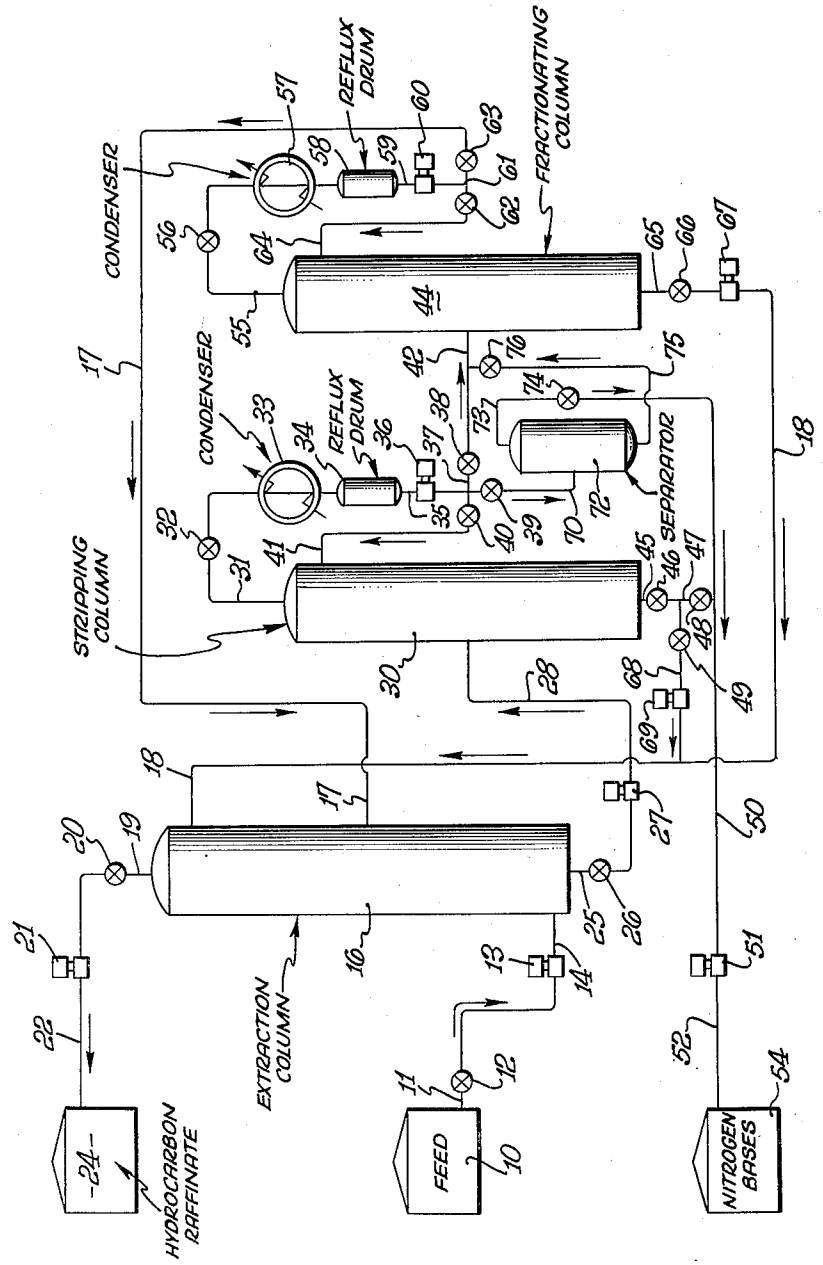
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RECOVERY OF NITROGEN BASES

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RECOVERY OF NITROGEN BASES

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This invention relates to the recovery of nitrogen containing compounds from hydrocarbon fractions in which they are contained such as may be obtained from shale oil, shale oil distillates, tar sand, or petroleum fractions.

It is well known that there is present in petroleum, oil shales and tar sands and in distillates thereof a small percentage of organic nitrogen compounds particularly in oils of naphthenic origin such as those found predominantly in California fields. Many of these nitrogen compounds show basic characteristics in that they are reactive with dilute acids and consequently they are known as "nitrogen bases."

