

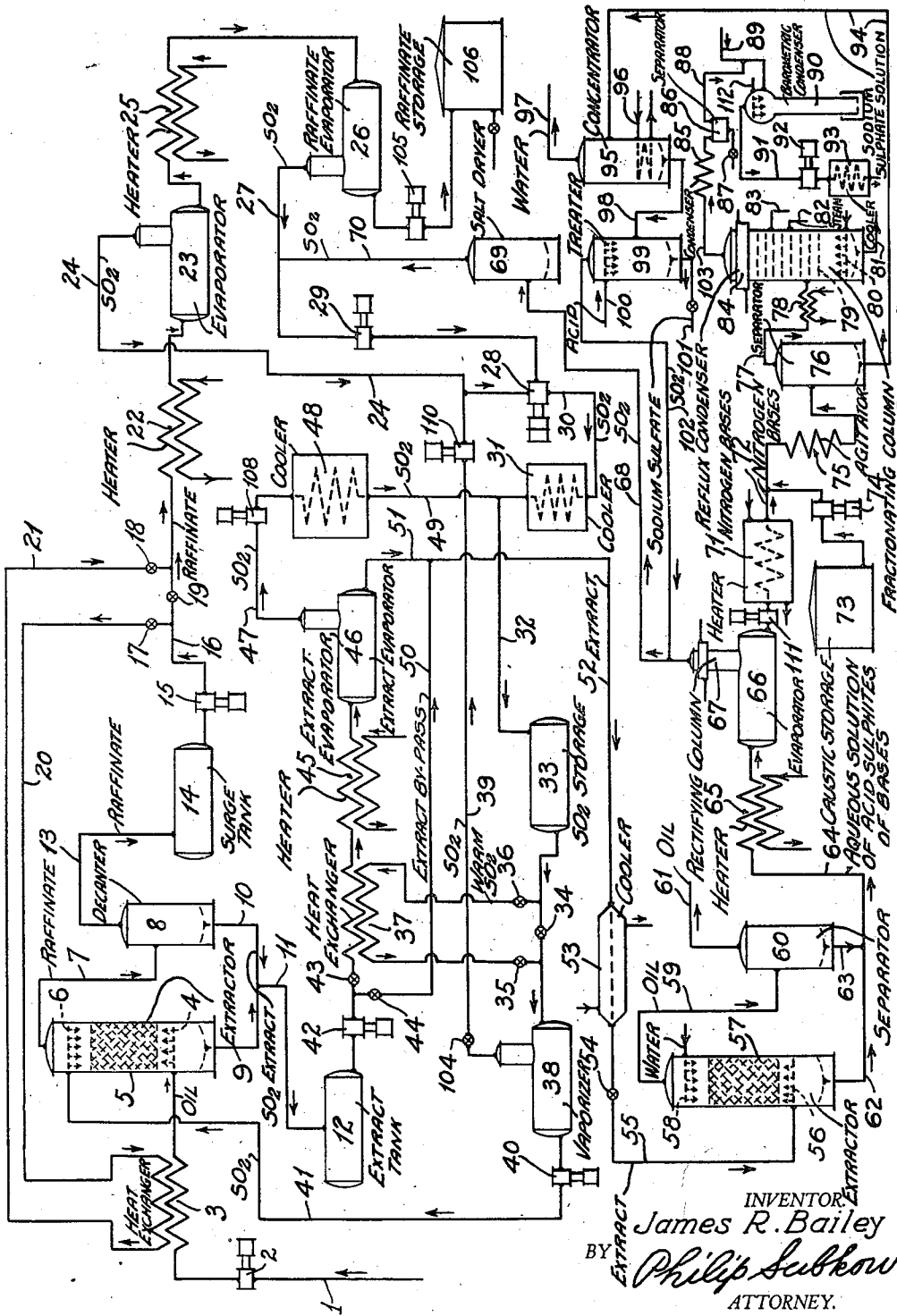
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J. R. BAILEY

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SEPARATION AND PURIFICATION OF NITROGEN BASES

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SEPARATION AND PURIFICATION OF
NITROGEN BASES

James R. Bailey, Austin, Tex., assignor to Union
Oil Company of California, Los Angeles, Calif.,
a corporation of California

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7 Claims. (Cl. 260—38)

This invention relates to a process for the recovery and separation of nitrogen bases, and more particularly to the recovery and separation of nitrogen bases from petroleum or shale oil and from the distillates obtained in the pyrolysis of cottonseed meal.

