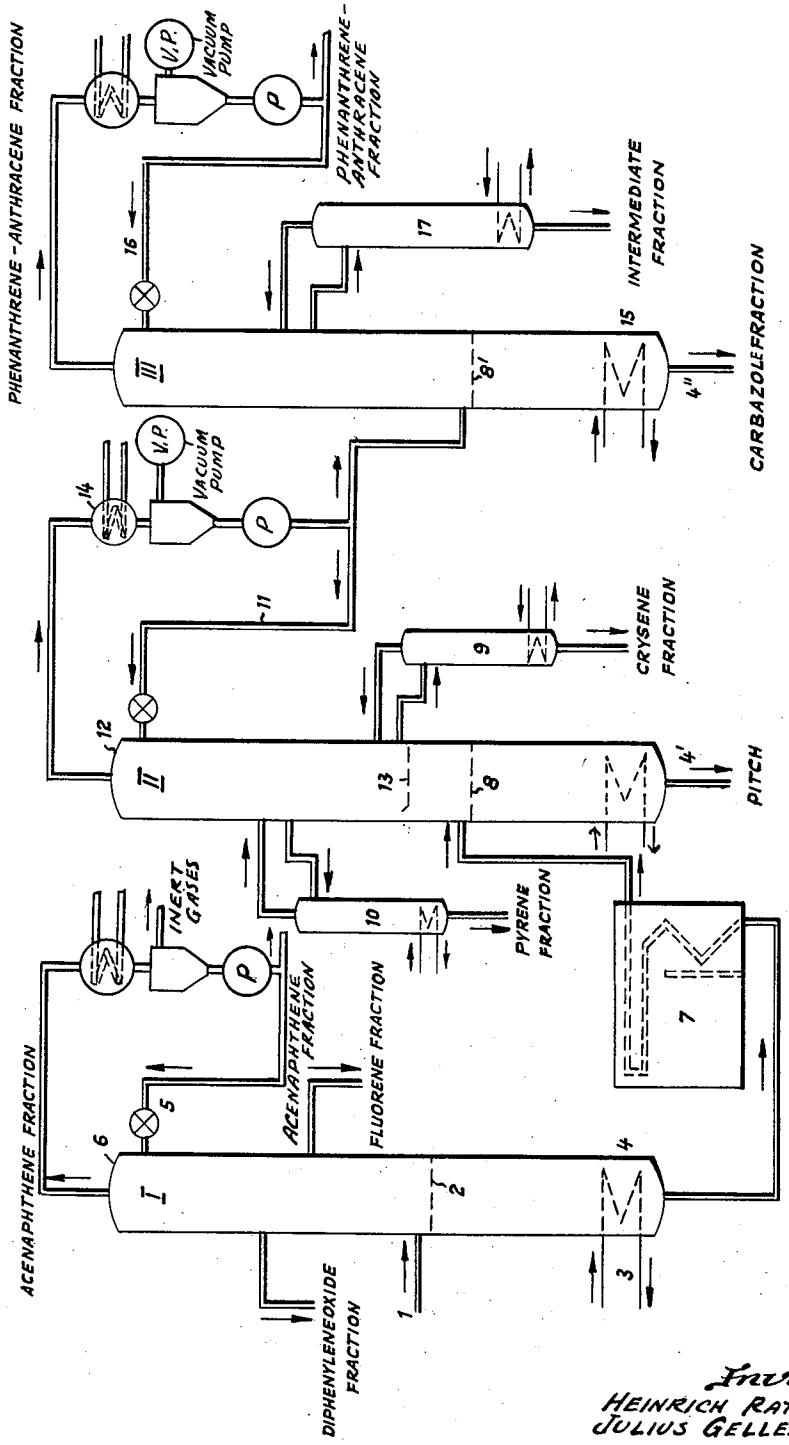
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FRACTIONAL DISTILLATION OF COAL TAR

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FRACTIONAL DISTILLATION OF COAL TAR

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This invention relates to a method of fractional distillation of coal tar and it has particular relation to a method of separating coal tar by continuous fractional distillation into desired volatile ingredients and a substantially non-volatile distillation residue.