These organic nitrogen compounds are found throughout the range of petroleum distillates from the lower boiling amines and cyclic nitrogen compounds such as pyridine to the high boiling more complex nitrogen containing compounds. Further, these nitrogen bases exhibit different degrees of basicity dependent apparently upon numerous factors such as type of structure, whether it be straight chain or cyclic, various substituents in the compound such as the location of side chains or alkylating groups which may give rise to steric hindrance thus affecting the basic nature of the compound, degree of saturation or unsaturation of the nitrogen compound or the like. Thus in a simple example, if pyridine is hydrogenated a simple amine is formed exhibiting stronger basic properties than does the pyridine itself. No definite criteria can be established as yet whereby the nature of these various nitrogen bases can be accurately predicated. However, such prediction is not necessary according to the present invention inasmuch as I am able to effectively separate any of these nitrogen bases from the hydrocarbon fractions containing them.

Methods of separation of nitrogen bases from hydrocarbons have been known in the art for some time. These methods include such processes as extraction of the hydrocarbon oil containing the nitrogen bases with sulfuric acid followed by neutralization of the extract with caustic soda whereupon the nitrogen bases are thrown out as an immiscible layer. Other methods involve the usage of various metal salts to form complex salts with the nitrogen base as for example $(Base)_2.ZnCl_2$ as obtained by contacting the nitrogen bases with zinc chloride. This method as described by Mahan and Bailey (J. A. C. S. 59, 449, 1937) further involves the decomposition of the double salt at elevated temperatures. Still others involve the usage of com-

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paratively weak acids such as those having dissociation constants in aqueous solutions in the order from about 10^{-3} to about 10^{-5} under conditions to form two fluid phases, at least one of which is liquid and comprises a fatty aqueous solution containing the acid and adsorbed nitrogen base, and the other which is liquid or vaporous and consists essentially of the organic substance from which at least a portion of the nitrogen bases have been removed.

The two phases are separated and the fatty acid solution is then stripped with steam or other hot convection medium to remove the nitrogen bases therefrom.

One of the more important disadvantages of these older methods of recovery is that only a relatively small portion of the nitrogen bases is recovered from the oil due possibly to the fact that these bases vary widely in their basic characteristics as above described.

It is an object of the present invention to provide an improved process for the recovery of nitrogen bases from various hydrocarbon fractions in which they are contained, this process being independent, with the exception of minor modifications, upon the type or basic characteristics of the nitrogen compound.

Another object of the invention is the recovery of larger amounts of nitrogen bases than are obtainable by methods heretofore known.

More specifically it is the object of my invention to provide a combination of solvents which when employed as hereinafter described will result in improved recovery of nitrogen bases and which may be readily recovered from the nitrogen base extract and reused in the process.

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

In its essentials my process comprises treating petroleum or a fraction thereof containing one or more nitrogen bases with a volatile acid or a non-volatile acid salt together with a mutual solvent for the acid and hydrocarbon to effect the improved recovery of the nitrogen base. It has been postulated that one reason for the comparatively inefficient separation of nitrogen bases from hydrocarbons is because of the poor solubility of the reagents normally employed in the extraction. I have found that this difficulty may be overcome by combining with the extractive solvent a mutual solvent which has the effect of increasing the solubility of the extractive solvent in the hydrocarbon resulting in improved recovery of the nitrogen bases.

As extractive solvents for this process I prefer to employ the volatile acids such as hydrochloric, formic, acetic, propionic, carbonic, sulfurous and the like. Generally included in the category of volatile acids according to the present invention are those acids which may be vaporized at a temperature below about 200° C. and preferably below about 150° C. In this regard hydrocarbon fractions containing nitrogen bases of strongly basic character will require the usage of the weaker of the above acids such as acetic, carbonic, or sulfurous acids. Those fractions containing very weak nitrogen bases whose acid salts will readily decompose on heating will permit the usage of the stronger volatile acids such as hydrochloric acid and formic acid, and the like.

Whereas the above volatile acids may be employed in the recovery of lower boiling nitrogen bases such as those boiling below the particular volatile acid employed we have found that from an operational standpoint it is preferable to modify the process and employ an aqueous solution of a non-volatile acid salt, in conjunction with the mutual solvents hereinafter disclosed, such as sodium dihydrogen phosphate, sodium monohydrogen sulfate and the like, which aqueous salt solutions permit the more ready recovery of the nitrogen bases from the extract. These non-volatile acid salts are inorganic salts having a replaceable acid hydrogen.

