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# UNITED STATES PATENT OFFICE

2,136,604

## SEPARATION AND PURIFICATION OF AROMATIC AND NONAROMATIC NITROGEN BASES

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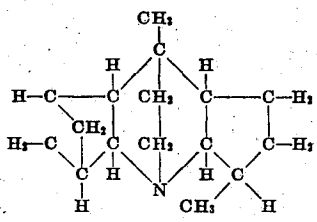
No Drawing. Original application October 17, 1932, Serial No. 638,195. Divided and this application December 14, 1936, Serial No. 115,783

11 Claims. (Cl. 260—269)

This invention relates to a process for the resolution of complex mixtures of nitrogen bases. More specifically it relates to a process for the resolution of complex mixtures of nitrogen bases such as may be extracted from natural sources, for instance petroleum oils (including the asphaltic type California oils), shale, or the pyrolytic distillates of cottonseed meal, into aromatic and hydroaromatic nitrogen bases. This application is a division of my copending application Serial No. 638,195 filed October 17, 1932 which in turn is a continuation in part of my application Serial No. 590,913 filed February 4, 1932.

As a general rule, a crude mixture of nitrogen bases, extracted from any of the sources previously referred to consists of bases which may be classified as aromatic and hydroaromatic, or naphthenic bases. One of the fundamental differences between the aromatic and the hydroaromatic nitrogen bases lies in their respective refractive indices. The hydroaromatic hydrogen bases exhibit a much lower refractive index than the aromatic ones. Thus, for instance, quinoline, isoquinoline and their homologues exhibit a refractive index of approximately 1.600 (based upon the D line of the sodium spectrum, observation made at 25° C.) while the hydroaromatic nitrogen bases possess refractive indices ranging from 1.4833–1.5129 under the same conditions. Therefore, the determination of refractive indices is of great help to determine the completeness of the separation of a mixture of nitrogen bases into aromatic and hydroaromatic bases.

A typical nitrogen base, illustrative of the aromatic type, is 2, 3, 8 trimethylquinoline, while the hydroaromatic type may be illustrated by the pyrindacine base $C_{16}H_{25}N$ which is generally considered to have the following structure:



and which may be considered as a piperidine derivative. In the aforesaid application, I have indicated that the 2, 3, 8 trimethylquinoline may be separated as an insoluble acid sulphate from the soluble acid sulphate of the $C_{16}H_{25}N$ base, both bases being concentrated in a fraction of nitrogen bases boiling at about 276° C., the fraction having been extracted with liquid sulphur dioxide from a California kerosene, produced from a McKittrick type crude oil. I have discovered that the method of separating the aromatic 2, 3, 8 trimethylquinoline from the hydroaromatic $C_{16}H_{25}N$, is universally applicable to, and extremely efficient in the removal of admixed hydroaromatic bases from aromatic nitrogen bases present in any crude mixture of these two types of bases. The method referred to above is also extremely helpful in removing the hydroaromatic nitrogen bases remaining admixed with the aromatic nitrogen bases after a preliminary separation of the nitrogen bases as to types has been carried out by some other method. A number of processes for the complete or partial separation of mixtures of nitrogen bases into aromatic and hydroaromatic bases have been disclosed and claimed in my copending application Serial No. 627,134.

It is, therefore, an object of my invention to provide a simple and efficient method of resolving a complex mixture of nitrogen bases into fractions comprising only aromatic or hydroaromatic nitrogen bases.

Briefly stated, my invention comprises a process for the resolution of mixtures of nitrogen bases of variable complexity into aromatic and hydroaromatic bases by the formation of the acid sulphates of the bases and their separation by means of water soluble organic solvents in which the acid sulphates of the aromatic bases are substantially insoluble and the acid sulphates of the hydroaromatic bases are readily soluble. Examples of such solvents are ketones, for instance acetone, alcohols, for instance ethyl or methyl alcohol and esters, for instance ethyl acetate.

My invention also comprises any of the specific procedures hereinafter disclosed.