These substances, particularly petroleum oil, especially the asphaltic petroleum found in California, contain varying amounts of nitrogen base compounds. Attempts to remove these nitrogenous compounds from crude oils before distillation by using inorganic acids of varying strength resulted in the extraction of only negligible amounts of basic nitrogenous material. The results showed clearly that the crude oil itself does not contain any substantial amounts of basic nitrogen compounds.

I have discovered that the process of distillation generates basic organic nitrogen compounds not present in the original crude oil. The temperatures at which this conversion occurs are the usual distillation temperatures for the separation of crude oil into its fractions such as gasoline, kerosene, gas oil, lubricating oil and are usually below the cracking temperatures used in the conversion of heavier hydrocarbons into lighter hydrocarbons. While these higher cracking temperatures are efficient for the generation of basic nitrogen compounds, the lower non-cracking temperatures also produce organic nitrogen bases from non-basic compounds in the oil. Undoubtedly the efficient agent is heat, and this conversion of non-basic into basic nitrogen compounds may be obtained as well by merely heating without distillation to the temperatures usually employed. The above temperatures vary from 275° F. to, and including 740° F. while the cracking temperatures are much higher, varying from 800° F. to 1200° F. In the process of distillation oil is heated to different temperatures to recover various fractions. These temperatures vary depending on the distillation system employed. Representative temperatures are, however, as follows: For the removal of primary gasoline, oil is heated to about 275° F. For the removal of secondary gasoline the oil is heated to about 350° F. Oil is heated to from 500–680° F. to remove kerosene. Gas oil is recovered at about 680° F. and up, while lubricating oils are distilled at about 740° F.

The object of this invention is to extract the nitrogen bases from oil containing these bases by means of solvents or direct acid contact and to separate the crude bases into more simple mixtures or individual compounds.

Another object is to separate the bases by fractional acid extraction.

Another object is to resolve the crude acid extract by fractional neutralization by repeated participation of the bases by alkali.

In separating the bases from their oil content, I have found it desirable to first remove the hydrocarbon oil and to thus concentrate the bases. There are several ways in which this can be accomplished. Thus, the nitrogen bases may be extracted from the oil by repeated washing with relatively dilute acid, preferably sulphuric acid. Another method is to separate the bases from a major portion of the diluting hydrocarbon oil by extracting with a solvent in which the nitrogen bases are soluble but in which a large portion of the diluting hydrocarbon oil is insoluble.

Among the solvents which may be used to extract the nitrogen bases, liquid sulphur dioxide is the most important and universally used. (See U. S. patent No. 911,553.) Other solvents such as furfural, aniline, nitrobenzene and isobutyl alcohol, accomplish the same purpose and may be substituted for the liquid sulphur dioxide.

The portion of the oil which is soluble in the solvent, which portion may be termed the extract, contains the nitrogenous bodies, but also contains a considerable proportion of hydrocarbon oils, such as aromatic and olefinic bodies which are soluble in these solvents to a considerable extent. I have found it desirable to remove as much of the diluting oils as possible by extracting the bases with a dilute acid. The resulting solution may then be completely or fractionally precipitated by an inorganic base such as sodium hydroxide or ammonia to produce a mixture of bases substantially free of contaminating hydrocarbon oil.

The so-called Edeleanu process described in the Patent 911,553 is particularly well adapted to this process. This invention will be better understood by reference to the drawing which shows one exemplification of this process in schematic form.

