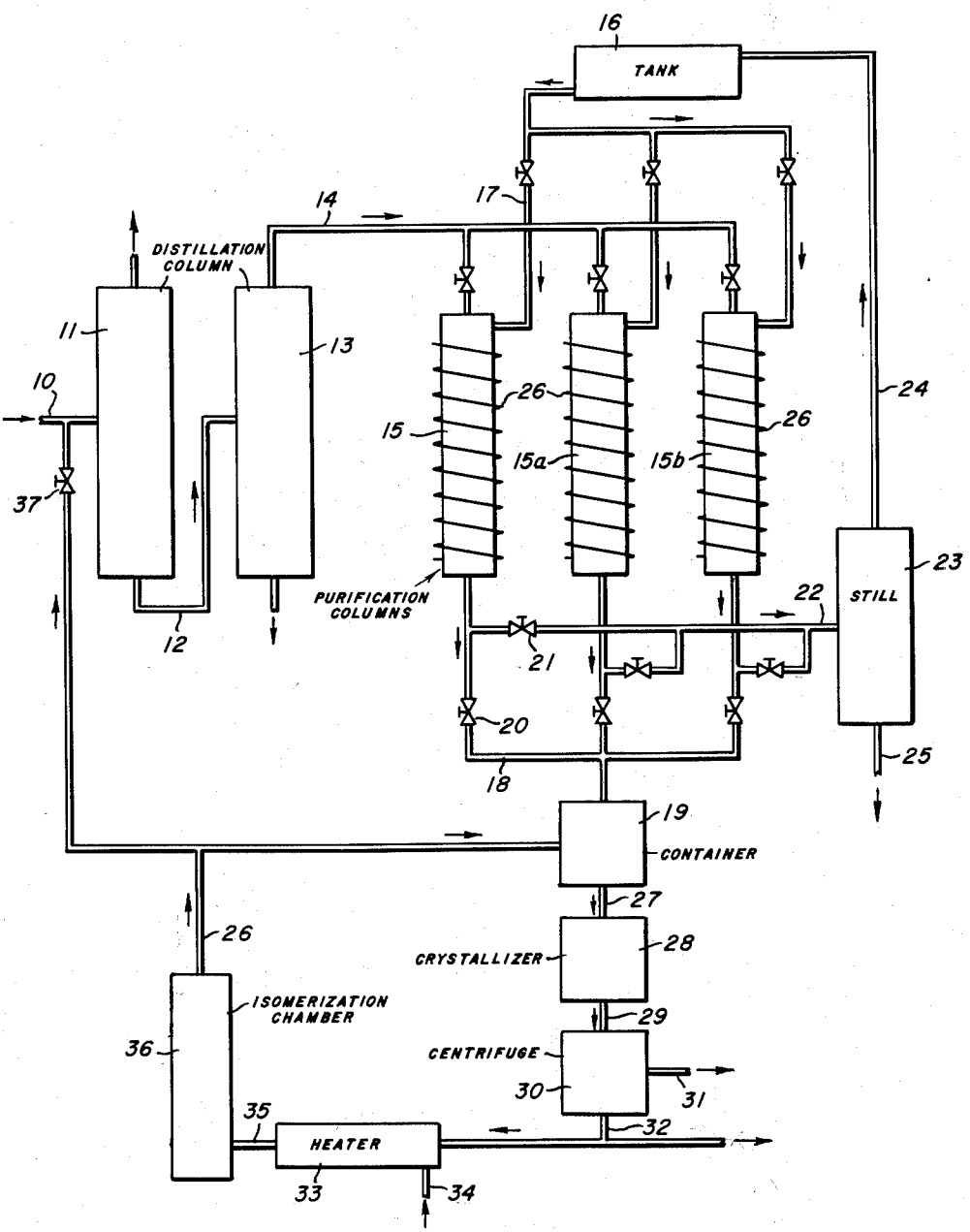
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METHOD FOR RECOVERING METHYLNAPHTHALENES

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METHOD FOR RECOVERING METHYLNAPHTHALENES

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The present invention relates to a method for recovering methylnaphthalenes from coal tar, and more particularly to the recovery of 2-methylnaphthalene, useful as an anthelmintic drug and in the synthesis of vitamin K.

