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SEPARATION OF PYRROLE

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This invention relates to the recovery of pyrrole from mixtures of heterocyclic nitrogen compounds in which it occurs.

Pyrrole occurs in admixture with picoline and other pyridine homologs in a number of natural sources of heterocyclic nitrogen compounds. For example, a mixture of heterocyclic nitrogen compounds recovered from certain coal tars contains a substantial proportion of pyrrole. These heterocyclic nitrogen compounds, including pyrrole, pyridine, and the various pyridine homologs such as picolines and lutidines, are customarily extracted from coke-oven distillates and other sources of these heterocyclic nitrogen compounds by means of an aqueous solution of mineral acid, usually sulfuric acid. After liberation of the nitrogen compounds from their acid solutions by means of alkali, the mixtures of nitrogen compounds are fractionally distilled. Compounds such as pyridine, boiling point 116° C., can generally be obtained in reasonably pure form by fractional distillation, but many of the remaining compounds cannot be separated by ordinary distillation methods alone. Instead, the fractions obtained, even when they are of relatively narrow boiling range, contain increasing numbers of the various heterocyclic nitrogen compounds in each fraction.

Although pyrrole alone boils at about 129.8° C., in admixture with heterocyclic nitrogen compounds such as picolines it forms azeotropes from which the pyrrole cannot be separated by ordinary fractional distillation. These azeotropes are of the high-boiling type, boiling generally within the range of about 140°–148° C. For example a mixture of 20% pyrrole and 80% of a 3- and 4-picoline mixture in about equal proportions was found to distil through the temperature range of 146.8°–147.0° C., whereas the 3- and 4-picoline mixture alone distilled at 144.4° to 144.5° C. and the pyrrole alone distilled at 129.8° to 129.95° C. Upon fractional distillation of a mixture of heterocyclic nitrogen compounds recovered from certain coal tars containing pyrrole, fractions taken within the range 140°–148° C., even closecut fractions boiling for example within about 1° of 147° C., have been found to contain, in substantial proportions, 3-picoline (beta-picoline), boiling point 143.8° C., 4-picoline (gamma-picoline), boiling point 144.8° C., generally a small amount of 2,6-lutidine, boiling point 143.8° C., and, in addition, a substantial quantity of pyrrole, boiling point 129.8 C. Mixtures of this kind have found limited practical application, mainly as special solvents, and are of relatively low economic value; in fact, the presence of even a few percent pyrrole limits the usefulness of picoline-lutidine mixtures for many solvent purposes because the presence of pyrrole makes the mixture water-insoluble. However, the pyrrole, which is thus detrimental in a picoline-lutidine mixture, is itself a rare chemical of considerable value. For example, pyrrole derivatives are of importance as pharmaceuticals, agricultural chemicals, e. g., insecticides, perfume bases, and antiseptics; however, the high cost of preparing pyrrole by the complicated procedures now in use limits its employment in these and other fields.

Since the components making up the heterocyclic nitrogen compound fractions containing pyrrole form constant-boiling azeotropes, fractional distillation is obviously unsatisfactory as a means for resolving the mixtures. Methods heretofore proposed in the published prior art for separating pyrrole from such mixtures have been generally unsatisfactory in products, yields, and production costs. One method proposed for such separation, for example, is to treat the heterocyclic nitrogen compound mixture with an excess of sulfuric acid to hold the picolines and other pyridine homologs in combination and subject the resulting mixture to prolonged steam distillation to remove the pyrrole which is only loosely held in the sulfuric acid-pyridine homolog mixture. This method has been found unsatisfactory, however, since the heating of pyrrole in the presence of sulfuric acid causes resinification of the greater part of the pyrrole to polymers insoluble in hydrocarbon oils, nitrogen bases or water, forming a jelly-like precipitate which it is impractical to separate. This method is thus ineffective for separation of pyrrole from pyridine homologs and, moreover, all or most of the valuable pyrrole is converted into a product of little or no utility. Methods for separation of pyrrole have also been disclosed in the published prior art involving forming potassium pyrroles. However, the yields and production costs of these methods have been found so unfavorable that the methods have not been considered feasible for industrial use.