The oil containing the organic nitrogen bases is introduced from a source, not shown in the drawing, passes through line 1, at a temperature of about 50° F., and is pumped by a pump 2, at a pressure of about 25 pounds, through heat exchanger 3 in heat exchange with the raffinate flowing from surge tank via pump 15, line 16, valve 17, lines 20 and 21 and valve 18 into heater 22. The flow of raffinate may be controlled by proper manipulation of valves 17 and 18. In case it is not desired to cool the incoming oil, valve 19

(which is closed when raffinate is circulating through heat exchanger 3) may be opened and by closing valves 17 and 18, the raffinate from tank 14 may be passed directly into heater 22.

5 The oil, leaving exchanger 3, cooled to about 20° F., is forced into the bottom of the SO₂ extractor 5 through jets 4 and meets a stream of liquid sulphur dioxide flowing through line 41 and jets 6. The SO₂ in its passage downward through 10 the oil dissolves therefrom the nitrogenous bodies together with the aromatic and olefinic fractions. The solution of these bodies in SO₂ being heavier than the original hydrocarbon oil drops to the bottom of the extractor 5. The hydrocarbon oil 15 (raffinate) being lighter than the sulphur dioxide "extract" rises to the top where it is removed through line 7. The raffinate contains some SO₂ in solution and some extract as entrained particles. The mixture is discharged into the "raffinate" or continuous decanter 8. The SO₂ extract which has settled in 8 is removed through line 10 and joins the extract withdrawn through line 9. Lines 9 and 10 join to form line 11 which carries the extract to the extract tank 12.

25 The raffinate freed of extract flows into surge tank 14 from which it is withdrawn by pump 15 and forced through line 16 either through line 20 and/or valve 19 as previously described. The raffinate then passes into heater 22 and then into an 30 SO₂ evaporator 23, operating at a pressure of about 75 pounds and a temperature of about 150° F. The dissolved SO₂ is removed through the top of evaporator 23 through line 24 and forced by means of compressor 28 into cooler 31 through 35 line 30, and from this cooler through line 32 and into the SO₂ storage tank 33. The raffinate leaving evaporator 23 is pumped through heater 25 where it is heated to about 200° F., and introduced into raffinate evaporator 26 operating at a pressure of about one-half pound absolute. The raffinate freed of SO₂ is withdrawn from evaporator 26 by pump 105 and introduced into the raffinate storage tank 106.

45 The sulphur dioxide gas liberated in evaporator 26 flows through line 27 and vacuum pump 29 into the suction side of compressor 28 from where it goes into storage as previously described.

50 The extract collected in tank 12 passes by means of pump 42 through valve 43 into heat exchanger 37 where it is preheated by warm liquid sulphur dioxide coming from tank 33 via valve 36. The cooled liquid sulphur dioxide coming from heat exchanger 37 through valve 35 passes into vaporizer 38, where the temperature of the SO₂ is lowered to approximately 20° F. by vaporizing a portion of the SO₂ under reduced pressure. The vaporized SO₂ passes via valve 104 into line 39 and then through booster compressor 110 to compressor 28 where it is re-compressed and passed 60 by means of line 30 into cooler 31 where it is liquefied and passed by means of line 32 to sulphur dioxide storage tank 33.

65 The extract collected in tank 12 is pumped by pump 42, valve 44 being closed, through heat exchangers 37 and heater 45 into the extract evaporator 46. The temperature of the extract on reaching the evaporator 46 is about 100° F., and the pressure is about 75 pounds. The evaporated SO₂ is removed through line 47, and compressor 70 108 into cooler 48 where it is liquefied and then through lines 49 and 32 into the SO₂ storage tank 33. The extract partially freed of SO₂ discharges from the evaporator 46 through lines 51 and 52 into a cooler 52.

75 By controlling the temperature and pressure in

the evaporator 46 the concentration of SO₂ in the extract leaving 46 may be controlled to give the acidity necessary for the extraction of the bases on subsequent extraction with water in extractor 57. An additional control is provided by the by-pass 50 which permits extract from 12 to be mixed with the extract from 46. Of course if it is desired, all of the extract may be by-passed directly to line 51.