In order to resolve a mixture of nitrogen bases into aromatic and hydroaromatic bases, it is necessary to isolate the bases from the medium in which they are present. Thus, in the case of

mixtures of bases present in petroleum distillates, it is necessary to remove the bases from their oil content. There are several methods by which this can be accomplished. For instance, the nitrogen bases may be extracted from the petroleum distillates by repeated washing with dilute sulphuric acid. Another method of extracting the nitrogen bases from petroleum distillate consists in extracting them with liquid sulphur dioxide according to the well known Edeleanu process (U. S. Patent 911,553). The extract phase thus obtained, contains large amounts of liquid sulphur dioxide, the nitrogen bases and the $SO_2$ soluble hydrocarbons present in the distillate. The major portion of the sulphur dioxide is then vaporized from the extract phase. The "extract" remaining after the major portion of the sulphur dioxide has been removed, contains in addition to small amounts of dissolved sulphur dioxide, a much higher concentration of nitrogen bases (partly as sulphur dioxide addition compounds, partly as free nitrogen bases) than was present in the original crude distillate. This extract is then treated with dilute sulphuric acid or water, for instance on countercurrent contact to extract the bases as acid sulphates or as acid sulphites in aqueous solution and the free nitrogen bases are obtained as a crude mixture by the addition of an inorganic base to the aqueous solution referred to above. These processes of extracting a mixture of nitrogen bases from natural sources have been fully disclosed and claimed in my copending application Serial No. 590,913 of which this application is a continuation in part.

My preferred method for resolving a mixture of nitrogen bases into aromatic and hydroaromatic bases is as follows:

A mixture of nitrogen bases, such as may be extracted from any of the natural sources referred to earlier in this specification, is dissolved in about twice its volume of acetone or alcohol. Concentrated sulphuric acid (sp. gr. 1.84) is then added slowly to the solution to precipitate substantially all of the aromatic nitrogen bases as insoluble acid sulphates which come down either in the form of a white crystalline precipitate or in the form of a white to yellow oily smear. When the aromatic bases are present in much larger proportions than the hydroaromatic, and this aromatic material consists of only two or three individual bases, the precipitate tends to be crystalline, but unless these conditions exist, it is oily. the acid sulphates of the hydroaromatic bases remain for the most part dissolved in the acetone or alcohol.

The amount of sulphuric acid required to quantitatively salify a given weight of a mixture of nitrogen bases is readily calculated from the nitrogen content of the latter. For instance, 100 grams of a mixture of nitrogen bases, which on analysis showed to contain 7% of nitrogen, would require approximately 51.58 grams of 95% sulphuric acid for conversion to acid sulphates. The most efficient conversion of the bases into acid sulphates is brought about by the addition of an equal molecular quantity of sulphuric acid as illustrated by the above figures. It has been observed that the weight of the insoluble acid sulphates increases at first with the amount of sulphuric acid added until a limit is reached, the limit being slightly less than an equal molecular quantity of sulphuric acid. After the limit has been reached, any subsequent addition of sulphuric acid tends to dissolve some of the precipitated acid sulphates. The fraction of the precipitate redissolving is principally composed of hydroaromatic acid sulphates which were at first precipitated together with the aromatic acid sulphates. Consequently, the precipitated acid sulphates contain a higher concentration of aromatic nitrogen bases when the volume of acid used per volume of base is increased. However, as previously stated, a very efficient precipitation, i. e., one in which the precipitates contain a high concentration of aromatic nitrogen bases may be carried out by using equal molecular quantities of sulphuric acid and nitrogen bases. The reaction mixture should be kept reasonably cool to prevent the formation of mesytiline or ether, due to a reaction between the sulphuric acid and the acetone or alcohol. It has been found desirable to add the sulphuric acid rather slowly as sometimes on a more rapid addition of the sulphuric acid, a carbonization of the nitrogen bases was observed. After all of the sulphuric acid has been added, the reaction mixture is cooled somewhat further, the insoluble acid sulphates of the aromatic nitrogen bases filtered off and the filter cake washed with a little acetone or alcohol to remove any of the remaining acid sulphates of the hydroaromatic nitrogen bases.