As mutual solvents for the process according to my invention I may employ any solvent in which both the extractive solvent and the hydrocarbon fraction are at least partially soluble and I prefer to employ those solvents which, like the volatile acid, boil below about 200° C. and preferably below about 150° C. Such solvents include for example the low boiling alcohols and ketones such as methyl alcohol, ethyl alcohol, isopropyl alcohol, acetone, methyl ethyl ketone and the like. The mentioned alcohols are all monohydric alcohols. Of these I have found methanol to be the most effective in improving the recovery of the nitrogen bases. Briefly the process according to my invention comprises a continuous countercurrent extraction of the hydrocarbon fraction with the mutual solvent and the extractive solvent together with water washing at the top of the extraction tower to avoid loss of solvent or the contamination of the hydrocarbon raffinate. This process and the modifications thereof which may be employed depending upon the nature of the nitrogen bases to be recovered may be more readily understood by reference to the accompanying process diagram.

In the drawing equipment and piping are shown to permit two types of operation depending upon the usage of a volatile acid or an aqueous solution of a non-volatile acid salt as the extractive solvent. If a volatile acid is to be employed as the extractive solvent a hydrocarbon feed containing the nitrogen bases is withdrawn from tank 10 by means of line 11 controlled by valve 12 and is pumped by pump 13 via line 14 into the bottom of extraction column 16. The volatile acid and the mutual solvent are introduced into extraction column 16 by means of line 17 entering column 16 at some point intermediate between the point of feed inlet and raffinate outlet. The volatile acid and mutual solvent entering extraction column 16 by means of line 17 has the effect of extracting the nitrogen bases from the hydrocarbon fraction the latter passing upwardly in the column and the nitrogen bases-solvent solution passes downwardly therein.

Water is introduced at a point above that of solvent introduction as for example by means of line 18 which has the effect of water washing the ascending hydrocarbon raffinate to remove residual amounts of the extractive solvent and the mutual solvent from the hydrocarbon. The water progresses downwardly in the column and is withdrawn together with the solvent-nitrogen base phase as hereinafter described. The hydrocarbon raffinate is withdrawn from the top of extraction column 16 by means of line 19 controlled by valve 20 and is pumped by pump 21 via line 22 into the hydrocarbon raffinate storage tank 24.

The lower phase in extraction column 16 comprising the volatile acid, the mutual solvent, nitrogen bases, and excess water employed in washing the raffinate is withdrawn from the bottom of the column by means of line 25, controlled by valve 26 and is pumped by pump 27 via line 28 into stripping column 30. In stripping column 30 the acid, solvent and water are stripped from the nitrogen bases and are taken overhead by means of line 31 controlled by valve 32 passing into condenser 33. From condenser 33 the overhead passes into reflux drum 34 from which it is withdrawn by means of line 35 and is pumped by pump 36 into line 37 controlled by valves 38, 39 and 40. A part of the condensate may be returned to stripping column 30 by means of line 41 to serve as reflux in the stripping or fractionating operation. The remainder of the condensate passes through valve 38 via line 42 into fractionating column 44.

Returning to stripping column 30 the nitrogen bases remaining as bottoms in the operation are withdrawn from the bottom of the column by means of line 45 controlled by valve 46 and are passed into line 47 controlled by valves 48 and 49. In the presently described method of operation these nitrogen bases pass through valve 48 and line 50 and are pumped by pump 51 via line 52 into the nitrogen base storage tank 54.

In fractionating column 44 the acid and mutual solvent are distilled overhead leaving the excess water as bottoms in the distillation. The overhead comprising the acid and mutual solvent is withdrawn from fractionating column 44 by means of line 55 controlled by valve 56 and is passed into condenser 57. From condenser 57 the condensate is passed into reflux drum 58 and from thence into line 59 and is pumped by pump 60 into line 61 controlled by valves 62 and 63 and part of the condensate is returned to fractionating column 44 by means of valve 62 and line 64 to serve as reflux in the distillation. The remaining portion of the condensate passes through valve 63 and through line 17 back to extraction column 16 to be reused in the extraction.