80 The cooled extract flows through line 55, is 10 expanded through valve 54 and perforated pipe 56 to about atmospheric pressure. However any degree of pressure may be maintained in extractor 57 by controlling valve 54. It is preferable to operate at the elevated pressure to overcome the 15 back pressure of the system. The extract passes through jets 56 into the bottom of the lead or ceramic lined extractor 57 where it is treated countercurrently with a stream of cold water, introduced through line and jets 58. The lighter 20 hydrocarbon oil freed of organic nitrogen bases flows through line 59 into the separator 60 where the oil is removed through line 61 and the aqueous layer through line 63. The water extract from the SO₂ extract contains small amounts of SO₂ 25 and all the nitrogen bases in the form of acid sulfites in solution. This water solution is discharged through line 62 and joins line 63 also carrying dissolved acid sulfites of the nitrogen bases withdrawn from the bottom of 60. Lines 30 62 and 63 join to form line 64 through which the aqueous solution of the bases passes through heater 65 into evaporator 66. The water is heated sufficiently to drive off any SO₂ dissolved therein. The remaining SO₂ is removed through rectifying 35 column 67, which is operated to reflux water and permit substantially dry SO₂ to pass. The SO₂ gas flows through line 68 into the salt dryer 69 where remaining water vapor is removed, through line 70, into the suction side of compressor 29. 40 The evaporator 66 may be operated at an elevated or sub-atmospheric pressure as desired.

45 The SO₂ freed solution of the nitrogen bases flows from evaporator 66, pump 111 through heater 71 into line 72 where it meets a stream of caustic solution introduced from tank 73 by means of pump 74. The solution passes through agitator 75 into separator 76 where the nitrogen bases freed by the addition of caustic, are removed at the top through line 77 and subsequently 50 pass through heater 78 into a fractionating column 79. Conventional reflux condenser 84 may be provided and steam may be introduced at the bottom through jets 80.

55 The nitrogen bases entering the fractionating column 79 are fractionated into various cuts which may be removed as side cuts 82, 83 and as a bottom fraction through 81. The vapors discharge through line 103 into condenser 85 and separator 86. In separator 86 the nitrogen base 60 vapors are condensed and removed via 87 while the water vapor passes uncondensed through line 88. The water vapors emerging from separator 86 through line 88 are introduced into the suction side of a conventional vacuum steam jet 65 89 and is introduced into a barometric condenser 90 where they meet a stream of water at about 60-70° F. entering through line 112. The uncondensed vapors which may include fixed gases pass through line 91 into the suction side of 70 vacuum pump 92 and subsequently are liquefied by flowing through cooler 93.

The sodium sulfite solution formed by the addition of sodium hydroxide to the nitrogen bases in solution is discharged from separator 76 through 75

line 94, into concentrator 95. The solution is heated sufficiently by steam coil 96 to drive off the major portion of the water which is removed by means of line 97. The concentrated sodium sulfite solution passes through line 98 into the lead lined treater 99 into which a stream of dilute sulfuric acid is introduced through line 100. The sulphur dioxide formed is removed through line 102 and passes through line 68 into the salt drier 69. The sodium sulfate solution is removed through line 101.

The fractionator 79 may be operated at any desired degree of pressure but it is preferred to operate at as low a pressure as possible in order to avoid the decomposition or cracking of the nitrogen bases. Pressures as low as 1-25 m.m. of mercury absolute pressure may be used and are obtainable in the above apparatus. The use of a vacuum steam jet and barometric condenser 90 permits of condensation of steam by ordinary cooling water.

It is well known that liquid sulphur dioxide extracts from petroleum distillates contain a large number of compounds such as unsaturated, aromatic and sulphur bodies. Experiments conducted on kerosene and heavier fractions indicate that the resulting product after SO_2 extraction is practically nitrogen free. These nitrogen bodies are found in the SO_2 soluble fraction. The exact condition in which the nitrogen bases are present in the liquid SO_2 extract is not known. I believe, however, that there is strong evidence that these nitrogen bases are present partly combined with sulphur dioxide as sulphur dioxide addition products and partly as free bases dissolved in the extract.

