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ISOLATION OF PYRROLE FROM PYRIDINE HOMOLOGUES BY AZEOTROPIC DISTILLATION WITH WATER

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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, mixture of 20% pyrrole and 80% of a 3- and 4-picoline mixture in about equal proportions was found to distill 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; but the high cost of preparing pyrrole by the complicated procedures now in use limits its employment in these and other fields.

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Since the components making up the heterocyclic nitrogen compound fractions containing pyrrole form constant-boiling azeotropes, conventional 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 in an attempt to remove the loosely held pyrrole. Methods for separation of pyrrole have also been disclosed in the published prior art involving forming potassium pyrroles. However, due to incomplete reaction and to undesirable side reactions, 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 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 discovered that pyrrole may be effectively and economically separated from mixtures thereof with other heterocyclic nitrogen compounds which are not separable from pyrrole by ordinary fractional distillation, e. g. such other compounds as the pyridine homologs 3-picoline,

4-picoline and 2,6-lutidine with which pyrrole is often associated, by fractional distillation of such mixtures in the presence of water as an azeotropic agent.

I have found that pyrrole, as well as the pyridine homologs with which it is generally associated, form binary azeotropes of the low-boiling type with water, and that when water is present in a pyrrole-containing heterocyclic nitrogen compound mixture, as above described, the low-boiling pyrrole-water and pyridine-homolog-water azeotropes (boiling within the range of about 90–100° C. at atmospheric pressure) are formed in preference to the high-boiling pyrrole-pyridine homolog azeotropes above described (boiling at about 145°–148° C. at atmospheric pressure). Therefore, when fractional distillation of a mixture of pyrrole and one or more pyridine homologs as above described is carried out in the presence of water, the various water azeotropes of the heterocyclic nitrogen compounds present distill over in the temperature range of about 90–100° C. at atmospheric pressure. I have further found that the boiling point of the pyrrole-water azeotrope is, surprisingly, slightly lower than the boiling points of the water azeotropes of the pyridine homologs with which the pyrrole is associated, so that upon fractional distillation a first distillate fraction may be taken, the oil component of which is highly enriched in pyrrole and, with sufficiently careful fractionation, may consist of substantially pure pyrrole.

When a pyrrole-rich material, rather than pure pyrrole, is taken as distillate product, it may be subjected to a second fractional distillation in the absence of water to take off pure pyrrole as distillate, leaving as still residue a mixture of pyrrole and one or more pyridine homologs in the form of the above-discussed high-boiling pyrrole-pyridine homolog azeotropic mixture. Such separation is based on the fact that the highest boiling mixture of pyrrole and the pyridine homologs under discussion is the above-mentioned azeotropic mixture in which pyrrole is generally present within the relatively narrow limits of 15% to 25%; accordingly, if a mixture is obtained containing substantially more than 25% pyrrole, upon boiling such a mixture pyrrole will distill off until the residual mixture attains its peak constant boiling point. This high-boiling residual pyrrole-pyridine homolog azeotropic mixture separated as still residue may be returned for further treatment by the process of my invention along with pyrrole-containing heterocyclic nitrogen compound material entering the first stage of my process.

The oil component of the material left in the still after the azeotropic distillation for separation of the water azeotrope of a pyrrole-enriched product, as above described, consists primarily of pyridine homologs (or a pyridine homolog if only one was originally present) and generally still contains some pyrrole. A pyridine homolog product substantially free of pyrrole may be recovered from this residual material either by continuing azeotropic distillation thereof in the presence of water until the material left in the still is substantially free from pyrrole or by subjecting the residual material low in pyrrole to straight fractional distillation in the absence of water to take off a substantially pure pyridine homolog product as distillate, leaving the pyrrole and a part of the pyridine homologs in the still in the form of the above-mentioned high-boiling pyrrole-pyridine homolog azeotropic mixture. The material of intermediate pyrrole content separated as distillate in the first of these methods or separated as still residue in the second method is preferably returned for reworking by the process of the invention.

By either of the methods discussed in the preceding paragraph a pyridine homolog product is recovered that is substantially free of pyrrole and therefore possesses satisfactory water-solubility characteristics. This product is generally a mixture of pyridine homologs, since the source material for pyrrole to which the process of the application is applied generally contains more than one pyridine homolog associated with the pyrrole. Such a mixture may, if desired, be further treated to resolve it into its individual pyridine homolog components.