In the processing of coal tar or similar hydrocarbon mixtures by fractional distillation, particular difficulties have been encountered in the separation of phenanthrene+anthracene and carbazol, as the vapor pressures of these compounds do not differ much from each other. Furthermore, as anthracene and carbazol show substantially similar solubility in organic solvents, it is likewise difficult to separate a mixture of these compounds by dissolution in organic solvents and subsequently crystallization. In spite of this difficulty, hitherto separation of anthracene and carbazol has been preferably carried out by this process, although, even when proceeding in several steps, the yields are relatively low and the process has also other disadvantages, such as the required heat-consuming redistillation of oil obtained in centrifuging, and the necessity of using extensive apparatus.

The main difficulty encountered in separating by fractional distillation fractions containing phenanthrene+anthracene and carbazol, consisted in the necessity of using temperatures, at which considerable decomposition of the material to be distilled, occured. For example, in the separation of the relatively low-boiling fluorene fraction from higher boiling tar ingredients, the use of a bottom temperature of 310 to 330° C. at a pressure of 150 to 250 mm. Hg is necessary. In view of the high number of trays in the fractionating column to be used, it is not possible to economically apply a still higher vacuum. On the other hand, as the use of temperatures above 330° C. in the distillation residue for a longer period of time, results in considerable thermal decomposition, the fluorene fraction has to be considered the highest-boiling coal tar ingredient, which could be recovered by direct distillation from the residue, with the use of a high reflux ratio.

The main object of the present invention is to provide a method of fractional distillation, in which the high-boiling ingredients of coal tar can be separated with high reflux ratio, without essentially exceeding for considerable periods of time, a temperature of about 330° C.

Other objects of the invention are the recovery of individual ingredients with a high degree of purity and in high yields. Further objects will be apparent from the following disclosure.

It has been unexpectedly found that in continuous rectification of coal tar according to the present invention, said peak temperature of about 330° C. need not be exceeded considerably and/or for a considerable period of time at any point of the rectifying plant and the anthracene+phenanthrene and carbazol fractions can be nevertheless recovered with the use of high reflux ratios.

According to the present invention, this is attained in the following manner.

In the first rectifying column or in the first columns of a continuously operated coal tar distillation plant according to the invention, low-boiling coal tar fractions up to and including the diphenylene oxide fraction, or, if desired, up to and including the fluorene fraction, are distilled off and the distillation residue of these distillations is freed from the last of said low-boiling fractions by highly efficient rectification with high reflux ratio in the manner described further below.

This residue, which has been thus sharply defined in its initial boiling point, is subsequently heated and evaporated under high vacuum. The pitch residue resulting in these steps is continuously discharged, while the vapors formed are passed to one or more, and separated in, rectifying columns. The vacuum and the temperature in the evaporation part of the column are thereby selected in such manner that at least the ingredients up to and including carbazol and eventually also heavy oils, like the pyrene and chrysene fractions, are present essentially in the vapor phase. This is the case if, at an absolute pressure of 10 to 40 mm. Hg, preferably 20 to 30 mm. Hg at 180° to 220° C. at the top of the column and 20 to 80 mm. Hg preferably 40 to 60 mm. Hg in the evaporation part of the column, the tar ingredients are introduced into this step of the process with a temperature of 350° to 380° preferably about 360° C. As this high temperature is maintained for a rather short period of time only, for example 1–3 minutes, it causes no substantial thermal decomposition of the tar ingredients.

The ingredients boiling above carbazol, such as primarily ingredients boiling in the range of pyrene and chrysene, can be recovered, if desired, directly from the same rectifying column. As in this part of the process particular stress is laid only on sharp fractionation of the carbazol fraction and not of said ingredients proper, a relatively low reflux ratio and a low number of normal trays, or a higher number of trays with low dipping and a design favorable to flow, can be used, and therefore, the above mentioned absolute pressure of for example 40–60 mm. Hg can be maintained without difficulty in the evaporation space.