The extract from the liquid sulphur dioxide treatment is forced under pressure into a separating chamber where some of the sulphur dioxide is distilled off. The remaining extract containing only small amounts of SO_2 is pumped into a contact chamber where it is washed with water. The SO_2 is converted into H_2SO_3 which reacts with the organic nitrogen bases to form soluble sulfites. A subsequent heating of this layer after separation from the petroleum fractions may liberate additional SO_2 which may be dried and recovered. The bases present in the aqueous layer may be liberated by treatment with caustic. The caustic solution is steam distilled and the bases recovered. It should be noted that this process may operate in a continuous manner and that the amount of basic materials required is reduced to a minimum as no acid is added to extract the bases.

This mixture of crude bases may be fractionated as shown and these fractions or the crude mixture itself may be further resolved by chemical methods into purer and simpler mixtures and even into pure compounds.

As was stated previously, the bases may be extracted either from the petroleum oil or from the extract or other concentrate of these bases by means of dilute acids such as sulphurous acid, sulphuric, nitric or other inorganic acids or by means of relatively strong organic acids such as acetic, chloracetic, oxalic acids or acidic substances such as picric acid, etc.

The result of the acid or solvent extraction is a complex mixture of aromatic and naphthenic nitrogen compounds, partly of the pyrrole type and partly of the pyridine and piperidine type. The number of the bases isolated from any fraction in which they occur is undoubtedly very large. Their nature depends, to a large extent,

upon the source from which they are isolated. They range from low boiling liquids to comparatively high melting solids. As a rule, a mixture of the aforementioned bases has a rather pungent odor and tends to darken on standing.

These crude mixtures may be purified and resolved into more simple mixtures and even pure components by several means. They may be first fractionally distilled or rectified into a plurality of relatively narrow cuts. These cuts, or if so desired the crude mixture, may be further resolved by converting them into salts. In this operation advantage is taken of the different basicity of these bases and their relative reactivity with various acids or salts.

A complex mixture of bases may be separated into several more simple ones, or pure compounds, by the addition of various reagents capable of forming salts with the nitrogen bases present. Some of the bases form easily separable salts with the common inorganic or organic acids.

Various salts are capable of forming salts or double salts with some of the bases present in a crude mixture, so that on separation of the products formed a simpler aggregate of bases is obtained or a base is removed from its impurities in pure form.

For instance, sodium ferrocyanide in dilute hydrochloric acid solution combines with some of the bases to form nicely crystallizing, well defined precipitates. These precipitates may be removed from the mixture leaving a more simple aggregate than was originally present. Mercurous chloride forms well defined precipitates with a number of the nitrogen bases. These precipitates are white and crystalline and by a repeated treatment of a mixture of bases with this compound are separated into more simple mixtures or a base may be separated from its impurities. In addition to the previously mentioned salts, other salts reacting in an identical manner may be used. They are salts of platinum, palladium, gold, cadmium, iron (ferrous and ferric), potassium dichromate, etc. Thus, with the 2,3,8 trimethylquinoline base, which may be isolated from the nitrogen bases present in kerosene distillate, gold chloride forms a salt of yellow color resembling the picrate of said base and recrystallizing from water in long, slender rods; platinum chloride forms a granular light orange colored salt, difficultly soluble in water and alcohol; potassium dichromate gives an orange yellow salt, but crystallized from water in a fine granulated condition; potassium ferrocyanide precipitates the difficultly soluble hydroferrocyanide of a light cream color which in boiling water decomposes with the evolution of prussic acid; zinc chloride gives a salt recrystallizing from alcohol in long slender prisms; the mercuric chloride salt is readily soluble in hot water and hot alcohol and separates from either solvent in long, slender rods; the stannous chloride salt has solubilities similar to the mercuric chloride salt and is best crystallized from glacial acetic acid in the form of rods.

