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ISOLATION OF HETEROCYCLIC NITROGEN COMPOUNDS FROM MIXTURES THEREOF

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This invention relates to the resolution of mixtures of heterocyclic nitrogen compounds, containing 3- and 4-picolines and other pyridine homologs.

The picolines, other homologs of pyridine, and pyrrole are customarily extracted, along with pyridine, from coal tar oils and other sources of these heterocyclic nitrogen compounds by means of an aqueous solution of mineral acids, usually sulfuric acid, and are liberated from the acid solutions by the addition of alkali hydroxide or carbonates. Mixtures of nitrogen compounds thus liberated are then fractionally distilled. Bases such as pyridine, boiling point 116° C., and 2-picoline, boiling point 129.4° C., can generally be obtained in reasonably pure form by fractional distillation, but for the most part the remaining compounds cannot be separated by distillation methods alone. Instead, the fractions obtained, even when they are of relatively narrow boiling range, contain increasing numbers of pyridine homologs and their isomers. Mixtures of this kind have found limited practical application mainly as special solvents and are of relatively low economic value. The individual compounds, however, if they could be readily isolated would be of far greater value, for example, in the preparation of derivatives, especially pharmaceutical products and dyes. The requirements for purity in these fields are extremely severe.

Of especially high potential value are the nitrogen compounds in the fractions having a boiling range of about 140°–148° C. When mixtures of heterocyclic nitrogen compounds are recovered from most types of coal tar, the fractions taken within the range 140°–148° C., even closely cut fractions within this boiling range, in general contain as components three pyridine homologs of substantially the same boiling point in roughly equal proportions; i. e., 2,6-lutidine, boiling point 143.8° C., 3-picoline (beta-picoline), boiling point 143.8° C., and 4-picoline (gamma-picoline), boiling point 144.8° C. Mixtures of heterocyclic nitrogen compounds recovered from some of the less common coal tars may contain substantial proportions of pyrrole instead of, or in addition to, the 2,6-lutidine. Although pyrrole alone boils at 129.8° C., with 3- and 4-picolines it forms high boiling azeotropes boiling about 145°–148° C., the components of which are inseparable by distillation methods. Derivatives of many of these compounds are becoming of increasingly greater importance as pharmaceuticals and agricultural chemicals. Nicotinic acid, for example, a member of the Vitamin B complex, may be readily obtained by oxidation of 3-picoline.

Since the three components making up the usual nitrogen base fractions boiling in the range 140°–148° C. (2,6-lutidine, 3-picoline, and 4-picoline) have substantially the same boiling points, and since pyrrole, present in some of these fractions, forms azeotropes with these bases, fractional distillation is obviously unsatisfactory as a means for resolving the mixtures. Other methods of resolving such mixtures heretofore described in the published prior art have been generally unsatisfactory in regard to products, yields, and production costs. Such other methods have usually depended upon fractional crystallization of the more common salts of the bases present, e. g., the chlorides, sulfates, oxalates, chlorates, picrates, ferrocyanides, and the like. Isolation or purification of individual bases by such methods has been found to be extremely cumbersome and generally insufficiently sharp to obtain compounds of a purity demanded in industry. These methods also have often presented other drawbacks such as prohibitive cost, explosive hazards, and toxicity.

It is an object of this invention to provide a commercially feasible method of obtaining pure or enriched 4-picoline and 3-picoline from mixtures of heterocyclic nitrogen compounds.

It is a further object of this invention to provide a commercially feasible process for resolving fractions of heterocyclic nitrogen compounds, particularly tar base fractions, boiling in the range 140°–148° C., which fractions contain 2,6-lutidine, 3-picoline, and 4-picoline in substantial proportions, and may contain a substantial proportion of pyrrole.