It is an object of this invention to provide a process for separating substantially pure pyrrole from admixture with other heterocyclic compounds not readily separable therefrom by distillation.

It is a further object of this invention to pro-

vide a commercially attractive method for recovering pyrrole from fractions of heterocyclic nitrogen compounds, particularly of coke-oven origin, boiling in the range from 140°–148° C., which fractions contain 3-picoline, 4-picoline, and pyrrole in substantial proportions, and may contain 2,6-lutidine.

We have discovered that pyrrole may be effectively and economically separated from mixtures thereof with other heterocyclic nitrogen compounds not separable from pyrrole by ordinary distillation, e. g. such other compounds as 3-picoline, 4-picoline, and 2,6-lutidine; in the process of our invention, a pyrrole-enriched product is separated from such heterocyclic nitrogen compound mixture by partially neutralizing the mixture with a relatively strong acid, as described below, under conditions that do not affect the nitrogen compounds deleteriously to a point where the mixture is slightly alkaline to methyl orange indicator, preferably having a pH in the range of from 4.4 to 5.0, and then subjecting the resulting mixture to steam distillation to separate as distillate a product enriched in pyrrole. The distillation residue may then be treated, e. g., with aqueous alkali, to liberate a heterocyclic nitrogen compound product low in pyrrole, i. e., enriched in the pyridine homologs that accompanied the pyrrole in the original mixture.

In the process of our invention, pure pyrrole and a pure pyridine homolog product may further be produced from the above products, i. e., the pyrrole-enriched material recovered as distillate, and the pyridine-homolog-enriched material recovered from the distillation residue, by fractionally distilling the pyrrole-enriched material to separate, as distillate, substantially pure pyrrole and by fractionally distilling the pyridine-homolog-enriched material to separate, as distillate, a substantially pure pyridine homolog product. In each of these two fractional distillations, the distillation residue consists of a constant-boiling pyrrole-pyridine homolog azeotrope of the high-boiling type, having a composition that is generally within the relatively narrow range of 15% to 25% pyrrole and 75% to 85% pyridine homologs, by weight; the exact composition of the high-boiling azeotrope will depend, at least in part, on the relative amounts of 3-picoline, 4-picoline and 2,6-lutidine in the pyridine homolog component of the mixture. The high-boiling pyrrole-pyridine homolog azeotrope remaining as residue from each of the two distillations is added to a new batch of pyrrole-containing heterocyclic nitrogen compound mixture to be treated by the process of our invention, while the pure pyrrole and pure pyridine homolog material are withdrawn as products.

Our invention further comprises a process in which the above-described separation of pyrrole is combined with steps for resolving into its components the above pyridine homolog material obtained as coproduct with the pyrrole. This pyridine homolog material generally contains 3-picoline, 4-picoline, and 2,6-lutidine. Thus our invention is applicable to resolving into its components a mixture of pyrrole, 3-picoline, 4-picoline, and 2,6-lutidine.

The process of our invention may be advantageously applied to the recovery of pyrrole from heterocyclic nitrogen compound mixtures obtained from coke-oven distillates, cracked petroleum, shale tar, bone oils, the products of destructive distillation of proteinaceous materials and from other natural, as well as synthetic, sources when these mixtures contain substantial amounts of pyrrole and other nitrogen compounds not readily separable therefrom by distillation, e. g., 3-picoline, 4-picoline, and 2,6-lutidine. When such a mixture of heterocyclic nitrogen compounds contains components of widely varying boiling points, the mixture is first subjected to fractional distillation whereby a fraction boiling in the range 140°–148° C. containing predominantly pyrrole and other nitrogen compounds not separable therefrom by ordinary distillation is obtained. Our invention comprises a process in which such a fractionation is combined with the above-described separation of pyrrole.

As above stated, a relatively strong acid should be employed in the partial neutralization. A strong mineral acid such as sulfuric acid or hydrochloric acid is preferably employed. However, any relatively strong acid, i. e., an acid having a minimum dissociation constant of 10^{-2}, preferably no lower than 10^{-1}, may be employed, provided such acid does not react deleteriously with the pyridine homologs or the pyrrole under the conditions of the process. Examples of such acids other than sulfuric and hydrochloric acids, include phosphoric acid, oxalic acid and benzenesulfonic acid.