After separation of the ingredients boiling above carbazol, a fraction of vapors is obtained, at 10 to 40 mm. Hg, corresponding to 180° to 220° C. at the top of the column, which is highly enriched in carbazol, anthracene, phenanthrene and eventually hydroanthracenes and fluorene. This fraction of vapors is discharged from the rectifying column and is divided in a subsequent group of columns, under a lower vacuum, corresponding for example to 100–300 mm. Hg, preferably about 150–200 mm. Hg, into several fractions. As no pitch ingredients are treated in said last mentioned group of columns, separation by distillation of the anthracene-phenanthrene-carbazol mixture can take place at high reflux ratio, i. e. with high supply of heat, and longer periods of treatment in the columns. It has been found that a reflux ratio of about 5–15 must be used in this fractionation if a sufficiently sharp separation is desired. At an absolute pressure of 100–300 mm. Hg, the highest temperature necessary in the last group of columns amounts to about 290°–320° C., i. e. it can be kept substantially below the temperature at which appreciable thermal decomposition occurs.

Separation of the phenanthrene-anthracene-carbazol mixture can take place in a main column which can be provided with one or more side columns. In these columns intermediate fractions can be separated from the mixture, whereby concentration of the desired phenanthrene + an-

thracene and carbazol fractions, can be considerably increased. A better product also results from obtaining the carbazol fraction not only in liquid form from the sump of the main column, but also in vapor form from the third or fifth tray above the sump, with subsequent condensation, whereby only the "heavy oils" consisting substantially of residual carbazol, and residual portions of the pyrene and chrysene fractions, are exposed to thermal stress in the sump of the main column.

Another way of protecting carbazol from thermal decomposition consists in that the ingredients boiling higher than carbazol—with the exception of pitch—are not separated from the carbazol before the last mentioned fractionation. In this case carbazol is separated from said higher boiling ingredients and recovered in a subsequent added column as the head product.

In addition to a fraction containing at least about 70–90% carbazol, the process of this invention yields a well rectified mixture of at least 70–80% anthracene and phenanthrene, from which the individual compounds can be separated easier than from analogous mixtures obtained in prior processes.

Another advantage is the higher yield, i. e. at least 90–98%, of the individual tar ingredients, resulting from elimination or considerable reduction of thermal decomposition.

A best mode of carrying into effect the method and the device according to the present invention are illustrated by way of example and without limitation by the following example and the appended drawing which diagrammatically illustrates a system or plant for carrying out the invention.

It is within the scope of the present invention to carry out the functions of the side columns shown by way of example, in the drawing, in normal columns. The term "column group" is used in this application to denote any of the main columns I, II, III and the side columns connected therewith, as well as modified arrangements in which main columns are substituted for the side columns shown for performing the functions of the side columns.

Example

Coal tar, which has been partially freed from water by evaporation in conventional manner and freed by distillation from other low-boiling ingredients, for example up to and including the naphthalene fraction and if desired also the diphenyl fraction, is fed with a temperature of about 250° C. through pipe **1** to charging tray **2** of rectifying column I, which contains for example a total of 20 trays, in its lower part. Heat is supplied to coil **3** of column I in such amount that the ingredients boiling lower than for example phenanthrene are substantially vaporized and thus separated from the unvaporized residue which contains practically all phenanthrene and other ingredients having equal and higher boiling points.

Reflux corresponding to the head product is supplied from the condenser, not shown, of column I through pipe **5** to column head **6** and the amount of reflux is so adjusted that the temperature in sump **4** remains practically constant at about 330° C. Absolute pressure in the sump of column I is maintained at about 250 mm. Hg. The temperature at the head of column I is maintained at about 205° C. by adjustment of the reflux. A reflux ratio of about 2.5–3.5 in column I has been found to give satisfactory results.

Under these conditions, the residue in sump **4**, contains only a small amount, such as 2–5% of ingredients boiling below phenanthrene and it contains practically all of the ingredients boiling in the range of phenanthrene and at higher temperatures. Acenaphthene fraction is discharged at the head of column I, while a diphenylenoxyde fraction and a fluorene fraction are obtained as side products as indicated in the drawing.