I have discovered that substantially pure 4-picoline may be isolated from a mixture containing 4-picoline and other heterocyclic nitrogen compounds (including other pyridine homologs) having boiling points close to 4-picoline by precipitating the 4-picoline from the mixture in the form of its calcium chloride addition compound. This is particularly surprising since 3- and 4-picolines and other pyridine homologs boiling close to 4-picoline have heretofore been thought to form addition compounds of substantially identical properties. The mixture from which 4-picoline is precipitated in accordance with my invention may advantageously be a close-cut fraction of heterocyclic nitrogen compounds (e. g., a tar base fraction) boiling in the range 140°–148° C., for example a fraction boiling in

the range 140°–145° C., containing as its principal components 2,6-lutidine, 3-picoline, and 4-picoline, or a fraction containing these bases and pyrrole, boiling in the range 145°–148° C. My invention may thus comprise fractionating a heterocyclic nitrogen compound mixture, e. g. a coal-tar base mixture, containing 4-picoline and other nitrogen compounds (including other pyridine homologs) of close boiling point, to obtain a close-cut fraction boiling predominantly in the range 140°–148° C., and precipitating 4-picoline from this fraction, in the form of its calcium chloride addition compound.

My invention further comprises a process in which separation of 4-picoline in the form of its calcium chloride addition compound is combined with steps for isolation of other pyridine homologs not readily separable therefrom by distillation, e. g., 3-picoline and 2,6-lutidine, as well as for isolation of pyrrole; thus my invention is applicable to resolving a mixture comprising essentially only 3-picoline and 4-picoline into its individual components, and is further applicable to resolving a mixture containing 2,6-lutidine or pyrrole or both, in addition to these picolines, into its individual components.

The process of my invention may advantageously be applied in the resolution of heterocyclic nitrogen compound mixtures obtained from coke oven distillates, cracked petroleum, shale tar, bone oils and from other natural, as well as synthetic, sources when these base mixtures contain substantial amounts of 4-picoline and other nitrogen compounds not readily separable therefrom by distillation, e. g., 3-picoline, and 2,6-lutidine or pyrrole. As above pointed out, in carrying out the process of my invention, such a mixture is advantageously first subjected to fractional distillation whereby a close-cut fraction containing predominantly the 4-picoline and other close boiling compounds is obtained. For example, as above pointed out, when nitrogen base mixtures are recovered from the more common coal tars, distillate fractions boiling in the range 140°–145° C. have been found to contain predominantly 3-picoline, 4-picoline and 2,6-lutidine, while distillate fractions of nitrogen compounds from other coal tars, boiling in the range 145°–148° C., have been found to contain substantial quantities of pyrrole, and small amounts of 2,6–lutidine, along with the 3- and 4-picolines. These mixtures cannot be readily resolved by distillation methods, but may advantageously be resolved by the process of my invention.

When a close-cut lutidine-picoline fraction thus obtained contains more than about 30% of 4-picoline, pure 4-picoline may be isolated directly therefrom by precipitation with calcium chloride in accordance with my invention, as illustrated in Example 1, below. I have generally found it advantageous, however, particularly when this base mixture contains less than about 30% of 4-picoline, to separate, first, all or most of the 2,6-lutidine and thereafter resolve the residual mixture containing predominantly 3-picoline and 4-picoline. Such a process is illustrated in Example 2, below. In the treatment of pyrrole-picoline fractions, it is desirable to remove the bulk of the pyrrole before precipitating the calcium chloride addition compound of 4-picoline in accordance with my invention.

The 2,6-lutidine and pyrrole may be separated from such a mixture by forming zinc chloride addition compounds of the picolines, and filtering or distilling to separate 2,6-lutidine and pyrrole. Zinc chloride is capable of forming addition compounds with 3-picoline, 4-picoline and 2,6-lutidine, two molar equivalents of base combining with one of zinc chloride; no stable addition compound is formed with pyrrole. The addition compounds of the two picolines are only sparingly soluble in water or alcohol, whereas the compound formed with 2,6-lutidine is decidedly more soluble. Also, the 2,6-lutidine compound of zinc chloride possesses a substantially higher vapor tension than do the corresponding compounds of 3- or 4-picoline at the same temperature.

Accordingly, to separate 2,6-lutidine and pyrrole from a mixture of 3-picoline, 4-picoline and 2,6-lutidine, zinc chloride is added to the mixture. An aqueous solution of zinc chloride may advantageously be employed and by proper selection of reagent proportions, for example by adding approximately the correct amount of zinc chloride for reaction with the picolines only, it is possible to precipitate the bulk of the isomeric picolines, whereas the 2,6-lutidine and pyrrole remain in solution and can be eliminated completely by filtration and washing of the crystals; alternatively, pyrrole may be removed and 2,6-lutidine almost completely removed by steam distillation of the mixture of water, crystals, and uncombined nitrogen compounds.