It has been established that some of the bases form insoluble salts with some of the salts previously mentioned while others do not react at all. By successive addition of small amounts of these salts, the original mixture is more and more completely broken up into simpler ones. When this procedure is carried out on a narrow cut of nitrogen bases obtained by fractional dis-

tillation, preferably under vacuum, the pure base may be obtained by selectively precipitating it from its admixtures.

The salts formed may be isolated by any suitable method. I may treat a complex mixture of nitrogen bases with a salt forming reagent, separate the salts that are formed, and resolve the salts into mixtures containing a purified and less complex mixture of bases.

The resolution of a complex mixture of nitrogen bases by the formation of salts may also be carried out by fractional acid extraction and fractional caustic precipitation. I have found that the bases in the individual fractions show a considerable difference in their pH values and that by partial acid extraction followed by fractional caustic precipitation, the distillate fractions or the crude bases themselves can be separated into much simpler mixtures. I have also found that through fractional distillation followed by fractional acid extraction, a large number of bases can be brought to a state of purity whereby final recrystallization of the appropriate salts will effect their complete purification.

In carrying out this fractional extraction, the base is treated with successive amounts of dilute acid such as sulphuric acid or picric acid or any of the acids previously mentioned. The unreacted base is separated from the acid solution of the bases. The unreacted base is again extracted with additional amounts of acid and the extraction and separation is repeated until all of the bases are removed by the acid. By regulating the strength of the acid, the bases may be extracted so that the relatively strong bases are separated from the relatively weak ones. Thus, the partition of acid between a number of bases of varying pH value will be such that the acid will be taken up by the strong bases in a greater degree than by the weak ones. The weaker the base, the less the formation of its salt. In this manner, we may resolve the bases into those of varying degrees of basicity. It will be recognized that by extracting with increasing or decreasing acid strengths, a further segregation according to the above principle into varying strength bases is possible.

The various salt solutions, each containing different fractions, may be further resolved into free bases by fractional precipitation by alkali. This operation is identical in principle to acid extraction since it also depends on the relative pH value of the bases. It operates oppositely to the acid extraction. Whereas with acid extraction, the stronger bases are preferentially removed, it is the weaker bases which are preferentially precipitated by the alkali. By regulating the strength of the alkali, a classification of the bases may be obtained. Thus, if we made three extractions with acids to obtain three classes of bases in three different salt solutions, then precipitate the bases by treating each salt solution with three different treatments with alkali, we will have then resolved the original mixture of bases into nine fractions of varying basicity and purity.

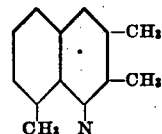
The fractional extraction with acids and bases tends to resolve the bases into varying basic strengths, also acts to separate the bases of pyridine type from the naphthenic bases, i. e. those of piperidine type. The pyridine bases being strong, will be preferentially dissolved by the acid and the piperidines will be preferentially liberated from the mixture of salts of these bases.

The above methods may be employed for the separation of pure components from the crude mixture of bases.

A kerosene boiling between 350-550° F., obtained from a California McKittrick asphaltic crude, was extracted with liquid SO₂. The SO₂ extract was freed of SO₂ and washed with dilute sulphuric acid. The acid solutions were neutralized with sodium hydroxide and the freed base was separated from the sodium sulphate solution. The crude bases were fractionally distilled, and distillates re-distilled to produce narrow cuts. The distillation was carried out under very high vacuum to minimize decomposition. The fraction boiling at atmospheric pressure at 276-277° C. was isolated. This fraction contains approximately 18% of a pure base which is 2,3,8, trimethylquinoline. A very satisfactory method for isolation of this base from the other bases in this fraction is to separate it in the form of the picrate admixed with the picrate of the base C₁₆H₂₅N, another base present in this fraction, by the addition of successive portions of 20 grams of picric acid in 50 c. c. of 50% acetic acid to 100 c. c. of the above distillation fraction dissolved in 350 c. c. of 50% acetic acid. The picrate of the latter base in contrast with that of the former is readily soluble in both benzene and alcohol and, therefore, a mixture of these salts is easily separated.

