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RECOVERY OF PYRROLE

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

Heterocyclic nitrogen compounds such as pyrrole, pyridine and the various pyridine homologs such as the 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, certain increasing numbers of the various heterocyclic nitrogen compounds in each fraction.

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. 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 close-cut 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, but are of relatively low economic value, since picoline-lutidine mixtures containing only a few percent of pyrrole are not water-miscible at ordinary temperatures. However, the pyrrole, which is thus detrimental in a picoline-lutidine mixture, is itself a rare chemical of great industrial value. For example, pyrrole derivatives are of importance as pharmaceuticals, agricultural chemicals, e. g., insecticides, perfume bases, and as antiseptics, and it is only the high cost of preparing pyrrole by the complicated procedures now in use that limits its employment in these and other fields.

Since the components making up the heterocyclic 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 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 heating in the presence of sulfuric acid converts pyrrole into dark polymeric substances insoluble in hydrocarbon oils, nitrogen bases or water, forming a jelly-like precipitate which it is impractical to separate, and when the pyridine homolog sulfates are reconverted to free nitrogen compounds by treatment with aqueous alkali, they are found to be still in admixture with a substantial amount of pyrrole. This method is thus ineffective for separation of pyrrole from pyridine homologs and, moreover, a large part of the valuable pyrrole is converted into a product of little or no utility.

It has further been proposed to recover pyrrole and its homologs from mixtures thereof with aromatic hydrocarbons recovered from organic degradation products, by treating the mixtures with potassium hydroxide to form potassium pyrroles. It has been found, however, that even when a large excess of solid potassium hydroxide is employed over the stoichiometric amount required to form potassium pyrroles in this prior art process, only a small proportion of the pyrroles can be separated in the form of their potassium compounds. The yield and the production cost in this method as practised in the prior art

have been found so unfavorable that the method is not 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 provide 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.

I have now discovered that pyrrole may be precipitated in the form of potassium pyrrole in surprisingly good yield and high purity from mixtures of pyrrole with other heterocyclic nitrogen compounds not separable from pyrrole by distillation, e. g., such other compounds as 3-picoline, 4-picoline and 2,6-lutidine, by making and maintaining the reaction mixture in which the potassium pyrrole is formed substantially completely anhydrous. The process of the invention thus involves removing from the reaction mixture substantially all water formed by the reaction while treating a pyrrole-containing heterocyclic nitrogen compound mixture, as above described, with potassium hydroxide to convert the pyrrole to potassium pyrrole. Under these conditions I have found that up to 85% of the pyrrole may be precipitated in the form of potassium pyrrole, even though no more than the theoretical amount of potassium hydroxide is employed for the reaction. The removal of water of reaction from a pyrrole-containing mixture treated with potassium hydroxide, I have found, may advantageously be effected by refluxing the reaction mixture with a water-entraining agent such as a hydrocarbon oil of coal-tar or petroleum origin, i. e. an aromatic, alicyclic, or aliphatic hydrocarbon of saturated or unsaturated character and boiling below the boiling point of the nitrogen compounds present, e. g., boiling below about 140° C., preferably in the range from about 80°–140° C.

The process of my 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 point, 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. My invention comprises a process in which such a fractionation is combined with the above-described separation of pyrrole in the form of potassium pyrrole.

My invention further comprises a process in which separation of pyrrole is combined with steps for isolation of the other heterocyclic nitrogen compounds present with pyrrole in these close-cut fractions. Thus my invention is applicable to resolving into its components a mixture of pyrrole, 3-picoline, 4-picoline and 2,6-lutidine.

In a preferred method of carrying out a process of my 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 approximately the calculated quantity of potassium hydroxide in either solid or concentrated aqueous solution form for reaction with pyrrole, in accordance with the equation

$$C_4H_4NH + KOH \rightarrow C_4H_4NK + H_2O$$

A small proportion of a hydrocarbon oil such as benzene or toluene, or a petroleum fraction boiling below about 140° C., is added to the mixture of nitrogen compounds, unless such hydrocarbons are naturally present in the nitrogen compound mixture which may be the case when a pyrrole source such as a low-boiling coal-tar oil or other natural pyrrole crude is treated. Preferably, an amount of hydrocarbon oil is employed such that it constitutes from 5% to 20% of the mixture. A mixture thus obtained with the added or naturally present hydrocarbons is agitated and heated to refluxing. Refluxing condensate consisting mainly of hydrocarbon oils with entrained water is not returned directly to the reaction charge, but is by-passed into a settling device where it separates into an upper layer of hydrocarbon oils, including dissolved nitrogenous compounds, and a lower water layer. The upper layer is continuously or intermittently returned to the still charge. The water layer is removed and the refluxing is continued until all the reaction water and any additional water originally present as moisture in the charge has been withdrawn.

The desired reaction proceeds smoothly under these conditions. Potassium pyrrole is soluble to some extent in the hot hydrocarbon-nitrogen compound mixture, but begins to crystallize in the course of the dehydration in small but well-formed granular crystals. The solubility of the potassium pyrrole in anhydrous cold solutions of reaction mixture is very small. The reaction mixture is cooled and potassium pyrrole crystals are isolated by filtration, e. g., centrifuging. The crystals may be washed with a little hydrocarbon solvent to remove adhering oils and may be dried by heating to 90°–95° C. under reduced pressure.