From these filtrates or steam distillates, bases greatly enriched in 2,6-lutidine or pyrrole containing, for example, from 60% to 90% of 2,6-lutidine can be isolated by salting out and drying, or by extraction of the aqueous solutions with suitable hydrocarbon solvents, e. g., benzene, toluene, xylene, or petroleum solvents. In order to recover substantially pure 2,6-lutidine, the 2,6-lutidine-rich base thus obtained may be admixed with a small proportion of zinc chloride to combine with picolines present and the filtration or steam distillation repeated. In this manner, the 2,6-lutidine product may be brought up above 95% purity. A pyrrole-enriched product may be similarly treated to obtain pure pyrrole.

Whether the zinc chloride addition compound of the 3- and 4-picolines is separated by filtration or by steam-distilling out volatile compounds such as 2,6-lutidine and pyrrole, the resulting mixture of picoline-zinc chloride addition compounds is treated with an alkali such as sodium hydroxide, sodium carbonate, or ammonia to set free the 3- and 4-picolines. Preferably, the mixed picoline-zinc chloride addition compounds are treated with one molecular equivalent (based on the zinc chloride) of sodium carbonate or two of sodium hydroxide, thus precipitating zinc carbonate or zinc hydroxide, respectively. This zinc carbonate or zinc hydroxide may eventually be recovered by filtration and washing, and may be reconverted into zinc chloride for further use in the process by means of hydrochloric acid.

The picoline base mixture liberated upon addition of the alkali to the picoline-zinc chloride addition compounds is removed by steam distillation and the bases are finally isolated from this distillate by salting out or by extraction with hydrocarbon solvents. Salting out of the picolines (or of other soluble nitrogen bases) from their water solutions may be carried out by adding solid sodium chloride or a saturated sodium chloride solution to the water solution of the picolines or other bases whereupon a separate supernatant liquid layer of base is formed. Alternatively, solid sodium hydroxide or concentrated

sodium hydroxide solution may be used to cause the soluble base to separate as a distinct layer from its water solution. Other salts or alkalies known in the art may also be used for this purpose.

Mixtures of 3- and 4-picolines thus obtained, or other mixtures comprising essentially 3- and 4-picolines obtained from coal tar or other sources, may be treated for isolation of 3-picoline and 4-picoline. As above pointed out, 3- and 4-picoline mixtures containing minor proportions of other bases such as 2,6-lutidine or pyrrole may also be treated directly to separate at least 4-picoline, particularly when its concentration is greater than about 30%.

In resolving 3- and 4-picoline mixtures, depending on the relative proportion of 3- or 4-picolines present, the base mixture may be treated first to precipitate 4-picoline in the form of its calcium chloride addition compound in accordance with my invention, and then treated to precipitate 3-picoline as phosphate in accordance with the process of copending application Serial No. 346,347, filed July 19, 1940, or these two operations may be reversed. 4-picoline is advantageously separated first when 4-picoline constitutes at least about 35% of the mixture. The residual base mixture, rich in 3-picoline, may then be treated for precipitation of a substantial proportion of the 3-picoline as phosphate. The residual base, containing both 3- and 4-picolines, remaining after precipitation of 3-picoline phosphate may then be added to fresh base mixture which is about to be treated for precipitation of the calcium chloride addition compound of 4-picoline.

When a 3- and 4-picoline mixture contains more than about 55% 3-picoline, the above steps may be reversed; i. e., the mixture may first be treated with phosphoric acid or phosphate in accordance with the process of the copending application referred to above to precipitate a substantial part of the 3-picoline as phosphate and the residual base mixture rich in 4-picoline may then be treated for precipitation of the calcium chloride compound of 4-picoline in accordance with my invention. My invention, involving the step of precipitating 4-picoline in the form of its calcium chloride addition compound combined with the step of precipitating 3-picoline as phosphate, thus makes possible the resolution of base mixtures of widely varying composition comprising essentially 3-picoline and 4-picoline.