A second method of isolation of 2,3,8, trimethylquinoline is offered through its acid sulphate. Preliminary tests are made to indicate the amount of 50% sulphuric acid to be used as well as the concentration of this base in different fractions. Through the sulphate test fractions boiling from 274 to 280° C. (748 m. m.) inclusive, were found to contain 2,3,8, trimethylquinoline with the maximum amount of around 20% in the 276 to 277° C. fraction. Since the sulphate of the base C₁₆H₂₅N is very soluble, it is not precipitated but can be subsequently separated as picrate. However, admixed with this sulphate there occurs in small amount the sulphate of a second base having the formula C₁₇H₂₃N. This latter base is an odorless solid melting at 43° and boiling at 278.9° C. (748 m. m.). It reacts with formaldehyde and with methyl iodide forms the corresponding quaternary ammonium salt at water bath temperature.

When either the picrate or sulphate is heated with ammonium hydroxide, the base separates as an oil which later solidifies. This is taken up with ether, the ethereal layer washed with water and ether allowed to evaporate. Recrystallized from 50% alcohol, the new product separates in lustrous, rectangular plates without end faces, melts sharply at 55 to 56° and boils with partial decomposition at 280° C. (747 m. m.). It is 2,3,8, trimethylquinoline



Characteristic of this substance is its faint fecal odor. It is readily soluble in the common organic solvents, very difficultly soluble in water even at boiling temperature and volatile with steam.

The picrate of the base because of its difficult solubility in all the common solvents may, like a sulphate, be employed in obtaining the amount of the 2,3,8, trimethylquinoline in different frac-

tions of the kerosene bases. Dissolved in hot glacial acetic acid, it separates on cooling in arborescent canary yellow crystals which blacken and decompose with gas evolution at 242-245° C. On heating in ammonium hydroxide solution the base is liberated.

The resolution of the bases into mixtures of varying degrees of basic strength is especially useful in the preparation of strong organic bases which are oil soluble. All of these bases are, of course, oil soluble. The stronger bases are useful as emulsifiers for oil. Thus, the fatty acid salts of these bases may be useful to form oil soluble soaps which may be used in making emulsifiable oil. Obviously, the stronger the base, the more efficient it will be for this purpose and the separation of the weaker bases from the stronger bases results in a purer, stronger and more efficient oil soluble base.

In like manner, the removal of the hydroaromatic bases from the aromatic base, i. e. the piperidine type bases from the pyridine type base results in a purer compound to be used as an intermediate in the preparation of phthalone dyes of the methyl quinoline type.

The 2,3,8 trimethylquinoline condenses on fusion with phthalic anhydride to form a phthalone dye intermediate which when sulphonated, forms a beautiful yellow dye. The reaction may be carried out by simply fusing the intermediate at a temperature of 200° C. for a period of four hours. The resulting dye is extremely stable.

In like manner, the crude mixture of pyridine type bases obtained preferably by fractional extraction to separate it from the hydroaromatic bases may be used instead of the pure 2,3,8, trimethylquinoline. The crude mixture of these bases contain a large number of quinolines which have the methyl group in proper position for condensation with phthalic anhydride. For example, 2,3 dimethylquinoline and 2,4 dimethylquinoline are present in the crude mixture. The quinolines methylated at the 2 position are capable of condensation with phthalic anhydride. Where such a condensation reaction is carried out with phthalic anhydride, the quinolines methylated in the above mentioned positions react. Thus, where we have a mixture containing other quinolines besides the ones methylated in the proper position, others not so constituted, addition of phthalic anhydride will cause a selective condensation, i. e. only the quinolines methylated in the proper positions react. By fractional acid extraction and caustic precipitation, a particular cut may be narrowed down to a point where the particular methylated quinolines predominate. Addition of phthalic anhydride will cause the formation of phthalone dyes. Thus by fractional acid extraction and caustic precipitation, a complex mixture of bases may be narrowed down to a point where phthalone dye formation is materially facilitated. The same results may of course, be obtained by fractional precipitation of the various bases as salts.