Methylnaphthalenes are present in coal tar as relatively minor constituents. A typical coal tar may contain about 1 percent of 1-methylnaphthalene and about 1.5 percent of 2-methylnaphthalene. A 230° to 260° C. cut, subsequently acid washed, may contain about 30% to 40% methylnaphthalenes. Known methods for the recovery of methylnaphthalenes from coal tar give low yields and involve many tedious and costly steps. As a result, the recovery of methylnaphthalenes from coal tar has not, to our knowledge, been practiced on a commercial scale. Accordingly, it is an object of our invention to provide a method whereby methylnaphthalenes of relatively high purity may be recovered from coal tar economically, in good yield, and on a substantial scale.

According to a preferred practice of our invention we

(1) Distil an acid-washed 230° to 260° C. cut of coal tar at atmospheric pressure to remove, as heads, impurities boiling below about 237° C.;
(2) Distil the cut further at subatmospheric pressure to remove high-boiling impurities, thereby preventing or minimizing formation of azeotropes and obtain a fraction containing about 90% mixed methylnaphthalenes;
(3) Chromatographically remove nitrogen and others of the remaining impurities;
(4) Crystallize out 2-methylnaphthalene;
(5) Isomerize the mother liquor from the crystallization, which mother liquor is relatively rich in 1-methylnaphthalene, to provide additional 2-methylnaphthalene;
(6) Recycle the isomerized mother liquor to the crystallizer to provide for the removal of the additional 2-methylnaphthalene.

A complete understanding of the invention may be obtained from the following detailed description and explanation which refer to the accompanying drawing illustrating the present preferred practice. The single figure of the drawing is a diagrammatic representation of a system for carrying out the method of our invention.

Referring in detail to the drawing, an acid-washed, coal tar fraction boiling between about 230° and 260° C. and containing between about 30 and 40 percent methylnaphthalenes, flows through pipe **10** to a distillation column **11** having 20 to 40 theoretical plates, preferably 40. The column may be operated at a reflux ratio of 1:1 to 5:1, preferably 5:1, to remove as heads a fraction boiling under about 237° C. The higher-boiling bottoms flow from the bottom of column **11** through pipe **12** to a distillation column **13**. Column **13**, unlike column **11**, which may be operated at substantially atmospheric pressure, is operated at a total pressure of less than 250 mm. of mercury, preferably between about 15 mm. and 50 mm. mercury absolute pressure. Column **13** may have 20 to 40 theoretical plates, preferably **40**, and may be operated at a reflux ratio of 1:1 to 5:1, preferably about 5:1, whereby there is obtained a cut boiling up to about 145° C. when the pressure is 50 mm. of mercury absolute.

The described successive atmospheric and vacuum distillations are required to separate a product comprising about 90% methylnaphthalness in high yield, for example, at least 80 percent recovery of the methylnaphthalenes originally present in the coal tar. This is so because the crude fraction boiling between about 230° and 260° C. contains numerous compounds, with many azeotropes and polyazeotropes present when such a fraction is distilled at atmospheric pressure. A number of these compounds do not form azeotropes at subatmospheric pressures. The initial heads removal to about 237° C. at atmospheric pressure, carries along some impurities as lower-boiling azeotropes that would boil with the methylnaphthalenes at subatmospheric pressure. This distillation has been found fairly critical to between about 236° and 238° C. When the heads fraction is taken below about 236° C., the impurities in the subsequent methylnaphthalenes fraction are significantly increased. When the heads fraction is taken above about 238° C. the impurities decrease, but the yield of methylnaphthalenes drops off appreciably and increasingly. A number of compounds with boiling points higher than that of the methylnaphthalenes boil in the methylnaphthalenes range as azeotropes at atmospheric pressure. It has been found unexpectedly that these compounds do not form azeotropes at subatmospheric pressure and thus a subatmospheric distillation permits separation of the methylnaphthalenes therefrom. An atmospheric distillation alone cannot produce a 90% methylnaphthalenes product from acid washed coal tar fractions. A subatmospheric distillation alone will produce a 90% methylnaphthalenes product, but in significantly lower yield.