The residue discharged from sump **4** is heated in a heater, e. g. a tube furnace **7**, to 350° to 380° C., preferably about 360° C., and introduced to tray **8** in main rectifying column II, which contains e. g. 20–30, preferably 25, trays and is operated at tray **8** under an absolute pressure of 20 to 80, preferably about 40 to 60 mm. Hg. By regulation of the reflux supplied through pipe **11**, a constant temperature of for example about 180° to 220° C. at 10 mm. to 40 mm. Hg, preferably 210° C. at 30 mm. Hg, is maintained at the head **12** of column II so that at a corresponding reflux between head **12** and the lowest tray **13** for side discharge, the vapors discharged at the head of column are substantially freed from ingredients boiling higher than carbazol and preferably contain practically all carbazol, phenanthrene and anthracene. Said ingredients boiling higher than carbazol amount, for example, to 2–5% in the carbazol-phenanthrene-anthracene fraction discharged at the head of column II. A reflux ratio of about 2.5–3.5 in column II has been found to give satisfactory results.

In column II chrysene and pyrene can be also recovered in side columns **9** and **10**, respectively, unless it is preferred to separate these fractions at last from the carbazol as mentioned above. These side columns are operated in such manner that the sumps of these columns are supplied with about the fourfold of the amount of heat necessary for vaporizing the fractions to be recovered from them.

Pitch is discharged at **4'** from column II, as indicated in the drawing.

The vapors discharged at the head of column II, which in addition to the above mentioned small amount of ingredients boiling above carbazol, contain phenanthrene, anthracene, carbazol, and ingredients boiling within the boiling range of these compounds, are passed to condenser **14** and from there to the column group III, respectively to the charging tray **8'** of column III, part of the condensed liquid being supplied as reflux through pipe **11** to column II by pump P. Column III contains, for example, 40–80, preferably 60 trays. Heat is supplied to sump **15** in an amount sufficient for maintaining a reflux ratio of e. g. 10.

The highly enriched carbazol fraction is discharged at **4''** while the anthracene-phenanthrene fraction is obtained at the head of column III. **16** indicates the tubing for the reflux which corresponds to the head product of column III. Column III is operated under an absolute pressure of, for example, 150 mm. Hg whereby the temperature in sump **15** is maintained at about 300° C.

An intermediate fraction containing ingredients boiling between the carbazol fraction and the phenanthrene+anthracene fraction is obtained in side column **17**. The sump of this column must be intensively heated so that, based on the product to be recovered from this side column, at least tenfold, and maximally thirty-fold revaporization take place in order to separate the intermediate products, as much as possible and economical, from anthracene and phenanthrene.

In carrying out the invention, it is necessary to operate the column, in which the anthracene-phenanthrene-carbazol fraction is evaporated (column II in the drawing) and the column, in which carbazol is separated from anthracene+phenanthrene (column III in the drawing), as well as the side columns connected with said columns, under vacuum, preferably operating the penultimate column (column II in the drawing) under the highest vacuum.

However, in order to eliminate thermal decomposition as much as possible, it has been found to be of advantage to operate also additional columns, or some of them, in which ingredients boiling lower than phenanthrene are treated, likewise under partial vacuum.

It will be understood from the above that, in carrying out the invention, by suitable selection and/or adjustment of the vacuum in the individual columns, the shifting of boiling points of the individual tar ingredients can be extensively utilized for regulating and increasing concentration of the various fractions, particularly of the

phenanthrene+anthracene fraction, and of the intermediate fraction.

Thus, in carrying out the present invention tar, which has been freed from the above mentioned lowest boiling ingredients, is subjected to continuous fractionation in a novel manner with high supply of heat to fractionation and high reflux, in separating the tar by rectification from ingredients boiling up to and including diphenylene oxide, or, if desired, up to and including the fluorene fraction, in a first part of the process; heating the resulting distillation residue to 350° to 380° C. in order to vaporize (under vacuum) high-boiling ingredients including ingredients at least up to phenanthrene, anthracene and carbazol, while continuously discharging distillation residue, in a second part of the process; and subsequently separating the condensed vapors resulting from said second part, by fractionation under vacuum into at least concentrated carbazol, substantially free from phenanthrene and anthracene, and a phenanthrene+anthracene fraction which is substantially free from carbazol.