The various examples set forth herein are not to be considered as limitations upon my invention. As to the scope thereof, reference is made to the appended claims.

I claim:

1. A method of separating organic nitrogen bases from petroleum fractions which comprises extracting said fractions with liquid sulphur dioxide to form an extract containing said organic nitrogen bases, hydrocarbon oil and liquid sulphur dioxide, removing a portion of the sulphur

dioxide from said extract and contacting the remaining extract with water, separating an aqueous phase containing nitrogen bases from an oil phase and liberating the nitrogen bases from said aqueous phase by addition thereto of an inorganic hydroxide.

2. A method of separating organic nitrogen bases from petroleum fractions which comprises extracting said fractions with liquid sulphur dioxide to form an extract containing said organic nitrogen bases, hydrocarbon oil and liquid sulphur dioxide, removing a portion of the sulphur dioxide from said extract and contacting the remaining extract with water, separating an aqueous phase containing nitrogen bases from an oil phase, liberating the nitrogen bases from said aqueous phase by addition thereto of a solution of an alkali metal hydroxide and separating the liberated nitrogen bases.

3. A method of separating organic nitrogen bases from petroleum fractions which comprises extracting said fractions with liquid sulphur dioxide to form an extract containing said organic nitrogen bases, hydrocarbon oil and liquid sulphur dioxide, removing a portion of the sulphur dioxide from said extract and contacting the remaining extract with water, separating an aqueous phase containing nitrogen bases from an oil phase, liberating the nitrogen bases from said aqueous phase by contacting said aqueous phase with an alkali metal hydroxide, separating the liberated nitrogen bases and fractionally distilling the liberated bases at pressures less than atmospheric.

4. A method of separating nitrogen bases from kerosene produced from asphalt base crude oil, which comprises extracting said kerosene with liquid sulphur dioxide, separating the sulphur dioxide extract from the portion of the kerosene insoluble in liquid sulphur dioxide, separating the sulphur dioxide from the extract to produce a crude mixture of bases, distilling said crude mixture to obtain a fraction containing components having a boiling range of 276-277° C. and adding picric acid to said fraction to precipitate the picrate of 2,3,8 trimethylquinoline, separating the picrate from the remainder of the fraction and liberating the 2,3,8 trimethylquinoline from the picrate by reaction with an inorganic hydroxide.

5. A method of separating nitrogen bases from kerosene produced from asphalt base crude oil which comprises extracting said kerosene with liquid sulphur dioxide, separating a sulphur dioxide extract from the portion of the kerosene insoluble in liquid sulphur dioxide, removing the sulphur dioxide from the extract to produce a crude mixture of nitrogen bases, extracting said crude mixture with an inorganic acid to form an aqueous solution of salts of the nitrogen bases, liberating the bases from said aqueous solution by means of an inorganic hydroxide, separating the nitrogen bases, fractionally distilling said separated bases to obtain a fraction containing components having a boiling point range of approximately 276° C. to 277° C., adding picric acid to said fraction to precipitate the picrate of 2,3,8 trimethyl quinoline, separating said picrate from the remainder of said fraction and liberating the 2,3,8 trimethyl quinoline from its picrate with an inorganic hydroxide.

6. A method of separating organic nitrogen bases from petroleum fractions which comprises extracting said fractions with liquid sulphur dioxide to form an extract containing said organic

nitrogen bases, hydrocarbon oil and liquid sulphur dioxide, removing a portion of the sulphur dioxide from the said extract, contacting the remaining mixture with water and separating an aqueous solution containing acid sulphites of the nitrogen bases.

7. A method of separating organic nitrogen bases from petroleum fractions which comprises extracting said fractions with liquid sulphur dioxide to form an extract containing said organic

nitrogen bases, hydrocarbon oil and liquid sulphur dioxide, removing a portion of the sulphur dioxide from the said extract, contacting the remaining mixture with water, separating an aqueous solution containing acid sulphites of the nitrogen bases and separating the nitrogen bases from said aqueous solution.

JAMES R. BAILEY.