In a preferred method of carrying out the process of our invention, a pyrrole fraction, as above described, suitably a fraction boiling in the range 140°–148° C. containing pyrrole, 3-picoline, 4-picoline, and small amounts of 2,6-lutidine, is mixed with a limited amount of sulfuric acid or hydrochloric acid, substantially less than the stoichiometric quantity of acid required for reaction with the nitrogen bases to form nitrogen base sulfates or hydrochlorides. As above indicated, the heterocyclic nitrogen compound mixture is thus partially neutralized to the point where it reacts slightly alkaline to methyl orange, i. e., to the point where it has a pH preferably in the range of about 4.4 to 5.0. When the amount of acid is thus carefully controlled, there will be no excess acid in the mixture and, accordingly, the pyrrole upon heating will not resinify as it does when heated in the presence of a strong acid, such as sulfuric acid or hydrochloric acid.

The mixture slightly alkaline to methyl orange, thus obtained, is subjected to steam distillation either at atmospheric pressure or under reduced pressure. When a dilute acid, e. g., 30% sulfuric acid, has been employed for the partial neutralization step, the steam distillation may be accomplished merely by heating the mixture to boil off water and a pyrrole-enriched nitrogen compound mixture. Steam distillation is continued until the distillate runs practically free of oil. The aqueous distillate is then made alkaline, e. g., by addition of caustic soda, to reduce the solubility of pyridine homologs present in the pyrrole-rich product in minor amount. The oil which separates out is decanted.

The distillation residue now low in pyrrole and consisting mainly of pyridine homolog sulfates or hydrochlorides is treated with alkali to liberate the nitrogen compounds which are decanted. Two products are thus recovered from the partial neutralization followed by steam distillation: a pyrrole-rich product and a pyridine homolog product low in pyrrole.

As indicated above, pyrrole tends to form

azeotropes of the high-boiling type with pyridine homologs such as the picolines. The constant-boiling mixture thus formed with a 3-picoline-4-picoline-2,6-lutidine mixture, as above stated, has a composition generally ranging from 15% to 25% pyrrole and 75% to 85% pyridine homologs by weight. Accordingly, both the pyrrole-rich product and the pyridine-homolog-rich product obtained above may be distilled to leave this high-boiling azeotropic mixture as still residue, in the first case taking off substantially pure pyrrole as distillate and in the second case taking off substantially pure pyridine homologs as distillate. The distillation residue consisting of the pyrrole-pyridine-homolog azeotropic mixture recovered from each distillation may be added to pyrrole-containing heterocyclic nitrogen compound mixture entering the process, while the pure pyrrole and pure pyridine homologs are withdrawn as products.

The pyridine homolog mixture thus recovered, generally containing 3-picoline, 4-picoline, and 2,6-lutidine, may be resolved into its components by methods described in copending applications, e. g. the methods of copending applications Serial No. 456,257, filed August 26, 1942, Serial No. 441,557, filed May 2, 1942, and Serial No. 452,369, filed July 25, 1942.

The following examples are illustrative of the process of our invention:

Example 1

798 pounds of an industrial beta-gamma picoline fraction (containing 16% pyrrole and 84% of a mixture of 3-picoline, 4-picoline, and 2,6-lutidine) were charged to a 500-gallon glass-lined kettle used as a still, along with 987 pounds of 27.6% aqueous sulfuric acid solution; the mixture had a pH of about 5. The kettle was equipped with a small condenser and a 175-gallon receiver with appropriate lines to run the system under vacuum. Distillation was carried out for 8 hours under 26 inches of vacuum. The distillate was separated into two layers: 796 pounds of water containing 0.64% nitrogen compounds and 246 pounds of crude pyrrole containing 8.5% water.

The distillation residue was neutralized with 782 pounds of 38% caustic soda mixed with 497 pounds of water. A pyridine homolog layer, low in pyrrole, was decanted. This amounted to 553 pounds and contained 26.5% water.