The bottoms from fractionating column 44 comprising substantially solvent-free water is withdrawn by means of line 65 controlled by valve 66 and is pumped by pump 67 via line 18 back to extraction column 16 to be reused as hereinbefore described.

The operation as described need be modified only slightly for the extraction of hydrocarbon fractions containing nitrogen bases boiling below the volatile acid extractive solvent and the mutual solvent. If such be the case the overhead from stripping column 30 will consist essentially of the nitrogen bases and will be passed directly

therefrom to the nitrogen base storage tank. The bottoms from stripping column 30 will consist in this case of the volatile acid, mutual solvent and water and will be passed directly to the fractionating column 44 to be resolved into an acid-mutual solvent fraction and a water fraction as described above.

If, however, it is desired to extract a low boiling nitrogen base from a hydrocarbon fraction it may be preferable to employ an aqueous solution of a non-volatile acid salt as hereinbefore described as the extractive solvent. If this be the case, hydrocarbon feed containing the low boiling nitrogen base will be withdrawn from tank 10 by means of line 11, controlled by valve 12 and pumped by pump 13 via line 14 into the extraction column 16 as before. The difference in the operation resides largely in the point of introduction of the various constituents into extraction column 16. If a volatile acid is employed it is introduced into the column together with the mutual solvent by means of line 17, but if an aqueous solution of a non-volatile acid salt is employed it is introduced at the top of the extraction column by means of line 18 and the mutual solvent is introduced as before by means of line 17. In this manner the mutual solvent has the effect of solubilizing the extractive solvent in the hydrocarbon below the point of introduction at line 17. The extractive solvent entering by means of line 18 and being in the form of an aqueous solution has the same effect as the introduction of water by means of line 18 as described in the above process; namely, that of extracting any residual mutual solvent remaining in the hydrocarbon raffinate.

The extractive solvent, mutual solvent, and water are withdrawn from the bottom of the column 16 by means of line 25 controlled by valve 26 and are pumped by pump 27 via line 28 into the stripping column 30. The hydrocarbon raffinate is withdrawn as above from extraction column 16 by means of line 19 controlled by valve 20, is pumped by pump 21 via line 22 into the hydrocarbon raffinate storage tank 24.

In the stripping column 30 the volatile nitrogen bases together with the mutual solvent, and in most cases water, are distilled overhead and are withdrawn from the column by means of line 31 controlled by valve 32 passing therefrom into condenser 33. The condensate collecting in reflux drum 34 after condensing in condenser 33 is withdrawn from the reflux drum by means of line 35 and is pumped by pump 36 into line 37 controlled by valves 38, 39 and 40 and a part thereof is passed through valve 40 via line 41 back to column 30 to serve as reflux in the distillation. The remainder of the condensate is passed through valve 39 via line 70 into the separator 72 wherein a phase separation occurs between the water and mutual solvent in one case and the nitrogen bases in the other.

The nitrogen base phase is withdrawn from the top of separator 72 by means of line 73 controlled by valve 74, is passed through line 50 and is pumped by pump 51 via line 52 into the nitrogen base storage tank 54.

The lower phase in separator 72 comprising mutual solvent and water is withdrawn therefrom by means of line 75, controlled by valve 76 and is passed via line 42 into fractionating column 44.

In fractionating column 44 the mutual solvent and water are separated by simple distillation, the solvent passing overhead by means of line 55

controlled by valve 56 into condenser 57 and subsequently into reflux drum 58. The condensed mutual solvent is withdrawn from reflux drum 58 by means of line 59, is pumped by pump 60 into line 61 controlled by valves 62 and 63 and a part thereof is returned via line 64 to fractionating column 44 to serve as reflux in the distillation. The remaining condensate is passed through valve 63 via line 17 back to the extraction column 16. The bottoms from the distillation in column 44 comprising substantially solvent-free water is withdrawn therefrom by means of line 65, controlled by valve 66 and is pumped by pump 67 through line 18 back to the extraction column 16.