The precipitation of 4-picoline in the form of its calcium chloride addition compound should be carried out in an anhydrous, non-alcoholic medium. Hydrocarbon oils such as benzene, toluene or solvents of paraffinic character may be used as diluent or suspension medium for crystals. Solid anhydrous calcium chloride, preferably finely ground, may be added directly to the base mixture dissolved in a hydrocarbon oil as above described and the mixture agitated for formation and precipitation of the calcium chloride-4-picoline addition compound.

A preferred method, however, involves mixing a concentrated aqueous solution of the required quantity of calcium chloride with the base mixture which is preferably dissolved in a low-boiling hydrocarbon oil. This mixture is then agitated and heated to refluxing temperature. Upon refluxing, water vaporizes and passes off with the hydrocarbon vapors. The reflux condensate passes through a side arm trap where the lower water layer may be removed while the upper hydrocarbon layer is returned to the still. All water in the reaction mixture is thus eventually removed. This method insures complete utilization of the calcium chloride and the formation of granular crystals which can be filtered or centrifuged most readily. This method, furthermore, makes it advantageous to reuse the calcium chloride cyclically since as will be hereinafter pointed out calcium chloride is eventually recovered in the form of an aqueous solution. The temperature at which this reaction is carried out will be approximately the boiling point of the solvent used, and is preferably carried out within the range of about 80° to 120° C., depending upon the solvent employed.

In carrying out the process of my invention, I have found it advantageous to precipitate only a portion of the 4-picoline from a 3- and 4-picoline mixture, since I have found that when the concentration of 4-picoline in a solution of essentially 3- and 4-picolines has fallen below about 25%, a substantial amount of 3-picoline-calcium chloride addition compound may precipitate along with 4-picoline-calcium chloride addition compound. In more complex mixtures containing 3- and 4-picolines, the limiting concentration of 4-picoline which must be left in the mixture, in order that the precipitated product be reasonably pure, depends upon the composition of the base mixture and is determined empirically. Each mol of calcium chloride combines with two mols of 4-picoline. In carrying out the process of my invention, therefore, calcium chloride is added in just one-half the molar quantity of 4-picoline it is desired to remove. It is obvious, of course, that where pure 4-picoline is not required, i. e., where the presence of a small amount of 3-picoline is not disadvantageous, a larger proportion of the 4-picoline may be precipitated from the picoline mixture.

The 4-picoline-calcium chloride addition compound is separated from the mother liquor by filtration or centrifuging followed by washing, e. g., with a hydrocarbon solvent. The solid addition compound, dried, or containing adhering solvent, is decomposed by the addition of water. The resulting mixture may separate into two layers—a lower layer containing the bulk of the calcium chloride and an upper one containing most of the 4-picoline; however, calcium chloride and picoline are distributed through both phases and it is advantageous, therefore, to separate the liberated base by steam distilltaion of the mixture. The water-soluble base can be separated from the aqueous distillate as pointed out above in connection with 2,6-lutidine; preferably, it is salted out by the addition of solid sodium chloride or a concentrated solution of sodium chloride. The calcium chloride solution remaining in the steam distillation still may be reused for precipitation of a new batch of 4-picoline.

The mother liquor from which the calcium chloride addition compound of 4-picoline was precipitated contains 3- and 4-picoline, hydrocarbon oil, and a trace of dissolved calcium chloride. This mixture is subjected to fractional distillation to recover the hydrocarbon oil for further use. The remaining mixture of 3- and 4-picolines is now greatly enriched in 3-picoline.

After the bulk of the 4-picoline has thus been removed from a 3-picoline-4-picoline mixture, or after the bulk of the 2,6-lutidine and 4-picoline has been removed from a 2,6-lutidine-3-picoline-4-picoline mixture, the resulting base mixture, rich in 3-picoline, is worked up for isola-

tion of 3-picoline in accordance with the process of copending application Serial No. 346,347.

In this process the base mixture is preferably diluted with methanol or ethanol, and the alcohol solution of the base is treated with a limited quantity of phosphoric acid and induced to crystallization by inoculation with 3-picoline phosphate, preferably at 0° to 10° C. To avoid precipitating 4-picoline or other materials with the 3-picoline phosphate, only a limited quantity of the 3-picoline phosphate should be precipitated; I have found it advantageous to precipitate 3-picoline phosphate until the remaining mother liquor contains the 3- and 4-picolines in a proportion of from 45/55 to 50/50.