It has been found that by operating the distillation and fractionation in the above described novel manner, heating to the high temperature of 350°–380° C. for a short period of time only, is sufficient and can be applied without the danger of thermal decomposition. Moreover, owing to the novel character of the fractionating procedure, an unusually high amount of heat can be introduced into and a correspondingly high reflux applied to fractionation, likewise without the danger of thermal decomposition. The mixture of phenanthrene, anthracene and carbazole is obtained in high concentration and substantially free from ingredients boiling above carbazol and this considerably facilitates separation of carbazol from said mixture.

It will be undersood from the above that this invention is not limited to the embodiments described above and illustrated in the drawing and can be carried out with various modifications. For example, column I of the drawing can be operated in such manner that the fluorene remains substantially in the residue formed in the sump of column I. In this case fluorene will be present in the phenanthrene-anthracene-carbazol fraction obtained at the head of column II of the drawing and can be recovered by an additional column forming part of column group III. Furhermore, the number and arrangement of side columns can be different from those shown in the drawing. These and other modifications can be made without departing from the scope of the invention, as defined in the appended claims.

Reference is made to our co-pending application Ser. No. 191,869, filed October 24, 1950, and now abandoned, of which this is a continuation-in-part.

In carrying out the present invention, the vacuum at the head of column I of the drawing amounts, for example to 100 to 200 mm. Hg and this column is operated with a reflux ratio of, for example, 2.5 to 3.5. The amount of heat supplied to the material in heater **7** and in the heating coils of the side columns **9** and **10** is sufficient to bring about a reflux ratio of, for example, 2.5 to 3.5 in column II. In the sump of column II the temperature is for example 320 to 350° C. and the vacuum corresponds, for example, about 20 to 80 mm. Hg. The condensed fraction fed to tray **8'** in column III has a temperature of, for example, 270 to 310° C. The temperature at the head of column III amounts, for example, to 250 to 290° C., and enough heat is supplied to this column to maintain, for example, a reflux ratio of 5–15 therein. The vacuum corresponds, for example, to 100 to 300 mm. Hg at the head and, for example, to 200 to 400 mm. Hg in the sump of column III. The temperature of the liquid fed to side column **10** and the corresponding temperature at the head of this column is, for example, 200 to 240° C. and in the sump thereof, for example, 330 to 390° C., while the vacuum corresponds, for example, to 15 to 45 mm. Hg at the head and to 30 to 90 mm. Hg in the sump of column **10**. Column **9** is operated, for example, with a feed temperature of about 220–260° C., a temperature at the head of about 220 to 260° C. and of 400 to 450° C. in the sump and with a vacuum of 15 to 50 mm. Hg at the head and 30 to 100 mm. Hg in the sump. Both columns **10** and **9** contain, for example, 10 to 20 trays. Column **17** is operated, for example, with a feed temperature and a temperature at the head of 260 to 300° C. and of 285 to 315° C. in the sump and with a vacuum of 125 to 325 mm. Hg at the head and of 225 to 425 mm. Hg in the sump. It contains, for example, 20 to 40 trays. A pyrene fraction of, for example 60% and a chrysene fraction of, for example, 40% is obtained from columns **10** and **9**, respectively and the intermediate fraction discharged from column **17** has, for example, a boiling range of 341°–352° C.

The side columns are connected with a main column and part of the liquid flowing downward in the main column is fed at the desired level as a side stream into the side column and is there subjected to fractionation with a suitable reflux ratio in order to obtain at the sump of the side column a fraction boiling at a higher temperature than the fraction escaping at the head of the main column. The head product of the side column is reintroduced into the main column. By supplying heat to the sump of such side column, the amount of heat introduced into the system of the main column can be increased.

The pitch discharged at **4'** from column II is, for example, either normal pitch having a softening point of about 70° C. or a hard pitch having a softening point of about 90–110° C. The head product of column III contains, for example 70–80% of anthracene+phenanthrene.