As a modification of the foregoing process, I may operate as follows: A mixture of nitrogen bases, extracted from a California kerosene with liquid sulphur dioxide in the manner outlined earlier in this specification, or from any of the sources previously referred to and containing both aromatic and hydroaromatic bases, is commingled with an equivalent of concentrated sulphuric acid which is slowly added to the solution at reduced temperatures. The acid sulphates of the nitrogen bases are then digested with acetone or alcohol in either of which the acid sulphates of the aromatic bases are difficultly soluble but in which the hydroaromatic acid sulphates are soluble to a considerable degree. The hydroaromatic acid sulphates tend to accumulate in the solvent while the white acid sulphates of the aromatic bases settle out from the solution as a precipitate or as an oily smear depending upon the concentration of aromatic bases as stated above.

The insoluble acid sulphates of the aromatic bases may be treated with an excess of caustic soda to liberate the free bases or they may be separated by fractional crystallization from appropriate solvents, or the sulphates may be directly converted to other salts, such as picrates, by the addition of an alcoholic solution of picric acid and the picrates of the bases separated by fractional crystallization from alcohol or other solvents. In closely cut distillation fractions, especially those fractions obtained by fractionally distilling a crude mixture of nitrogen bases extracted from a California kerosene, there are usually not more than 2 or 3 aromatic nitrogen bases present. After these bases have been freed from the admixed hydroaromatic bases, fractional crystallization as salts from appropriate solvents, such as outlined above, leads to the isolation of single compounds in a number of instances.

The hydroaromatic bases may be recovered as free bases by distilling off the solvent from the acetone or alcohol solution of the acid sulphates and adding sodium hydroxide or ammonium hydroxide to the acid sulphates remaining as a residue.

The addition of the sulphuric acid to any mixture of nitrogen bases obtained from petroleum (including the California asphaltic petroleums) shale or from a pyrolytic distillation of cotton-

seed meal, may also be carried out fractionally. In fractionally precipitating the acid sulphates of the nitrogen bases or of any fraction thereof, the bases are dissolved in the appropriate amount of solvent, such as acetone or alcohol, small portions of concentrated sulphuric acid are added while cooling the mixture, and the precipitates, consisting chiefly of aromatic acid sulphates, are withdrawn after each addition of sulphuric acid.

In addition, my process may operate as an aid in separating a pure nitrogen base from a fraction of nitrogen bases.

The completeness of the separation of the aromatic bases from the hydroaromatic ones by my process, may be ascertained by measuring the decrease or increase in refractive index of the mixture. The removal of the aromatic bases from a mixture containing aromatic and hydroaromatic bases will tend to decrease the refractive index of the mixture and will indicate to an operator the extent of separation at any stage of the process.

The following example is given by way of illustration:

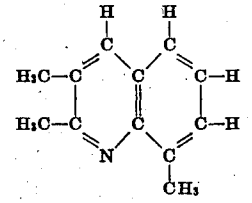
A fraction of nitrogen bases boiling at approximately 285° C. was obtained by fractionally distilling under reduced pressure a crude mixture of nitrogen bases extracted from a crude California kerosene by the liquid sulphur dioxide extraction process referred to earlier in this specification.

A sample of this fraction weighing 152 grams and having a refractive index, $n$ 30/$D$=1.5395, was dissolved in twice its volume of acetone and 52 c. c. of concentrated sulphuric acid was added while cooling and stirring the mixture. A voluminous white precipitate of acid sulphates, weighing 37.857 grams was formed. The acid sulphates were then filtered off, washed with 30 c. c. of acetone and dried at 110° C. The bases were liberated from the acid sulphates in the usual manner by the addition of caustic soda. They weighed 21.8 grams and had a refractive index of $n$ 30/$D$=1.5886. The residual bases remaining dissolved in the acetone as acid, sulphates, after distilling off the acetone, were taken up in water and the bases freed with ammonium hydroxide. They weighed 128.2 grams and had a refractive index of $n$ 30/$D$=1.5262. The aromatic nitrogen bases separated as acid sulphates from this fraction form picrates on the addition of picric acid to them. These picrates recrystallize very nicely from 95% ethyl alcohol. The advantage of the picrate recrystallization from ethyl alcohol lies in the fact that the picrates of the aromatic bases are much more insoluble than the picrates of the hydroaromatic bases, so that a further purification may be brought about by retaining in the solution some of the dissolved picrates of the hydroaromatic bases and precipitating the insoluble picrates of the aromatic nitrogen bases.