Potassium pyrrole is, itself, a useful product: it may be employed in the preparation of various pyrrole derivatives, e. g. proline, which have varied uses in pharmaceutical and other fields. The potassium pyrrole is also a most advantageous source for substantially pure pyrrole. Pyrrole is readily liberated from the potassium pyrrole by the addition of water, the resulting mixture settling to a lower layer of potassium hydroxide solution and an upper layer of pyrrole. The pyrrole layer is decanted, dried, and distilled, giving a product of 99% to 99.5% purity. Compounds such as picolines present, even in amount less than 1% in the pyrrole product, may be removed by extracting the material with a small quantity of dilute oxalic acid solution and thereafter washing with water. A pyrrole product of substantially 100% purity may thus be obtained. The aqueous lower layer of potassium hydroxide solution may be cyclicly reused in the process, preferably after being dehydrated to some extent by free evaporation.

The mother liquor remaining after filtration of the potassium pyrrole crystals may be treated to recover a pyridine homolog mixture. This may generally be accomplished merely by frac-

tional distillation; however, if necessary, the mother liquor may be washed with sulfuric acid to extract the pyridine homologs which may then be freed from their sulfate solution by addition of aqueous alkali. 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 method of my copending application Serial No. 456,257, filed August 26, 1942, or the methods of copending applications Serial No. 441,557, filed May 2, 1942, and Serial No. 452,369, filed July 25, 1942.

The following example is illustrative of the process of my invention:

An iron kettle, equipped for agitation and supplied with a reflux condenser and settling trap for collecting condensate, was charged as follows:

1500 parts by weight of a mixture of heterocyclic nitrogen compounds having approximately the following composition:

	Per cent
Pyrrole	19
3-picoline	42
4-picoline (approximately)	33

and the remainder consisting of 2,6-lutidine and traces of 2,4-lutidine.

300 parts by weight of potassium hydroxide, in pellet form, containing approximately 255 parts by weight of pure potassium hydroxide.

215 parts by weight of toluene.

The reaction mixture was agitated and heated to refluxing, the inside of the kettle attaining a temperature of 130° C. A total of 95 parts of water was removed over a period of 16 hours of refluxing. The kettle charge was cooled to 25° C. and the crystalline potassium pyrrole isolated by filtration. Crystals were washed with benzene and dried at 90°–95° C., 438 parts by weight of dry material being obtained.

Potassium pyrrole was decomposed by addition of 350 parts of water, the resulting mixture being allowed to settle in a lower layer of potassium hydroxide solution and an upper layer of pyrrole. The isolated pyrrole was found to contain 0.6% by weight of picolines. These were removed by extracting the material with a small quantity of dilute oxalic acid solution and with water. The product, on a moisture-free basis, amounted to 225 parts by weight or about 78% of the pyrrole present in the crude mixture. It was distilled for color and found to have the following characteristics:

Specific gravity at 25/4° C.	0.9691
Refractive index n_D at 25° C.	1.5095
True boiling point	129.8° C., corrected
Odor	Ethereal, resembling chloroform

The material was water-white when freshly distilled.

The mother liquor remaining after isolation of potassium pyrrole crystals was separated by fractional distillation into toluene and pyridine bases. The latter contained from 2% to 3% of residual pyrrole.

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.

I claim:

1. A process for recovering pyrrole from a mixture of heterocyclic nitrogen compounds from coal tar, containing pyrrole along with pyridine homologs including a picoline selected from the group consisting of 3-picoline and 4-picoline, which process comprises fractionating said mixture to obtain a fraction boiling in the range of about 140°–148° C., treating said fraction with potassium hydroxide in amount sufficient to react with the pyrrole to form potassium pyrrole, refluxing the resulting mixture together with a small proportion of hydrocarbon oil boiling below about 140° C., with separation of water from the reflux condensate, until substantially all water has been removed from the reaction mixture, and separating the potassium pyrrole which precipitates.

2. A process for recovering pyrrole from mixtures of pyrrole with 3-picoline and 4-picoline, which comprises treating the mixture with potassium hydroxide in substantially the stoichiometric amount to react with the pyrrole to form potassium pyrrole, refluxing the resulting mixture together with about 5% to 20% by weight, based on the total mixture, of hydrocarbon oil boiling in the range of about 80° to 140° C., with separation of water from the reflux condensate, until substantially all water has been removed from the reaction mixture, cooling the resulting substantially anhydrous reaction mixture, separating the potassium pyrrole which precipitates, and reconverting said potassium pyrrole to pyrrole by treatment with water.

3. A process for recovering pyrrole from a mixture of heterocyclic nitrogen compounds containing pyrrole along with pyridine homologs including a picoline selected from the group consisting of 3-picoline and 4-picoline, which process comprises fractionating said mixture to obtain a fraction boiling in the range of about 140°–148° C., treating said fraction with potassium hydroxide in amount sufficient to react with the pyrrole to form potassium pyrrole, refluxing the resulting mixture together with a small proportion of hydrocarbon oil boiling below about 140° C., with separation of water from the reflux condensate, until substantially all water has been removed from the reaction mixture, and separating the potassium pyrrole which precipitates.

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