The term "reflux ratio" is used in the present application to denote the ratio between the amount of reflux and distillate, respectively, into which the condensed head vapors are divided. The terms diphenylene oxide fraction, acenaphthene fraction, fluorene fraction, pyrene fraction and chrysene fraction are used to denote fractions which are obtained in the manner described and the name of which indicates the main ingredient of the respective fraction. The vacuum in the main column, and thus simultaneously in the side columns, is maintained and regulated, for example, by a vacuum pump arranged behind the condenser of a main column. In front of the vacuum pump a washing device or a low temperature trap is arranged in order to avoid loss of material.

The pyrene and chrysene fraction can be recovered not only as side product from column II, as described above and shown in the drawing, but also together with the head product of column II. In this latter case, pyrene and chrysene are recovered in the subsequent fractionation, by discharging the carbazol in a side column and the pyrene and chrysene fraction as the sump product of column III. Or a further column can be added, in which carbazol is obtained as head product and pyrene and chrysene as sump product.

The method of the present invention results in essential improvements and advantages, particularly in better separation, higher purity and concentration and also higher absolute yields of the individual products. By the separation of ingredients boiling above carbazol, fractionation of the ingredients boiling between carbazol and anthracene is facilitated. In the presence of said ingredients boiling above carbazol, the partial pressure of the lower boiling ingredients would be reduced and this would result in higher distillation temperatures and, therefore, increased danger of thermal decomposition. Furthermore, by regulation of the reflux ratio at the head of column II, the degree of separation between the carbazol fraction and higher boiling ingredients can be consider-

ably improved by the method of the invention. This separation can be further improved by introducing considerable additional heat through the sumps of columns 9 and 10. Separation of the ingredients in column I can be regulated and improved by corresponding regulation of the amount of heat supplied to sump 4. Finally, in the fractionation step in column III the amount of heat applied can be increased through the sump of columns III and 17 far above the limits hitherto known, whereby separation and concentration of the ingredients is further improved.

The term "normal column" is used herein to denote a conventional rectifying column connected with the other columns of the apparatus in series.

What is claimed is:

1. A method of continuous fractional distillation of coal tar, comprising the following steps: (*a*) separating coal tar by continuous fractional distillation into low-boiling ingredients and a distillation residue substantially free from low-boiling ingredients up to diphenylene oxide in a first fractionation; (*b*) heating said distillation residue to 350°–380° C. and evaporating therefrom under vacuum in the range of 40–80 mm. high-boiling ingredients at least up to phenanthrene, anthracene and carbazol, subjecting the resulting vapors to continuous rectification under vacuum in the range of 20–40 mm., and continuously discharging a vapor fraction containing at least phenanthrene, anthracene and carbazol, and continuously discharging the distillation residue in a second fractionation; condensing said vapor fraction and subjecting it to continuous rectification with high supply of heat for 2–4 fold evaporation of the products and high reflux equal to 1–3 times the products to be recovered under vacuum in the range of 100–200 mm. in order to separate it at least into a residue of concentrated carbazol substantially free from phenanthrene and anthracene and a fraction of anthracene+phenanthrene substantially free from carbazol in a third fractionation.

2. A method as claimed in claim 1, in which, in the first fractionation, the low-boiling ingredients include also fluorene and, in the second fractionation, the high-boiling ingredients include also pyrene and chrysene and the latter are separated from the vaporized anthracene-phenanthrene-carbazol mixture by taking off a side stream with a feed temperature of about 200°–240° C. in order to separate pyrene and a second side stream with a feed temperature of about 220°–260° in order to separate chrysene in the second fractionation zone.

3. A method as claimed in claim 1, in which at least part of the low-boiling ingredients is distilled off under partial vacuum, in the first fractionation.

4. A method as claimed in claim 1, in which the residue from the first fractionation is heated to about 360° C. prior to the introduction of said residue into the second fractionation.

5. A method as claimed in claim 1, in which coal tar freed from low boiling ingredients up to the diphenyl fraction is used as starting material.