The pyrrole product and the pyridine homolog product were fractionally distilled. From the crude pyrrole, a pure pyrrole product amounting to 35% of the charge was taken as distillate, leaving a high-boiling pyrrole-pyridine-homolog azeotrope as still residue. From the crude pyridine homolog material a pure pyridine homolog product amounting to 85% of the still charge was taken as distillate, leaving as still residue a high-boiling pyrrole-pyridine-homolog azeotrope. The high-boiling pyrrole-pyridine-homolog azeotrope remaining as still residue in each case was set aside for further treatment with the next batch of industrial beta-gamma picoline.

Example 2

Another sample of the same beta-gamma picoline fraction used in Example 1 was charged to a still with an amount of 30% sulfuric acid solution sufficient to neutralize the mixture to a point just on the alkaline side of the methyl orange end point (pH about 5), as described in Example 1. In this case, steam distillation was carried out at atmospheric pressure for 8 hours. Crude pyrrole was recovered from the distillate and crude pyridine homolog material from the still residue, as described in Example 1.

In this case the crude pyrrole contained a somewhat higher content of pyridine homologs owing to some dissociation of neutral pyridine homolog sulfates upon distillation at atmospheric pressure. Fractional distillation of the crude pyrrole produced about 14% of pure pyrrole as distillate, the still residue being the high-boiling pyrrole - pyridine - homolog azeotrope. Fractional distillation of the crude pyridine homolog material liberated from the steam distillation residue produced about 80% of a pure pyridine homolog product as distillate, the still residue being the high-boiling pyrrole-pyridine homolog azeotrope.

Example 3

A sample of the same beta-gamma picoline fraction used in Examples 1 and 2 was charged to a still, along with enough 30% hydrochloric acid to bring the mixture to a point just on the alkaline side of the methyl orange end point (pH about 5). Steam distillation was then carried out at atmospheric pressure, and a crude pyrrole and crude pyridine homolog material recovered, as in the above examples.

Upon fractional distillation of the crude pyrrole, pure pyrrole in the amount of 55% of the still charge was taken as distillate. Upon fractional distillation of the crude pyridine homolog material, pure pyridine homolog product amounting to 78% of the still charge was taken as distillate.

Example 4

A sample of the same beta-gamma picoline fraction used in Examples 1, 2, and 3 was treated by the same general procedure outlined in Example 3, except that the steam distillation was carried out under a vacuum of about 26 inches mercury, thus holding the steam temperature around 60° C.

Upon fractional distillation of the crude pyrrole, pure pyrrole amounting to 10.7% of the still charge was taken as distillate. Upon fractional distillation of the crude pyridine homolog material, a pure pyridine homolog product amounting to 57% of the still charge was taken as distillate.

Since certain changes may be made in carrying out the above process without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

We claim:

1. In a process for separating pyrrole from a mixture thereof with pyridine homologs not readily separable therefrom by distillation, the steps that comprise adding to the mixture an acid that does not affect the nitrogen compounds deleteriously, said acid having a dissociation constant not lower than about 10^{-2}, in amount substantially less than the stoichiometric amount for reaction with the nitrogen bases present, and subjecting the resulting mixture to steam distillation to separate as distillate a nitrogen compound product enriched in pyrrole.

2. In a process for separating pyrrole from a mixture thereof with pyridine homologs not readily separable therefrom by distillation, the steps that comprise substantially neutralizing

the mixture with an acid that does not affect the nitrogen compounds deleteriously, said acid having a dissociation constant not lower than about 10^{-1}, to a point where the mixture has a pH not lower than about 4.4, and subjecting the resulting mixture to steam distillation to separate as distillate a nitrogen compound product enriched in pyrrole.

3. In a process for separating pyrrole from a mixture thereof with pyridine homologs not readily separable therefrom by distillation, the steps that comprise substantially neutralizing the mixture with a strong mineral acid that does not affect the nitrogen compounds deleteriously to a point where the mixture has a pH not lower than about 4.4, and subjecting the resulting mixture to steam distillation to separate as distillate a nitrogen compound product enriched in pyrrole.