Returning to stripping column 30 wherein the separation of water, nitrogen bases and mutual solvent from the non-volatile acid salt solution was accomplished, the non-volatile acid salt solution is withdrawn from the bottom of the column by means of line 45, controlled by valve 46 passing into line 47 controlled by valves 48 and 49. This aqueous solution of the non-volatile acid salts is passed through valve 49 and line 68 and is pumped by pump 69 into line 18 wherein it is commingled with any water which may have been distilled therefrom in stripping column 30 and which is recovered in fractionating column 44 and returned via line 18 to recombine with the salt solution.

It is apparent from the above description of my process that it exhibits a wide flexibility of methods of operation, of extractive solvents which may be employed, of mutual solvents which may be employed and of nitrogen base containing hydrocarbon fractions which may be treated. The essential element of my invention as is apparent to one skilled in the art comprises the use of a mutual solvent to increase the solubility of the extractive solvent, whether it be a volatile acid or a non-volatile acid salt, in the hydrocarbon fraction in order to obtain improved recoveries of nitrogen bases from these hydrocarbon fractions. This is the essential element of my invention and I do not wish to be limited on the grounds of the foregoing description to any particular modification in the operation or to any particular extractive solvent or mutual solvent.

I have, however, found certain compounds which appear to be effective as extractive solvents and certain compounds which appear to be effective as mutual solvents. As extractive solvents I have found that the volatile acids such as hydrochloric acid, formic acid, acetic acid, propionic acid, carbonic acid and sulfurous acid are satisfactory for the operation. In the use of these acids it is necessary to use a certain amount of discretion in the choice of the particular acid to be employed dependent upon the characteristics of the nitrogen base or bases to be recovered. If these nitrogen bases are of strongly basic nature it is advisable to employ one of the weaker of the above acids inasmuch as a strong acid such as hydrochloric acid will result in the formation of a difficultly decomposable salt whereas such will not be the case if a weak acid is employed. Further, as extractive solvents, particularly as extractive solvents for the recovery of the low boiling nitrogen bases such as for example those which boil below about 100° C. I have found that aqueous solutions of various non-volatile acid salts such as sodium dihydrogen sulfate, sodium monohydrogen phosphate and the like are satisfactory.

As mutual solvents I have found that any compound or mixture of compounds capable of increasing the solubility of the extractive solvent in the hydrocarbon may be employed. This definition covers a wide range of compounds but I have found that the alcohols such as methyl alcohol, ethyl alcohol, isopropyl alcohol, and the like, and particularly methanol are the preferred compounds to be employed as mutual solvents.

The foregoing description of the elements and various processes of my invention is not meant to be limited in any way inasmuch as many modifications thereof will occur to those skilled in the art without departing from the spirit or scope of my invention and of the following claims:

1. A process of recovering nitrogen bases of a plurality of types from hydrocarbon fractions containing the same which comprises extracting the hydrocarbon fraction with an extractive solvent comprising an aqueous solution of a compound selected from the class of compounds consisting of the volatile acids boiling below about 200° C. and the non-volatile acid salts having a replaceable hydrogen and a mutual solvent for said extractive solvent and hydrocarbons comprising a compound selected from the class of compounds consisting of the low molecular weight monohydric alcohols and ketones to remove the nitrogen bases substantially completely from said hydrocarbon fraction, water washing the extracted hydrocarbon raffinate, combining the resulting wash water with the extract phase, separating the nitrogen bases from the extract and reusing the water, selective solvent and mutual solvent in the extraction.

2. A process of recovering nitrogen bases of a plurality of types from hydrocarbon fractions containing the same which comprises extracting a hydrocarbon fraction with an extractive solvent comprising an aqueous solution of a volatile acid boiling below about 200° C. and a mutual solvent for said extractive solvent and hydrocarbons comprising a compound selected from the class of compounds consisting of the low molecular weight monohydric alcohols and ketones to remove the nitrogen bases substantially completely from said hydrocarbon fraction, water washing the extracted hydrocarbon fraction combining the resulting wash water with the extract phase, separating the nitrogen bases from the extract phase, separating the volatile acid and mutual solvent from the excess water in the extract phase and reusing the volatile acid, mutual solvent and water in the extraction.