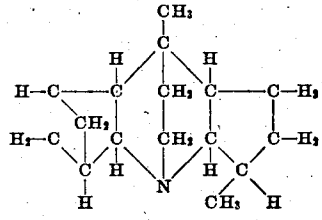
As stated earlier in this invention, the amount of the sulphuric acid added in the separation of the aromatic from the hydroaromatic bases is of importance.

The following example is illustrative of the influence of the amount of sulphuric acid added and at the same time indicates how my process may operate as an aid in isolating a pure nitrogen base from a fraction of nitrogen bases having a narrow boiling point range.

A fraction of nitrogen bases boiling at approximately 275° C. was obtained by fractionally distilling under reduced pressure a mixture of nitrogen bases extracted from a California kerosene according to the process outlined earlier in this specification. This fraction, having a refractive index $n$ 60/$D$=1.5155, contains considerable amounts of 2, 3, 8 trimethylquinoline



(refractive index $n$ 60/$D$=1.5828) and a hydroaromatic base $C_{16}H_{25}N$



(refractive index $n$ 60/$D$=1.4588).

Samples of this fraction of 100 c. c. each were dissolved in either alcohol or acetone and varying amounts of 95% sulphuric acid were added while cooling the solution. The sulphates in each case were weighed and the refractive indices of the bases freed from these sulphates taken. The results are shown in the following table:

*Table I*

| C. c. of bases | C. c. of $H_2SO_4$ | Grams of acid sulphates | N 60/D of free bases |
|---|---|---|---|
| 100 | 22 | 46.5 | 1.5220 |
| 100 | 23 | 34.1 | 1.5568 |
| 100 | 26 | 24.4 | 1.5648 |

The results, as shown in this table, indicate that with the smaller amount of sulphuric acid added, a greater weight of insoluble acid sulphates is obtained (which is due to the precipitation of some of the hydroaromatic bases as acid sulphates) and that when a limit is reached (which in this specific example seems to be between 22 and 23 c. c. of sulphuric acid) the hydroaromatic acid sulphates tend to go into solution decreasing the weight of the insoluble acid sulphates but increasing the refractive index due to a higher concentration of aromatic bases in the specific precipitates. The latter were removed, in great part, without liberating the bases from the acid sulphates by extraction of the hydroaromatic acid sulphates with boiling acetone. The insoluble acid sulphates after recrystallization from alcohol yielded bases with a refractive index and approximately 1.5800 at 25° C.

The pure 2, 3, 8 trimethylquinoline, referred to above, may be obtained by treating the acid sulphates of the bases having refractive indices of 1.5568 and 1.5648 (see Table I) or the nitrogen bases having a refractive index of 1.5800 obtained as outlined above, with picric acid which, on simple addition to the acid sulphates (both the picric acid and the acid sulphates being preferably dissolved in alcohol) forms the picrates of the bases present. The picrate of 2, 3, 8 trimethylquinoline, being far less soluble in alcohol than the accompanying picrates of the hydroaromatic or other aromatic bases, is easily isolated by frac-

tional recrystallization from alcohol and the free base obtained by addition of an inorganic base such as sodium hydroxide or ammonium hydroxide to the picrate.

The free 2, 3, 8 trimethylquinoline is an important dye intermediate. An extremely fast yellow dye of a brilliant color may be derived from this methylated quinoline by simply condensing the same with phthalic anhydride at a temperature of 200° C. The manufacture of this phthalone dye as well as phthalone dyes which may be prepared from any fractions of methylated quinolines which may be obtained from a mixtures of nitrogen bases by the process outlined in this invention are disclosed and claimed in my copending application Serial No. 628,770.

The following specific example will illustrate how an individual aromatic nitrogen base may be isolated from admixed hydroaromatic bases by the process herein disclosed:

A mixture of nitrogen bases extracted from a California kerosene by the liquid sulphur dioxide process outlined earlier in this specification was carefully fractionally distilled under reduced pressure and a fraction boiling at approximately 247–253° C. (atmospheric pressure) collected.