Crystals of 3-picoline phosphate are filtered or centrifuged and freed from adhering mother liquor by washing with methanol or ethanol. 3-picoline phosphate is decomposed by admixture with aqueous solutions of sodium hydroxide and the liberated base is separated and dehydrated.

The mother liquor is worked up for recovery of alcohol and a base mixture of 3- and 4-picolines in roughly equal proportions by treatment with sodium hydroxide and distillation. The recovered mixture of 3- and 4-picolines is returned to the process cycle, being first treated with calcium chloride to isolate the 4-picoline calcium chloride addition compound and then with phosphoric acid for isolation of 3-picoline.

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

Example 1—Isolation of 4-picoline directly in the form of its calcium chloride addition compound from base mixtures containing predominantly 2,6-lutidine, 3-picoline, and 4-picoline

The material used in this example consisted of a mixture of heterocyclic bases containing about 34% 2,6-lutidine, about 29% 3-picoline, and about 37% 4-picoline together with other bases present in small amounts. The boiling range of the material was 140.4° to 144.1° C., specific gravity .946 at 25° C.

An iron kettle equipped for agitation and fitted with a reflux condenser was charged with 1000 parts by weight of this heterocyclic base mixture, 170 parts by weight of toluene, and 340 parts by weight of an aqueous solution containing 145 parts of pure calcium chloride and 2 to 3 parts of magnesium chloride present as an impurity. The mixture was agitated and heated to refluxing. The condensate was passed through a side arm trap in which it separated into two liquid layers; the upper layer consisting predominantly of toluene with a smaller proportion of heterocyclic bases dissolved therein was allowed to return continuously to the kettle. The lower layer consisting of water containing a small percentage of dissolved bases was withdrawn to bring about dehydration of the kettle charge. Formation of the crystalline addition compound of 4-picoline and calcium chloride began in the course of the dehydration and was practically complete at the end, the crystals showing only a slight solubility even in the hot mixture of toluene and bases. The charge was cooled to room temperature. The heavy slurry of crystals was filtered on a suction filter and the crystals washed with toluene to remove adhering free bases. The total weight of the precipitate was 665 parts, or 370 parts of crystals on a toluene-free basis. The crystals consisted of an addition compound in which calcium chloride and 4-picoline were combined in a molar ratio of 1:2.

The crystals were decomposed by the addition of 300 parts by weight of warm water. At about 95° C. the resulting mixture separated into two layers. The lower aqueous layer was evaporated to a slightly reduced volume. The distillate yielded a small quantity of 4-picoline. The toluene-4-picoline layer was fractionally distilled separating successively: (1) water and toluene; (2) toluene; and (3) 4-picoline. A small still residue of calcium chloride remained behind. A total of 230 parts by weight of 4-picoline was obtained. This material was found to contain 92% of 4-picoline and 8% of 3-picoline, no 2,6-lutidine being present.

Bases which did not combine with calcium chloride obtained as mother liquor and wash liquors from the filtration of the addition compound were fractionally distilled to separate them from admixed toluene and traces of dissolved calcium chloride. A total of 746 parts by weight of bases was obtained.

From this base mixture, 2,6-lutidine and 3-picoline may be isolated by treatment with zinc chloride and with phosphoric acid, as indicated above, and as pointed out more particularly in the following example.

Example 2—Resolution of 2,6-lutidine-3-picoline-4-picoline mixture

Another portion of the same heterocyclic base mixture used in the previous example was charged into an iron kettle equipped for agitation. An equal weight of a 50% aqueous zinc chloride solution was added; this amount of zinc chloride was calculated to combine with approximately the amount of 3- and 4-picolines present, leaving the bulk of the 2,6-lutidine free. The charge was heated to the boiling point of water at which temperature the zinc-chloride picoline addition compounds remained molten. The agitated mass was steam distilled to remove the bulk of the uncombined 2-6-lutidine, a small proportion of the isomeric picolines passing over with the lutidine. The distillate was admixed with an equal volume of saturated salt solution to salt out the bases which were then withdrawn as a separate supernatent layer. The separated bases completely dehydrated and distilled contained 85% of 2,6-lutidine. The mass in the kettle was subjected to further steam distillation to remove additional base mixture of lower 2,6-lutidine content. These lutidine-rich base mixtures could be treated with an additional quantity of zinc chloride and again steam distilled to produce a higher quality 2,6-lutidine.