6. A method of continuous fractional distillation of coal tar, comprising the following steps: (*a*) separating coal tar by continuous fractional distillation into low-boiling ingredients up to diphenylene oxide and fluorene, and a distillation residue substantially freed from these low-boiling ingredients, at least part of this fractional distillation being carried out under partial vacuum in a first fractionation; heating said distillation residue after its discharge from said fractionation to about 360° C. and introducing the heated residue into a second fractionation, in which it is subjected to rectification under an absolute pressure of about 20–80 mm. Hg in order to distill off at least substantially all phenanthrene, anthracene and carbazol from said residue, subjecting the resulting vapors to continuous rectification under said absolute pressure and continuously discharging the pitch formed as distillation residue in this fractionation; condensing the rectified vapors containing at least phenanthrene, anthracene and carbazol and subjecting the condensate to continuous rectification in a third fractionation under an absolute pressure of 100–300 mm. Hg, in order to separate it at least into a residue of concentrated carbazol substantially free from phenanthrene and anthracence and a fraction of anthracene+phenanthrene, which is substantially free from carbazol.

7. A method as claimed in claim 6, in which a reflux ratio of 2–3 is used in the second fractionation and a reflux ratio of 8–15 is used in the third fractionation.

8. A method as claimed in claim 6, in which, in the third fractionation, the condensate of the rectified vapors is separated into a residue of concentrated carbazol substantially free from phenanthrene and anthracene, a fraction of anthracene+phenanthrene substantially free from carbazol, as the lowest boiling fraction of this rectification and an intermediate fraction boiling between the carbazol fraction and the anthracene+phenanthrene fraction and having a boiling range of about 341°–352° C.

9. A method as claimed in claim 6, in which, in addition to phenanthrene, anthracene and carbazol, the pyrene fraction and chrysene fraction are also vaporized in the second fractionation and the fraction containing phenanthrene, anthracene and carbazol, is discharged as head product, while the pyrene fraction, as well as the chrysene fraction are branched off as side streams which are subjected to further rectification in the second fractionation zone.

10. A method as claimed in claim 6 in which the fraction introduced into the third fractionation is separated into a residue of concentrated carbazol substantially free from phenanthrene and anthracene, a fraction of anthracene + phenanthrene substantially free from carbazol, as the lowest boiling fraction of this rectification and an intermediate fraction boiling between the carbazol fraction and having a boiling range of about 341°–352° C. and the anthracene + phenanthrene fraction, the fraction of anthracene + phenanthrene being discharged as head product and the intermediate fraction is branched off as side stream and subjected to further rectification in the third fractionation zone.

11. A method of continuous fractional distillation of coal tar, comprising (*a*) separation of coal tar into low boiling ingredients up to diphenylene oxide and into a first residue substantially free from said low-boiling ingredients in a first fractionation; (*b*) continuously discharging said residue from said first fractionation, indirectly heating it to 350°–380° and subsequently introducing it into a second fractionation under vacuum in the range of 20–40 mm., in which it is continuously separated into a vaporized head fraction containing phenanthrene, anthracene and carbazol, a first side stream consisting of a pyrene fraction and a second side stream consisting of a chrysene fraction, and a pitch residue containing the non-volatile ingredients, all of said fractions and residue being continuously discharged from said second fractionation zone; (*c*) continuously introducing the phenanthrene-anthracene-carbazol fraction into a third fractionation under vacuum in the range of 100–200 mm., in which it is continuously separated into a vaporized head fraction containing phenanthrene + anthracene and being substantially free from carbazol, a distillation residue consisting of concentrated carbazol substantially free from anthracene + phenanthrene and a side-stream consisting of an intermediate fraction, boiling between the phenanthrene+anthracene fraction and the carbazol fraction and having a boiling range of about 341°–352° C.

12. An apparatus for continuous fractional distillation of coal tar, comprising at least one fractionating column for the removal of low-boiling ingredients, said column being adapted to be operated under partial vacuum; a fractionating column containing 20 to 30 trays, and be-

ing provided with two side columns; and a further fractionating column containing 40 to 80 trays and being provided with at least one side column, said last mentioned two columns and their side columns being adapted to be operated under vacuum, the removal of low-boiling ingredients and said first and second fractionating columns of the apparatus being connected in series; and a heater for heating the residue discharged from the fractionating zone for the removal of low-boiling ingredients.

13. An apparatus as claimed in claim 12, in which normal columns are used instead of the side columns.

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