The process of my invention may advantageously be 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 from pyrrole by distillation, particularly such pyridine homologs as 3-picoline, 4-picoline, and 2,6-lutidine. Compounds such as 2-picoline and 2,4-lutidine are often present in small amounts. When the source material for the pyrrole is a mixture of heterocyclic nitrogen compounds containing components of widely varying boiling points, the mixture is first preferably subjected to ordinary fractional distillation (i. e., without the addition of an azeotropic agent), whereby a fraction boiling in the range 140°–158° C. containing predominantly pyrrole and other nitrogen compounds not separable therefrom by ordinary distillation is obtained.

In a preferred method of carrying out the process of my invention, a pyrrole fraction as above described, for example an industrial beta-gamma-picoline fraction of the tar base mixture separated from the coal tar obtained in the high temperature carbonization of coal (which fraction contains about 15–20% pyrrole, the remainder consisting primarily of 3-picoline and 4-picoline, with some 2,6-lutidine, 2-picoline and 2,4-lutidine present), may be subjected to fractional distillation in the presence of water as azeotropic agent. If the fraction treated contains any substantial quantity of 2-picoline, it is preferred either to strip out this material first by ordinary fractional distillation in the absence of water before the azeotropic distillation is carried out, or to carry out the azeotropic fractional distillation in equipment capable of a high degree of fractionation, since the 2-picoline-water azeotrope boils closer to the pyrrole-water azeotrope than do the other pyridine homolog-water azeotropes.

The azeotropic fractionation may be carried out either in batch or continuous operation. In either case, sufficient water should be present in the still and column system to provide at least 55 parts by volume (liquid basis) of water vapor for every 45 parts by volume (liquid basis) of pyrrole present as vapor in the system, since in the azeotropic mixture of pyrrole and water the components are present in this proportion. In batch operation, all the water required for the distillation may be added at the beginning or

water may be added to the still continuously or intermittently during the course of distillation. In continuous operation the necessary water is, of course, added continuously or intermittently as the pyrrole crude is fed. I have found it advantageous to employ only slightly more water than is necessary to take off the desired pyrrole product as water azeotrope since the residual material may then quickly be dehydrated preparatory to separating a pure pyridine homolog product by fractionation in the absence of water.

As above suggested, I have found that by employing a high degree of fractionation in the azeotropic distillation, a distillate may be obtained, the oil component of which consists of substantially pure pyrrole, i. e. 99% pyrrole. I have further found that, with reworking of all materials of lower pyrrole content separated, up to 80% or more of the pyrrole present in the crude may eventually be recovered as a product of this purity. When the production of a product of such purity requires a fractionation that is considered to be too time-consuming in commercial operation, which may be the case when a crude relatively low in pyrrole is employed as source material in the process, a pyrrole product of somewhat lesser purity, e. g. containing from about 50% to 95% pyrrole in the oil component of the distillate, may advantageously be taken as azeotropic distillate fraction and this pyrrole product, after removal of water therefrom, may be subjected to ordinary fractional distillation to separate pure pyrrole as distillate. The still residue in this last fractionation will consist of the high-boiling pyrrole-pyridine homolog azeotrope above referred to containing 15–25% pyrrole and 75–85% pyridine homologs by weight. This material may advantageously be reworked by the process of the invention, by adding it to pyrrole crude entering the process, for recovery of its pyrrole content.

The oil component of the material left in the still after the above-described azeotropic distillation for separation of the water azeotrope of pure pyrrole or a pyrrole-enriched product, is a heterocyclic nitrogen compound material from which most of the pyrrole has been removed, but which contains substantially all the pyridine homologs originally present. Although the pyrrole content of this residual material is low, there may be more pyrrole present than is desirable for a pyridine homolog product of satisfactory water-solubility. It is generally desirable, therefore, to remove additional pyrrole from this material. To accomplish this, the material is preferably first dehydrated (e. g. by stripping out the water as distillate or by treating with a solid dehydrating agent such as solid caustic soda) and then subjected to ordinary fractional distillation. In this fractionation a pure pyridine homolog product is taken off as distillate and a pyrrole-pyridine homolog mixture containing these constituents in the proportion of their high-boiling azeotropic mixture is withdrawn as still residue. This residue is also advantageously returned for reworking by the process of the invention.