The vacuum-distilled product comprising a mixture of 1-methylnaphthalene (30 to 37%), 2-methylnaphthalene (55 to 65%), and impurities (under 10%), flows from the top of column **13** through a pipe **14** to the top of and downwardly through a chromatographic purification column **15** packed with silica gel, alumina, activated clay, or any other suitable adsorbing material, preferably silica gel. Such chromatographic purification is important, since it has been found effective for removing nitrogenous and other deleterious constituents that interfere with an isomerization, hereinafter to be more fully described.

After about 2.5 parts by weight of the 90% methylnaphthalenes fraction have passed through the chromatographic column **15** for each part by weight of silica gel in the column, a desorbent liquid, e.g. methanol, flows from tank **16** through pipe **17** in a total amount of 1.5 parts by weight for each part by weight of adsorbent in column **15**. This desorbent liquid, being more polar than the methylnaphthalenes and even more polar than the impurities which in turn are more polar than the methylnaphthalenes, pushes the methylnaphthalenes and impurities through the column ahead of it. Effluent from the bottom of column **15** first is a 95% methylnaphthalenes fraction, which flows through pipe **18** directly to container **19**. By observation or known control means, just prior to flow of impurities, valve **20** is closed and valve **21** is opened to permit flow of impurities and methanol through pipe **22** to still **23**, where the methanol and the impurities are separated and flowed respectively through pipes **24** and **25**.

After column **15** has drained, it still is saturated with methanol which represents about 25% by weight of the silica gel. The methanol is removed by heating the column at 110° to 150° C. for about two hours to drive off the methanol and thus regenerate the column. The column, after cooling, is ready for re-use. Column heating may be effected by coils **26**, a steam jacket or other heating means. For continuous operation, additional chromatographic purification columns, such as col-

umns 15*a* and 15*b*, may be employed in parallel arrangement and with appropriate valves and piping, as illustrated. In addition to methanol, the desorbant liquid may be chosen from other highly polar solvents such as ethanol, propanol and isopropanol. Methanol is preferred because of its low boiling point.

As described, the chromatographically purified methylnaphthalenes flow from the bottom of column **15** through a pipe **18** as a mixture comprising about 95 percent methylnaphthalenes and 5 percent impurities, to a container **19** where they may be admixed with an isomerization product flowing thereto through pipe **26**, as will be more fully described. From container **19**, the admixture flows through pipe **27** to a crystallizer **28** wherein the methyl naphthalenes are cooled to between about —10° C. and —15° C., which is below the freezing point of 2-methylnaphthalene (34° C.) but above the freezing point of 1-methylnaphthalene (—31° C.). Mostly 2-methylnaphthalene and some 1-methylnaphthalene crystallize out in a cold slurry of the crystals in a mother liquor comprising about 47 to 50 percent of 2-methylnaphthalene and 39 to 43 percent of 1-methylnaphthalene. The slurry flows from the crystallizer through a pipe **29** to a centrifuge **30**, to separate crystals and mother liquor for removal through pipes **31** and **32** respectively. The crystals comprise about 90 percent 2-methylnaphthalene, about 5 percent 1-methylnaphthalene, with the remainder as impurities.

It is preferred to process the mother liquor to obtain additional 2-methlynaphthalene by flowing the liquor in pipe **32** to a heater **33** wherein it is admixed with hydrogen from pipe **34** and vaporized to a temperature between about 400° and 425° C., and then flowing the vapors through pipe **35** to an isomerization chamber **36**, which may be a column packed with a suitable catalyst, such as 13 percent alumina on silica.

Hydrogen serves to prolong the life of the catalyst. About 3 volumes to 10 volumes hydrogen per volume of methylnaphthalenes vapors may be used, a 5:1 ratio being preferred. The isomerization catalyst becomes spent after about 7 parts by weight of methylnaphthalenes have been passed through one part by weight of catalyst. The catalyst may be regenerated with oxygen at about 450° to 500° C.