4. In a process for separating pyrrole from a mixture thereof with pyridine homologs not readily separable therefrom by distillation, the steps that comprise substantially neutralizing the mixture with an acid that does not affect the nitrogen compounds deleteriously, said acid having a dissociation constant not lower than about 10^{-2}, to a point where the mixture has a pH not lower than about 4.4, subjecting the resulting mixture to steam distillation to separate as distillate a nitrogen compound product enriched in pyrrole, and fractionally distilling the pyrrole-rich product to separate substantially pure pyrrole as distillate.

5. In a process for recovering pyrrole from a mixture thereof with pyridine homologs not readily separable therefrom by distillation, the steps that comprise substantially neutralizing said mixture with a strong mineral acid that does not affect the nitrogen compounds deleteriously to a point where the resulting mixture has a pH in the range of about 4.4 to 5, subjecting the resulting mixture to steam distillation to separate as distillate a nitrogen compound product enriched in pyrrole, treating the steam distillation residue to liberate a nitrogen compound product enriched in pyridine homologs, and subjecting each of these nitrogen compound products to fractional distillation to separate as distillates therefrom substantially pure pyrrole and a substantially pure pyridine homolog product respectively.

6. In a process for recovering pyrrole from a mixture thereof with pyridine homologs not readily separable therefrom by distillation, the steps that comprise substantially neutralizing said mixture with a strong mineral acid that does not affect the nitrogen compounds deleteriously to a point where the resulting mixture tests slightly alkaline to methyl orange indicator, subjecting the resulting mixture to steam distillation to separate as distillate a nitrogen compound product enriched in pyrrole, and subjecting this nitrogen compound product to fractional distillation to separate as distillate therefrom substantially pure pyrrole.

7. In a process for recovering pyrrole from a mixture thereof with pyridine homologs not readily separable therefrom by distillation, the steps that comprise substantially neutralizing said mixture with sulfuric acid to a point where the resulting mixture has a pH in the range of about 4.4 to 5, subjecting the resulting mixture to steam distillation to separate as distillate a nitrogen compound product enriched in pyrrole, treating the steam distillation residue with alkali to liberate a nitrogen compound product enriched in pyridine homologs, and subjecting each of these nitrogen compound products to fractional distillation to separate as distillates therefrom substantially pure pyrrole and a substantially pure pyridine homolog product respectively.

8. In a process for recovering pyrrole from a mixture thereof with pyridine homologs not readily separable therefrom by distillation, the steps that comprise substantially neutralizing said mixture with sulfuric acid to a point where the resulting mixture has a pH in the range of about 4.4 to 5, subjecting the resulting mixture to steam distillation under reduced pressure to separate as distillate a nitrogen compound product enriched in pyrrole, and subjecting this nitrogen compound product to fractional distillation to separate as distillate therefrom substantially pure pyrrole.

9. In a process for recovering pyrrole from a heterocyclic nitrogen compound mixture containing, besides pyrrole, pyridine homologs not readily separable therefrom by distillation, the steps that comprise fractionating said mixture to obtain a pyrrole distillate cut boiling in the range 140°–148° C., substantially neutralizing said cut with sulfuric acid to a point where the resulting mixture has a pH in the range of about 4.4 to 5, subjecting the resulting mixture to steam distillation to separate as distillate a nitrogen compound product enriched in pyrrole, treating the steam distillation residue with alkali to liberate a nitrogen compound product enriched in pyridine homologs, and subjecting each of these nitrogen compound products to fractional distillation to separate as distillates therefrom substantially pure pyrrole and substantially pure pyridine homolog material respectively.

10. In a process for recovering pyrrole from a mixture thereof with pyridine homologs not readily separable therefrom by distillation, the steps that comprise substantially neutralizing the mixture with an acid that does not affect the nitrogen compounds deleteriously, said acid having a dissociation constant not lower than 10^{-2}, to a point where the mixture tests slightly alkaline to methyl orange indicator, subjecting the resulting mixture to steam distillation to separate as distillate a nitrogen compound product enriched in pyrrole, treating the steam distillation residue to liberate a nitrogen compound product enriched in pyridine homologs, subjecting the product enriched in pyridine homologs to fractional distillation to separate as distillate a substantially pure pyridine homolog product and resolving this pyridine homolog product into its individual component pyridine homologs.

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