

UNITED STATES PATENT OFFICE

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ISOLATION OF QUINOLINE FROM A MIXTURE OF NITROGEN BASES

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4 Claims. (Cl. 260—283)

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This invention relates to the separation of quinoline from mixtures thereof with other nitrogen bases. This application is a continuation-in-part of application Serial No. 346,347, filed July 19, 1940, now Patent No. 2,408,975, dated October 8, 1946.

Quinoline is customarily extracted along with other nitrogen bases from coke oven distillates and other sources of heterocyclic nitrogen bases by means of an aqueous solution of a mineral acid, usually sulfuric acid. After liberation of the bases from these acid solutions by means of alkali, the base mixtures thus obtained are customarily fractionally distilled to obtain fractions predominating in a particular base. By fractionating tar bases liberated from a quinoline-containing oil, fractions predominating in quinoline may be obtained; in some cases, a relatively wide-boiling fraction, e. g. one having a boiling range of 233° to 240° C., may be separated; in other cases, a close-cut fraction, e. g. one having a boiling range 237.5° to 239.5° C., is taken. Quinoline fractions as ordinarily produced heretofore might contain as much as 80% to 92% quinoline, the remainder consisting of other nitrogen bases of boiling range close to quinoline and not readily separable by distillation, e. g. trimethylanilines, isoquinoline, quinaldine, and other bases. Mixtures of this kind have found limited practical applications and are of low economic value. Pure quinoline, however, is a product of great commercial interest, for example, in the preparation of its derivatives, especially pharmaceutical products and dyes. Pure quinoline is becoming of particular importance at present since it is a suitable starting material for the preparation of nicotinic acid, a member of the vitamin B complex.

I have discovered that phosphoric acid forms an acid phosphate ($C_9H_7N.H_3PO_4$) of limited water solubility and that this phenomenon may be employed to effect separation of substantially pure quinoline from other nitrogen bases with which it may be admixed. Of such other bases, I have found that isoquinoline, which may form an appreciable part of the impurities in the quinoline fractions, forms a phosphate that is extremely soluble in water. Quinaldine, on the other hand, I have found, forms a phosphate having a water solubility substantially the same as that of quinoline phosphate; hence, a crude fraction treated with phosphoric acid for recovery of quinoline should contain relatively small amounts of quinaldine, not over 5%, and preferably less than 2%, by weight.

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Quinoline fractions treated in accordance with my invention for recovery of quinoline may have a quinoline content of as low as about 70%. Preferably, however, in order to obtain a fraction containing not more than 5% quinaldine, preferably less than 2%, the crude quinoline fraction should be subjected to reasonably close fractional distillation to obtain a fraction containing from 80% to 92% quinoline. In accordance with this invention, such fractions are caused to react with phosphoric acid in the presence of an aqueous medium. Preferably, an amount of phosphoric acid corresponding to the stoichiometric amount required to react with all the bases present is used; an excess of phosphoric acid over and above the stoichiometric amount may be used, if desired. The amount of water present should be such as to retain in solution substantially all of the nitrogen bases present except the quinoline and to avoid undue solution of quinoline phosphate.

In a preferred method of carrying out this invention, a predetermined amount of phosphoric acid is added to a crude quinoline fraction and the temperature of the reaction mixture permitted to rise. After all the phosphoric acid has been added, precipitation of the quinoline phosphate is effected by cooling the reaction mixture to a temperature within the range of 0° to 30° C., lower temperatures being advantageous as the solubility of the phosphate decreases substantially on cooling. The quinoline phosphate thus preferentially precipitated is separated from the dissolved phosphates and other bases by filtration, or by centrifuging, and washing, preferably with cold water, or with water containing a few per cent of phosphoric acid or of monosodium phosphate to reduce the solubility of quinoline phosphate.

The washed quinoline phosphate may be dried to produce crystal quinoline phosphate containing no water of crystallization. The resultant product which is in the form of clean crystals is a useful product for direct use commercially for the manufacture of quinoline derivatives. Free quinoline may be obtained by hydrolyzing the quinoline phosphate. For example, quinoline phosphate or a solution thereof may be treated with an aqueous alkaline material, such as caustic soda, lime or ammonia. The freed quinoline may be further purified by dehydration and distillation.

Ordinary commercial grades of phosphoric acid may be used to precipitate the quinoline phosphate. Mono- or disodium phosphate with the

equivalent sulfuric acid may be used, however, instead of the more expensive free phosphoric acid, i. e. the phosphoric acid may be formed in situ. Most advantageously, alkali phosphate recovered after liberation of the quinoline from its phosphate may be cyclically reused, mixing it with sufficient sulfuric acid to neutralize the alkaline bases present, avoiding, however, any substantial excess which would reduce the quantity of precipitated quinoline phosphate.

The following examples are illustrated of the process of my invention. All parts are by weight. boiling range 236.6° to 237.8° C. and a specific gravity of 1.09 at 25° C. containing 91.5% quinoline, 4% isoquinoline, 5% quinaldine, and approximately 4% other nitrogen bases were suspended in 500 parts water, and 520 parts of 85% phosphoric acid were gradually added, dissolving the quinoline. The temperature of the solution rose to 80° C. due to the generated heat of neutralization. This solution was cooled to about 20° C. while being agitated. Quinoline phosphate ($C_9H_7N.H_3PO_4$) precipitated in small but well-formed crystals. The reaction mixture was filtered by suction and washed with 300 parts of water at about 10° C., successive small portions being applied to the crystals. On a dry basis, 641 parts of quinoline phosphate were thus obtained.