3. A process of recovering nitrogen bases of a plurality of types from hydrocarbon fractions containing the same which comprises extracting a hydrocarbon fraction with an extractive solvent comprising an aqueous solution of a non-volatile acid salt having a replaceable hydrogen and a mutual solvent for said extractive solvent and hydrocarbons comprising a compound selected from the class of compounds consisting of the low molecular weight monohydric alcohols and ketones to remove the nitrogen bases substantially completely from said hydrocarbon fraction, contacting the resultant hydrocarbon raffinate with fresh extractive solvent to wash residual amounts of mutual solvent from said raffinate, separating the nitrogen bases and mutual solvent from said extractive solvent in the extract phase, separating the nitrogen bases from said mutual solvent and reusing said mutual solvent and said extractive solvent in the extraction.

4. A process according to claim 2 wherein the volatile acid is selected from the class of acids consisting of hydrochloric acid, formic acid, acetic acid, propionic acid, carbonic acid and sulfurous acid.

5. A process according to claim 3 wherein the acid salt is selected from the class of compounds consisting of sodium dihydrogen phosphate and sodium monohydrogen sulfate.

6. A process according to claim 2 wherein the mutual solvent is methanol.

7. A process according to claim 3 wherein the mutual solvent is methanol.

8. A process of recovering nitrogen bases of a plurality of types from hydrocarbon fractions containing the same which comprises extracting the hydrocarbon fraction with an aqueous solution of hydrogen chloride and methanol to remove the nitrogen bases substantially completely from said hydrocarbon fraction, water washing the extracted hydrocarbon raffinate, combining the wash water with the acid-methanol-nitrogen base extract, distilling the water, methanol and acid from the nitrogen bases extracted from the hydrocarbon fraction and separating the excess water from the acid and methanol, returning the latter to the extraction step and the water to the water washing step.

9. A process of recovering nitrogen bases of a plurality of types from hydrocarbon fractions containing the same which comprises extracting the hydrocarbon fraction with acetic acid and methanol to remove the nitrogen bases substantially completely from said hydrocarbon fraction water washing the extracted hydrocarbon raffinate, combining the wash water with the acid-methanol-nitrogen base extract, distilling the water, methanol and acid from the nitrogen bases extracted from the hydrocarbon fraction and separating the excess water from the acid and methanol, returning the latter to the extraction step and the water to the water washing step.

10. A process of recovering nitrogen bases of a plurality of types boiling below about 200° F. from hydrocarbon fractions containing the same which comprises extracting the hydrocarbon fraction with an aqueous solution of a non-volatile acid salt having a replaceable hydrogen and a mutual solvent for said aqueous solution of a non-volatile acid salt and hydrocarbons comprising a compound selected from the class of compounds consisting of the low molecular weight monohydric alcohols and ketones, to remove the nitrogen bases substantially completely from said hydrocarbon fraction washing the extracted hydrocarbon raffinate with fresh extractive solvent, adding the extractive solvent from said washing to the extraction step, separating the extract phase from the raffinate phase, separating the nitrogen bases and mutual solvent from the aqueous solution of the non-volatile acid salt and excess water in the extract phase, separating said nitrogen bases from said mutual solvent by simple phase separation, returning said solvent to the extraction step and said aqueous non-volatile acid salt together with the excess water to the water washing step of the process.

11. A process of recovering nitrogen bases of a plurality of types from hydrocarbon fractions containing the same which comprises extracting the hydrocarbon fraction with acetic acid and methanol to remove the nitrogen bases substantially completely from said hydrocarbon fraction,

water washing the extracted hydrocarbon fraction, combining the resulting wash water with the extract phase, separating the nitrogen bases from the extract phase, separating acetic acid and methanol from the excess water in the extract phase and reusing the acetic acid and methanol in the extraction.

12. A process according to claim 3 wherein the acid salt is sodium monohydrogen sulfate and the mutual solvent is methanol.

13. A process according to claim 2 wherein the volatile acid is sulfurous acid and the mutual solvent is methanol.

14. A process according to claim 2 in which the

volatile acid is hydrochloric acid and the mutual solvent iis acetone.

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