The vapors from column **36** flow through pipe **26** to container **19**, the isomerization serving to increase the 2-methylnaphthalene content of the mother liquor from about 47–50% to about 56–60%. As hereinabove described, the isomerization increases the quantity of 2-methylnaphthalene available for recovery by admixture with the product from pipe **18** flowing to container **19** and thereafter to crystallizer **28** and centrifuge **30** for separation of 2-methylnaphthalene and recycling of mother liquor for isomerization in column **36**.

It is evident that the hereinabove described procedures may be varied, for example, to draw off a product of mixed methylnaphthalenes before or after any of the process steps, the purity thereof increasing as the process steps proceed. The ratio of the weight flow rates in pipes **26** and **18** may vary between about 0 to 1 and 2.6 to 1 respectively. It is also evident that, with intermediate product removal in a cyclic operation, the impurities in the system increase. As a means for correcting this situation, when the vapors in pipe **26** have a content below about 55% of 2-methylnaphthalene, they may be drawn off as a varying side stream or completely by appropriately opening valve **37** to pipe **10** and distillation column **11**.

It will be apparent that distillation columns **11** and **13**, columns **15**, **15***a*, **15***b* and **36**, container **19**, crystallizer **28**, centrifuge **30** and heater **33** may be of any design known to effect the desired result. In particular, the distillation columns may be bubble-tray towers containing 20 to 40 trays. The container **19** may be a lower tower or a simple pot in which the vapor from pipe **26** is bubbled through and condensed in a pool of liquid. The columns **15**, **15***a*, **15***b* and **36** may be packed with an appropriate adsorbent and catalyst respectively.

A specific example of the practice of the invention is set forth below.

A coal tar creosote fraction boiling between about 230° and 260° C. which was subsequently washed with dilute sulfuric acid, containing 14.5% of 1-methylnaphthalene and 21.0% of 2-methylnaphthalene, was distilled in column **11** to remove a fraction boiling under 237° C. as heads and again distilled in column **13** at a pressure of about 50 mm. mercury absolute pressure, to separate a fraction boiling up to 145° C. at 50 mm. of mercury and containing 90% methylnaphthalenes as 33% of 1-methylnaphthalene and 57% of 2-methylnaphthalene. The two columns each had 40 theoretical plates, and were operated at a 5:1 reflux ratio. Chromatographic purification followed in column **15**, packed with silica gel, the liquid subsequently used as desorbent for impurities being methanol. The admixture in container **19** comprised 2.6 parts isomerized methylnaphthalenes from pipe 26 to 1 part of chromatographically purified methylnaphthalenes from pipe **18**, all parts by weight. The admixture flowing from container **19** was crystallized at —10° C., the slurry centrifuged, the mother liquor vaporized in admixture with 5 volumes heated hydrogen and isomerized at a temperature of about 425° C. at a contact time of 3 to 4 seconds in column **36** packed with a 15% alumina on silica catalyst. The centrifuged product comprised 2-methylnaphthalene (90%) pure in a 70% yield of methylnaphthalenes originally present and corresponding to a 106% yield of the 2-methylnaphthalene originally present.

In the above example, the product from distillation column **13** was a mixture of methylnaphthalenes (90% pure) in an 82.5% yield of methylnaphthalenes originally present. From chromatographic purification column **15**, a mixture of methylnaphthalenes (95% pure) was obtained in a corresponding 81% yield of the methylnaphthalenes originally present. From the centrifuge **30**, when the isomerization step was omitted, there was obtained 2-methylnaphthalene (90% pure) in a 24% yield and a mother liquor of mixed methylnaphthalenes (95% pure) in a 57% yield of methylnaphthalenes originally present.