To the kettle residue containing the zinc chloride addition compounds of 3- and 4-picolines was added a sufficient quantity of 50% aqueous sodium hydroxide solution to liberate the picolines. These were removed by steam distillation and were salted out of the aqueous distillate. The base mixture thus recovered had a boiling range of 141.5° to 145.5° C. and contained approximately 7% 2,6-lutidine, 41% 3-picoline, and 52% 4-picoline.

The iron reaction kettle of Example 1, equipped for agitation and provided with a reflux condenser, was charged with 1100 parts by weight of this 3- and 4-picoline mixture, 170 parts by weight of toluene, and 612 parts by weight of an aqueous calcium chloride solution containing 312 parts by weight of pure calcium chloride. The kettle charge was dehydrated as described in Example 1, cooled, and crystals of the precipitated 4-picoline addition compound isolated by filtra-

tion and washed with toluene. Crystals as well as combined mother and wash liquors were worked up as described in Example 1. The following products were obtained:

(a) From the 4-picoline-calcium chloride crystals a base mixture, 384 parts by weight, containing 95% 4-picoline and 5% 3-picoline;

(b) From the mother and wash liquors a base mixture, 650 parts by weight containing 64% 3-picoline, 25% 4-picoline, and 11% 2,6-lutidine.

An enamel-lined kettle provided with an agitator and cooling jacket was charged with 600 parts by weight of base mixture (b), above, and 550 parts by weight of pure methanol. While agitating and cooling, 280 parts by weight of 85% phosphoric acid was gradually added. The mixture was then gradually cooled to 5° C. and held at this temperature for 15 hours. A heavy crystalline precipitate of 3-picoline phosphate was separated out. The kettle charge was centrifuged and the isolated crystals washed with fresh methanol at 5° C. The dry crystals amounted to 375 parts by weight.

The crystals were dissolved in 500 parts of water and 3-picoline was liberated by the addition of 180 parts of sodium hydroxide in 200 parts of water. The liberated 3-picoline was separated as an upper layer from the hot aqueous solution of sodium phosphate. Partial evaporation of this solution gave a small additional yield of 3-picoline salted out from the distillate. The 3-picoline was dehydrated and distilled to improve the color, 179 parts by weight being obtained. The material had a purity of 97%.

Mother liquor and methanol wash liquors were combined and the methanol recovered by fractional distillation. The still residue consisting of free bases, water, and base phosphates, was mixed with a solution of 40 parts of sodium hydroxide in 100 parts water. Liberated bases were separated, dehydrated, and distilled. An additional small yield of bases was obtained by partial evaporation of the aqueous phosphate solution, the bases being contained in the distillate.

The recovered bases consisted of a mixture of 3- and 4-picolines and 2,6-lutidine, together with some 2-picoline and 2,4-lutidine. The latter two components present originally in the natural mixture of bases in small proportions had accumulated in these recovered bases. It was found advantageous, therefore, to submit these bases to fractional distillation and again recover a narrow-boiling center cut of bases containing predominantly 2,6-lutidine, 4-picoline and 3-picoline which may then be further resolved as described in these examples.

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 separating components of a mixture containing substantial proportions of 4-picoline and of other heterocyclic nitrogen compounds not readily separable from 4-picoline by distillation, comprising precipitating 4-picoline from such mixture in the form of its calcium chloride addition compound.

2. In a process for separating components of a nitrogen base mixture containing predominantly 4-picoline and other pyridine homologs not readily separable therefrom by distillation, the step which comprises treating this base mixture with calcium chloride in an anhydrous non-alcoholic medium to precipitate a portion of the 4-picoline in the form of its calcium chloride addition compound.

3. A process for separating components of a mixture containing at least about 30% 4-picoline and containing other heterocyclic nitrogen compounds, including other pyridine homologs, not readily separable from 4-picoline by distillation, comprising precipitating from the mixture in a non-aqueous, non-alcoholic medium the calcium chloride addition compound of 4-picoline.