Alternatively, the residual material from the azeotropic distillation for separation of the water azeotrope of the pyrrole product may be subjected to further azeotropic distillation, with water as the azeotropic agent, until the material left in the still is substantially free of pyrrole. The additional pyrrole-containing material taken off in this continued azeotropic distillation generally is not sufficiently high in pyrrole to make its withdrawal as a pyrrole product economically attractive. It is preferable to rework this pyrrole-containing material also by the process of the invention for the recovery of its pyrrole content. The still residue remaining from this continued azeotropic distillation consists of a product the oil component of which is a pyridine homolog material substantially free from pyrrole.

The azeotropic distillation may be carried out at atmospheric pressure, or at pressures above or below atmospheric. I have found that at pressures below atmospheric there is a slightly greater spread between the boiling points of the pyrrole-water azeotrope and the pyridine homolog-water azeotropes than there is at atmospheric or higher pressures; however, the improvement obtained at reduced pressures is not sufficiently great to make it generally advantageous in commercial operation to use reduced pressure. Accordingly, atmospheric pressure is preferred for commercial operation.

At atmospheric pressure the boiling point of the pyrrole-water azeotrope is between about 93° and 93.5° C., whereas the boiling points of the water azeotropes of 3-picoline, 4-picoline and 2,6-lutidine are all above about 96.5° C. A separation of pyrrole on the one hand, and 3-picoline, 4-picoline and 2,6-lutidine on the other may thus readily be brough about by fractional distillation of their water azeotropes, maintaining a top column temperature of about 93° to 96° C. at atmospheric pressure. When 2-picoline is present, its water azeotrope has a boiling point at atmospheric pressure of about 94.8° C., and careful fractionation is therefore required to separate it from the pyrrole-water azeotrope.

The water and oil components of the various water azeotropes obtained may readily be separated. Since pyrrole is substantially insoluble in water, any aqueous condensate that includes a nitrogen compound mixture containing at least about 2.0% pyrrole stratifies upon standing into a water layer and an oil layer that may be separated by decantation. Water-soluble pyridine homolog mixtures may be separated from aqueous condensates containing them either by addition of a strong caustic, which causes the pyridine homolog oil to form a separate layer, or by azeotropic distillation with benzol.

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

Example 1

200 parts by volume of a mixture containing 25% pyrrole and 75% of 3- and 4-picolines was fractionally distilled in the presence of three times its volume of water. Distillation was carried out at total back flow until the vapor temperature reached a constant minimum of 93.0° C. The distillation was then carried out at full forward flow until the temperature had risen to 93.5° C. These alternate operations, i. e. distillation with total back flow and distillation with full forward flow were then repeated, with the temperature varying as indicated from 93.0° to 93.5° C., until about 36 parts by volume of oil had been removed as distillate. This oil had a pyrrole content of from 98%–99% and accounted for 70% of the pyrrole in the crude charged.

Azeotropic distillation was continued until about 40 parts by volume additional oil had been taken over as distillate in the form of a water azeotrope. This oil contained about 35% pyrrole. The oil component of the material left in the still

consisted of a 3- and 4-picoline mixture substantially free from pyrrole.

The intermediate oil fraction containing about 35% pyrrole could be returned for reworking by the process of the invention along with entering crude.

Example 2

In this run a fraction (boiling range about 140° to 147° C.) of a pyridine oil separated from coal tar made by high-temperature carbonization was employed. This fraction contained about 19% pyrrole, the remainder consisting predominantly of 3- and 4-picolines with some 2,6-lutidine and traces of 2-picoline and 2,4-lutidine being present.

A charge of 400 parts by volume of such a fraction and 100 parts by volume of water was fractionally distilled. Over a period of 12 hours, 65% of the pyrrole in the charge was collected as an oil distillate product containing 98%–99% pyrrole.

The oil component of the still residue still contained 7% pyrrole. This pyrrole could be substantially removed by continued azeotropic distillation, taking off as distillate a water azeotrope of an oil containing 30%–50% pyrrole, which oil could be returned for further reworking by the process of the invention. A pyridine homolog mixture substantially free of pyrrole would thus be left as the still residue.

Example 3

The material employed in this run was the beta-gamma-picoline fraction of a pyridine oil recovered from coal tar made by high-temperature carbonization. This fraction contained about 15.8% pyrrole, about 20% 2-picoline, and about 64% of 3-picoline, 4-picoline and 2,6-lutidine.