While the above example illustrates a preferred method of operation, other conditions of operation may be used without departing from the spirit of the invention. The distillation column **11** of 20 to 40 theoretical plates may be operated at substantially atmospheric pressure and at reflux ratios from about 1:1 to 5:1. The distillation column **13** may be operated at pressures from about 1 to 250 mm. mercury absolute pressure and at reflux ratios as low as 3:1. The chromatographic adsorbent may be alumina, activated clay or other adsorbent as well as silica gel. The crystallization may be effected at about 5° C. to about —25° C., the preferred range being —10° to —15° C. In the isomerization, the temperature may be from about 375° to 505° C., 400° to 425° C. being preferred. The catalyst may be a silica-alumina mixture of about 94 to 75% silica and 6 to 25% alumina. The contact time may be 1 to 20 seconds, and the hydrogen admixture may be in a ratio between about 3:1 and 10:1, 5:1 being preferred.

The invention is characterized by several distinct advantages that make it possible to recover better yields of high-purity products from coal tar than has been possible heretofore. In the first place, a product of higher purity results from the elimination of azeotropes and azeotrope formers in the atmospheric and subatmospheric pressure distillations of an acid-washed, coal tar fraction boiling from about 230° to 260° C. at substantially atmospheric pressure. Secondly, the chromatographic purification permits separation of nitrogenous and other impurities. More important, this separation is essential, for otherwise the isomerization of 1-methylnaphthalene to 2-

methylnaphthalene could not be effected with any degree of efficiency.

Although we have disclosed herein the preferred practice of our invention, we intend to cover as well any change or modification therein which may be made without departing from the spirit and scope of the invention.

We claim:

1. A method for recovering 2-methylnaphthalene from an acid-washed, coal tar fraction boiling between about 230° and 260° C. and containing methylnaphthalenes in admixture as 1-methylnaphthalene and 2-methylnaphthalene, which consists in distilling said coal tar fraction at atmospheric pressure and removing therefrom material boiling below about 237° C., further distilling the remaining fraction boiling above about 237° C., between about 1 mm. and 250 mm. mercury absolute pressure and collecting a fraction containing about 90 percent methylnaphthalenes, passing said collected fraction through a chromatographic adsorbent chosen from the group consisting of silica gel, alumina and activated clay, cooling purified methylnaphthalenes effluent from said chromatographic adsorbent to between about +5° and −25° C. and separating crystals of substantially pure 2-methylnaphthalene from mother liquor, heating said mother liquor and hydrogen to a vapor, passing said vapor into contact with a silica-alumina catalyst at an isomerization temperature between about 375° and 505° C. and recycling the resulting isomerized product to said cooling step.

2. A method as defined in claim 1, characterized by following said chromatographic adsorption step by passing a desorbent fluid more polar than the constituents in said collected fraction through said adsorbent and recovering further purified methylnaphthalenes effluent therefrom.

3. A method as defined in claim 2 characterized by using methanol as desorbent fluid.

4. A method as defined in claim 1, characterized by crystallizing said purified methylnaphthalenes effluent to between about −10° and −15° C.

5. A method as defined in claim 1, characterized by recycling a portion of said isomerized product to said atmospheric pressure distillation step.

6. A method for recovering 2-methylnaphthalene from an acid-washed, coal tar fraction boiling between about 230° and 260° C. and containing methylnaphthalenes in admixture as 1-methylnaphthalene and 2-methylnaphthalene, which consists in distilling at a reflux ratio between about 1 to 1 and 5 to 1 said coal tar fraction at substantially atmospheric pressure and removing therefrom material boiling below about 237° C., further distilling said fraction at a reflux ratio between about 1 to 1 and 5 to 1 and collecting a fraction boiling up to about 145° C. at about 50 mm. mercury absolute pressure, passing said collected fraction through silica gel, desorbing said silica gel by passing methanol therethrough and collecting further purified methylnaphthalenes effluent product therefrom, cooling combined product from the adsorption and desorption steps to about −15° C. and separating crystals of substantially pure 2-methylnaphthalene from mother liquor, heating mother liquor and hydrogen in a ratio of about 1 to 5 respectively to about 425° C., passing said heated admixture over a silica-alumina catalyst and thereafter recycling the resulting isomerized product to said cooling step.

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