4. In a process for separating components of a fraction of heterocyclic nitrogen compounds including 4-picoline, boiling predominantly in the ranger 140°–148° C., the step which comprises treating compounds in this fraction with calcium chloride in an anhydrous, non-alcoholic medium to precipitate a portion of the 4-picoline in the form of its calcium chloride addition compound, separating the precipitated calcium chloride addition compound of 4-picoline, and treating this separated compound to liberate 4-picoline.

5. A process for separating components of a fraction of pyridine homologs boiling predominantly in the range of about 140° to 145° C., containing at least about 30% 4-picoline and a substantial proportion of 3-picoline, which process comprises treating this base fraction with calcium chloride in an anhydrous non-alcoholic liquid medium to precipitate a portion of the 4-picoline in the form of its calcium chloride addition compound, separating the precipitated calcium chloride addition compound of 4-picoline, treating this separated compound with water to liberate 4-picoline, and separating the 4-picoline thus liberated.

6. In a process for separating a heterocyclic nitrogen compound mixture into its components, the steps which comprise fractionating the mixture to obtain a fraction of 4-picoline and other heterocyclic nitrogen compounds, including other pyridine homologs, boiling in the range 140°–148° C., treating bases in this fraction with calcium chloride in an anhydrous, non-alcoholic medium to precipitate a portion of the 4-picoline in the form of its calcium chloride addition compound, and treating this compound to liberate 4-picoline.

7. In a process for separating a tar base mixture into its components, the steps which comprise fractionating the base mixture to obtain a fraction of pyridine homologs boiling in the range 140°–145° C., containing 4-picoline, 3-picoline, and 2,6-lutidine, treating this base mixture to separate 2,6-lutidine, treating the remaining bases with calcium chloride in an anhydrous, non-alcoholic medium to precipitate a portion of the 4-picoline in the form of its calcium chloride addition compound, separating the precipitated calcium chloride addition compound of 4-picoline, and treating this separated compound to liberate 4-picoline.

8. In a process for resolving a heterocyclic base mixture containing substantial proportions of 3-picoline and 4-picoline, the combination of steps which comprises subjecting the mixture to a plurality of treatments to precipitate the calcium chloride addition compound of 4-picoline and to precipitate 3-picoline as phosphate, and separating each of these products directly after its precipitation.

9. In a process for resolving a heterocyclic base mixture comprising predominantly 2,6-lutidine,

3-picoline, and 4-picoline, the steps which comprise treating the base mixture to separate 2,6-lutidine, treating the resulting 3- and 4-picoline base mixture with calcium chloride to precipitate the calcium chloride addition compound of 4-picoline, separating the calcium chloride addition compound of 4-picoline thus precipitated, recovering a residual base mixture high in 3-picoline, and precipitating 3-picoline as phosphate from this residual base mixture.

10. In a process for resolving a pyridine homolog fraction boiling predominantly in the range 140°–145° C., and comprising predominantly 2,6-lutidine, 3-picoline, and 4-picoline, the steps which comprise treating the base mixture with zinc chloride to form addition compounds of the picolines, separating 2,6-lutidine from the picoline zinc chloride addition compounds thus formed, reconverting the picoline zinc chloride addition compounds to free bases, treating the resulting 3- and 4-picoline base mixture with calcium chloride to precipitate the calcium chloride addition compound of 4-picoline, separating the calcium chloride addition compound of 4-picoline thus precipitated, recovering a residual base mixture high in 3-picoline, and precipitating 3-picoline as phosphate from this residual base mixture.

11. In a process for separating components of a mixture containing at least about 30% of 4-picoline and substantial proportions of other heterocyclic nitrogen compounds, including other pyridine homologs, not readily separable from 4-picoline by distillation, the steps which comprise adding an aqueous solution of calcium chloride to said mixture, heating the resulting mixture to vaporize substantially all water therefrom and thus cause the calcium chloride addition compound of 4-picoline to precipitate, separating the precipitated 4-picoline-calcium chloride addition compound, decomposing this compound by addition of water, recovering 4-picoline and an aqueous calcium chloride solution separately from the resulting aqueous mixture, and employing the calcium chloride solution thus recovered for treatment of additional heterocyclic nitrogen compound mixture.

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