A portion of this fraction, weighing about 100 grams, was dissolved in twice its volume of acetone and 50 c. c. of concentrated sulphuric acid (sp. gr. 1.84) was slowly added to the solution which had been cooled to below 50° F. The aromatic base 2, 8 dimethylquinoline which is practically the only aromatic base present in this fraction precipitated as a white to yellow crystalline acid sulphate, while the hydroaromatic bases present in this fraction remained in solution. The precipitate was washed with a little acetone to remove any remaining acid sulphates of the hydroaromatic nitrogen bases and then dried at a temperature slightly above the boiling point of water. The free nitrogen base was obtained by adding an inorganic base such as sodium hydroxide to the acid sulphate. The total yield of 2, 8 dimethylquinoline was about 10% of the original weight of bases used. The boiling point of the base was 253° C. and it was characterized by a faint fecal odor. This quinoline also is a useful intermediate for manufacturing quinphthalone dyes.

In order to distinguish between the aromatic quinolines and substituted quinolines the acid sulphates of which are insoluble in my organic solvents and those bases yielding soluble acid sulphates, I have chosen to call the latter type of bases "hydroaromatic bases".

The bases yielding soluble acid sulphates are not completely hydrogenated in the same manner as piperidine or coniine which is evidenced by the fact that they are not susceptible to dehydrogenation (see Bailey et al., Journ. Chem. Soc. 55, 4145, 1933), but for want of a better term and in view of the fact that the identity of the bases yielding soluble acid sulphates has not yet been fully established I have labeled them as hydroaromatic.

The examples disclosed in this invention are not to be considered as limitations imposed thereon but are merely illustrative of the generic invention and many variations may be made within the scope of the appended claims.

I claim:

1. A process for resolving a mixture of organic nitrogen bases, as derived from petroleum, shale and pyrolytic distillate of cottonseed oil, and containing aromatic and hydroaromatic nitrogen bases which comprises forming the acid sulphates of said aromatic and hydroaromatic nitrogen bases and separating said acid sulphates by treating the same with acetone in which the aromatic acid sulphates are substantially insoluble but in which the hydroaromatic acid sulphates are soluble and separating the solution of the hydroaromatic acid sulphates from the insoluble aromatic acid sulphates.

2. A process for resolving a mixture of organic nitrogen bases, as derived from petroleum, shale and pyrolytic distillates of cottonseed oil, and containing aromatic and hydroaromatic nitrogen bases which comprises forming the acid sulphates of said aromatic and hydroaromatic nitrogen bases and separating said acid sulphates by treating the same with alcohol in which the aromatic acid sulphates are substantially insoluble but in which the hydroaromatic acid sulphates are soluble and separating the solution of the hydroaromatic acid sulphates from the insoluble aromatic acid sulphates.

3. A process for resolving a mixture of organic nitrogen bases, as derived from petroleum, shale and pyrolytic distillates of cottonseed oil, and containing aromatic and hydroaromatic nitrogen bases which comprises treating the bases with sulphuric acid to form the acid sulphates of the said bases and separating the acid sulphates of the bases by treating the same with a solvent selected from the class consisting of lower alkyl ketones, alcohols and esters in which the aromatic acid sulphates are substantially insoluble, but in which the hydroaromatic acid sulphates are soluble and separating the solution of the hydroaromatic acid sulphates from the insoluble aromatic acid sulphates.

4. A process as defined in claim 3 in which the amount of sulfuric acid added for the production of acid sulfates of the bases is slightly less than an equivalent molecular amount.

5. A process according to claim 3 in which the sulfuric acid treatment of the nitrogen bases is realized by a relatively slow addition of such sulfuric acid to prevent carbonization of the bases.

6. A process for resolving a mixture of organic nitrogen bases, as derived from petroleum, shale and pyrolytic distillates of cottonseed oil, and containing aromatic and hydro-aromatic nitrogen bases, which comprises forming the acid sulfates of said aromatic and hydro-aromatic nitrogen bases, separating the aromatic acid sulfates from the hydro-aromatic acid sulfates by extracting the acid sulfate mixture with an inert solvent selected from the class consisting of lower alkyl ketones, alcohols and esters, in which the aromatic acid sulfates are substantially insoluble but in which the hydro-aromatic acid sulfates are soluble, and separately removing the solution of the hydro-aromatic acid sulfates from the insoluble aromatic acid sulfates.