2000 parts by volume of such a fraction was first preliminarily dried by treatment with solid caustic soda and then subjected to normal fractional distillation (i. e. in the absence of an azeotropic agent) up to an end temperature of about 145° C. to remove the 2-picoline. The remaining 1600 parts by volume of 2-picoline-free material was fractionally distilled in the presence of 400 parts by volume of water. The degree of fractionation was adjusted to provide a distillate the oil component of which tested about 60% pyrrole rather than attempting to produce 98%–99% material. During the entire distillation the vapor temperature was held at around 95° C. The distillate after removal of water and drying over solid caustic soda measured 330 parts by volume and contained 61.6% pyrrole. The oil component of the still residue measured 1270 parts by volume and tested 6.0% pyrrole.

As in the above examples, the small amount of pyrrole remaining in the still residue could be substantially completely removed by continuing the azeotropic distillation with water. A distillate oil of intermediate pyrrole content would thus be removed and this material as above pointed out could be returned for reworking in the process of the invention. Preferably, however, a pure pyridine homolog product would be recovered by drying the still residue whose oil component tested 6% pyrrole and carrying out normal fractional distillation thereof. The pure pyridine homolog product would thus be separated as distillate.

The 330 parts by volume of pyrrole concentrate testing 61.6% pyrrole was fractionally distilled (alone) to produce as distillate fractions 140 parts of 99% pyrrole (taken off at 129.8°–130.9° C.) and 40 parts by volume of 54.2% pyrrole oil which was added to the next batch of pyrrole concentrate to be fractionally distilled. The still residue, 150 parts by volume of a 30% pyrrole oil, was returned for reworking by the process of the invention with the next batch of pyrrole crude entering the process.

In the above examples, each of the fractional distillations, azeotropic and straight, could be carried out in continuous fashion rather than batchwise, as described, with continuous return of oil fractions of intermediate pyrrole content to the stage of the process where oil of approximately the same pyrrole content is being treated, and with continuous return to the azeotropic distillation column, as azeotropic agent, of the water separated from the azeotropic distillate by stratification. As above pointed out, at least 80% of the pyrrole in the entering crude may thus eventually be recovered in the 99% pyrrole oil withdrawn as product.

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. In a process for separating pyrrole from a mixture thereof with pyridine homologs not readily separable from pyrrole by normal fractional distillation, the step that comprises subjecting the mixture to fractional distillation in the presence of water to separate as distillate the water azeotrope of an oil enriched in pyrrole.

2. In a process for separating pyrrole from a mixture thereof with at least one of the bases 3-picoline, 4-picoline and 2,6-lutidine, the step that comprises subjecting the mixture to fractional distillation in the presence of water to separate as distillate the water azeotrope of substantially pure pyrrole.

3. In a process for separating pyrrole from a mixture thereof with at least one of the bases 3-picoline, 4-picoline and 2,6-lutidine, the steps that comprise subjecting the mixture to fractional distillation in the presence of water to separate as distillate the water azeotrope of a pyrrole concentrate containing from about 50% to 95% pyrrole, and subjecting this pyrrole concentrate to normal fractional distillation to separate substantially pure pyrrole as distillate.

4. In a process for separating pyrrole from a mixture thereof with pyridine homologs not readily separable from pyrrole by normal fractional distillation, the steps that comprise subjecting the mixture to fractional distillation in the presence of water to separate as distillate the water azeotrope of an oil enriched in pyrrole, and separating a pyridine homolog product substantially free from pyrrole by distillation of the residual material.

5. In a process for separating pyrrole from a pyrrole-containing pyridine homolog fraction containing 2-picoline and at least one of the bases 3-picoline, 4-picoline and 2,6-lutidine, the steps that comprise subjecting the mixture to normal fractional distillation to separate 2-picoline as distillate, and subjecting the residual mixture to fractional distillation in the presence of water to separate as distillate the water azeotrope of an oil enriched in pyrrole.

6. In a process for separating pyrrole from a

pyrrole-containing pyridine homolog fraction boiling predominantly within the range of about 140–148° C. and containing at least one of the bases 3-picoline, 4-picoline and 2,6-lutidine, the step that comprises subjecting the mixture to fractional distillation in the presence of water, at a top column temperature ranging from about 93° to 96° C. at atmospheric pressure, to separate as distillate the water azeotrope of an oil enriched in pyrrole.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,335,823	Cislak et al.	Nov. 30, 1943
2,363,157	Stasse	Nov. 21, 1944
2,350,447	Cole	June 6, 1944