The quinoline phosphate thus obtained was purified by suspending it, without drying, in 1000 parts of water. To remove traces of hydrocarbon oils, the solution of quinoline phosphate may be heated to boiling and partially evaporated; alternatively, the aqueous mixture may be subjected to steam distillation to drive off the hydrocarbon oils. Quinoline was liberated from the phosphate solution by adding a solution of 150 parts of sodium hydroxide in 300 parts of water, the mixture stratified, the upper quinoline layer separated and washed with water, residual water removed by distillation, and the quinoline thus obtained distilled. The material thus recovered boiled at 237.5° to 237.7° C., had a melting point of -15.9° C. and purity of 98.2% quinoline.

Example 2.—300 parts of crude quinoline fraction boiling in the range of 232.5° to 240.5° C., having a specific gravity of 1.089 at 25° C. and containing approximately 81% quinoline, were added to a solution formed by adding 300 parts of monosodium phosphate ($NaH_2PO_4.H_2O$), 800 parts of water and 110 parts of concentrated sulfuric acid (94%). A clear solution resulted. Traces of hydrocarbon oils of the same boiling range as the quinoline fraction were removed from this solution by evaporating it until 200 parts of water had been distilled off. The resultant solution was cooled to induce precipitation of the quinoline phosphate. Crystallization began at about 55° C., the mass being cooled with agitation to about 20° C.

The crystal slurry was filtered on a suction filter and the crystals washed with successive portions of an aqueous solution containing 5% monosodium phosphate to remove adhering mother liquor, a total of 400 parts of the solution being used for this purpose. The quinoline phosphate was suspended in 500 parts of water and the quinoline liberated by adding a solution of sodium hydroxide in amount sufficient to convert the phosphoric acid present into monosodium phosphate. The quinoline thus obtained was washed with water, dried, and distilled. 161 parts of refined quinoline were obtained having a melting point of -17.1° C. and a purity of 95.6%.

The sodium phosphate solution was regenerated by the addition of a quantity of sulfuric acid equivalent to the sodium hydroxide used in liberating the quinoline. The thus regenerated solution may be cyclically reused in the treatment of a further batch of crude quinoline. The mother liquor from the quinoline phosphate which contains the phosphates of other nitrogen bases present in the crude quinoline, besides a small proportion of quinoline, may be mixed with sodium hydroxide sufficient to liberate these bases.

The pure dry quinoline had a clean, sweet odor and remained light-colored for an extended time in contrast to the crude material which had a pungent odor and discolored rapidly after distillation.

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 quinoline from a mixture thereof with closely-related, like-boiling nitrogen bases, in which mixture quinoline constitutes at least 70% by weight of the total bases present and in which quinaldine is present only in relatively small amounts, the step that comprises treating the mixture in the presence of water with a quantity of phosphoric acid sufficient to react with a substantial portion of the nitrogen bases to precipitate quinoline phosphate from an aqueous solution of the mixture, the amount of water present being sufficiently high to retain in solution substantially all the nitrogen bases except quinoline, and sufficiently low to cause substantial precipitation of quinoline phosphate.

2. In a process for separating quinoline from a nitrogen base mixture containing at least 70% quinoline, not over 5% quinaldine, and isoquinoline, the steps that comprise treating the mixture in the presence of water with a sufficient quantity of phosphoric acid to react with a substantial portion of the nitrogen bases present to precipitate quinoline phosphate from the mixture, and separating the precipitated phosphate, the amount of water present being sufficiently high to retain in solution substantially all the nitrogen bases except quinoline, and sufficiently low to cause substantial precipitation of quinoline phosphate.

3. In a process for separating quinoline from a nitrogen base mixture containing from 80% to 92% quinoline, less than 2% quinaldine, and isoquinoline, the steps that comprise treating the mixture in the presence of water with a sufficient quantity of phosphoric acid to react with substantially all the quinoline present to precipitate quinoline phosphate from the mixture, and separating the precipitated phosphate, the amount of water present being sufficiently high to retain in solution substantially all the nitrogen bases except quinoline, and sufficiently low to cause substantial precipitation of quinoline phosphate.

4. In a process for separating quinoline from a nitrogen base mixture containing at least 70% quinoline, less than 2% quinaldine, and isoquinoline, the steps that comprise treating the mixture in the presence of water with a quantity of phosphoric acid at least as great as the stoichiometric amount equivalent to all the nitrogen bases present, the amount of water present being sufficiently high to retain in solution substantially all the nitrogen bases except quinoline, and suffi-

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ciently low to cause substantial precipitation of quinoline phosphate, heating the resultant mixture to remove therefrom traces of hydrocarbon oils of the same boiling range as the quinoline fraction, cooling to precipitate quinoline phosphate, separating the quinoline phosphate from the resultant slurry, and converting the separated phosphate to free quinoline.

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Certificate of Correction

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December 21, 1948.

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It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows:

Column 3, line 11, for the word "illustrated" read *illustrative*; line 13, before "boiling" insert *Example 1.—500 parts of crude quinoline of*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 12th day of April, A. D. 1949.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.