7. A process according to claim 6 in which the acid sulfates of the aromatic and hydroaromatic nitrogen bases are formed by treating said nitrogen bases with sulfuric acid.

8. A process for obtaining an aggregate of aromatic nitrogen bases free from hydro-aromatic bases and an aggregate of hydro-aromatic bases free from aromatic bases which comprises extracting a California kerosene, distilled from an asphalt base crude oil, with liquid sulfur dioxide to obtain an extract phase containing large amounts of liquid sulfur dioxide and the nitrogen bases present in the kerosene distillate together

with the sulfur dioxide soluble portion thereof, vaporizing the major portion of the sulfur dioxide, commingling the extract so obtained with water to obtain an aqueous solution of the acid sulfites of the nitrogen bases, adding an inorganic base to the said aqueous solution to isolate a crude mixture of nitrogen bases containing aromatic and hydro-aromatic nitrogen bases, isolating said crude mixture of nitrogen bases, adding sulfuric acid to said nitrogen bases to form the acid sulfate of the said bases, treating said acid sulfates with an inert solvent selected from the class consisting of lower alkyl ketones, alcohols and esters in which the aromatic acid sulfates are substantially insoluble but in which the hydro-aromatic acid sulfates are soluble and separating the insoluble acid sulfates of the aromatic nitrogen bases from the solvent solution containing substantially only the dissolved acid sulfates of the hydro-aromatic nitrogen bases.

9. A process for resolving a mixture of organic nitrogen bases, as derived from petroleum, shale and pyrolytic distillates of cottonseed oil, and containing aromatic and hydroaromatic nitrogen bases which comprises treating the bases with sulphuric acid to form the acid sulphates of the said bases and separating the acid sulphates of the bases by treating the same with acetone in which the aromatic acid sulphates are substantially insoluble but in which the hydroaromatic acid sulphates are soluble and separating the solution of the hydroaromatic acid sulphates from the insoluble aromatic acid sulphates.

10. A process for resolving a mixture of organic nitrogen bases, as derived from petroleum, shale and pyrolytic distillates of cottonseed oil, and containing aromatic and hydroaromatic nitrogen bases which comprises treating the bases with sulphuric acid to form the acid sulphates of the said bases and separating the acid sulphates of the bases by treating the same with alcohol in which the aromatic acid sulphates are substantially insoluble, but in which the hydroaromatic acid sulphates are soluble and separating the solution of the hydroaromatic acid sulphates from the insoluble aromatic acid sulphates.

11. A process for obtaining aggregates of nitrogen bases as derived from petroleum, shale and pyrolytic distillates of cottonseed oil, and containing only aromatic or hydroaromatic bases, free from admixture, which comprises extracting a mixture of nitrogen bases from a petroleum distillate containing the same, forming the acid sulphates of the extracted bases, extracting the acid sulphates with an organic solvent selected from the class consisting of lower alkyl ketones, alcohols and esters in which the acid sulphates of the aromatic bases are difficultly soluble and the acid sulphates of the hydroaromatic bases are readily soluble, separating the insoluble acid sulphates of the aromatic nitrogen bases, adding an inorganic base to the said insoluble acid sulphates to liberate the free aromatic bases, substantially free from admixed hydroaromatic bases, vaporizing the solvent from the solution of the acid sulphates of the hydroaromatic nitrogen bases and adding an inorganic base to the residue to obtain the free hydroaromatic nitrogen bases substantially free from admixed aromatic ones.

JAMES R. BAILEY.

## CERTIFICATE OF CORRECTION.

Patent No. 2,136,604. November 15, 1938.

JAMES R. BAILEY.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, line 21-22, for the word "hydrogen" read nitrogen; page 3, second column, line 61, for "and" read of; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 18th day of April, A. D. 1939.

Henry Van Arsdale

(Seal) Acting Commissioner of Patents.