

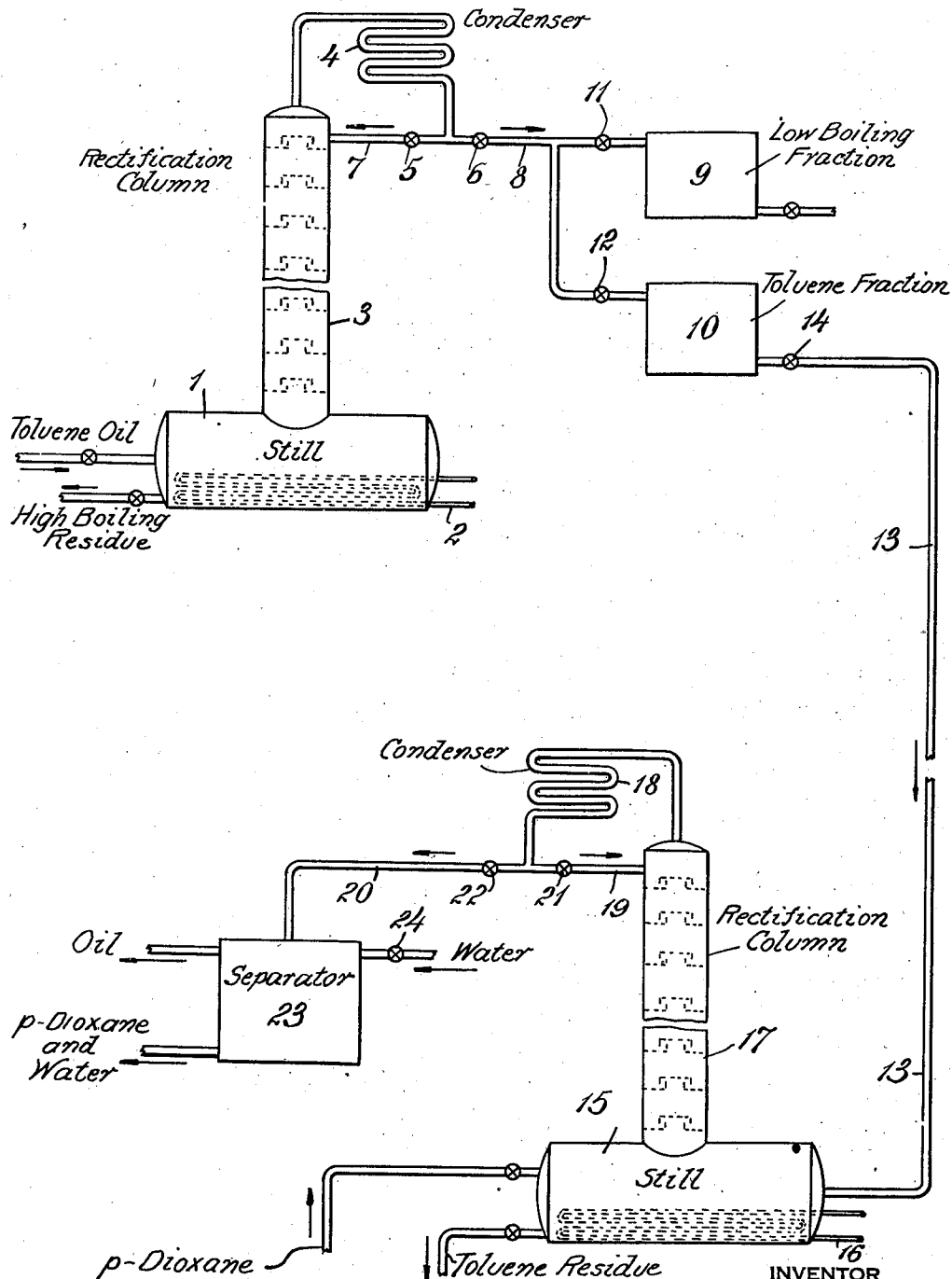
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PROCESS FOR THE RECOVERY OF TOLUENE

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PROCESS FOR THE RECOVERY OF TOLUENE

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This invention relates to a process for recovering toluene from mixtures containing it and other organic liquids.

Numerous hydrocarbon oils are known which contain toluene in varying proportions. For example, catalytic treatment of a suitable petroleum fraction in the presence of hydrogen, gives an oil consisting chiefly of hydrocarbons of both aromatic and non-aromatic character, and containing about 20% toluene. Gasoline fractions obtained by the distillation of certain types of petroleum frequently contain substantial proportions of toluene, although mainly consisting of other hydrocarbons. Oils of petroleum origin having a considerable content of aromatics, including toluene, may be treated by well known selective-solvent processes to produce fractions rich in aromatics; for example, extraction of suitable fractions of such petroleum oils with sulfur dioxide may yield fractions of high toluene content. In such cases toluene is accompanied by non-aromatic oils which may be largely paraffinic, naphthenic or olefinic in character. A considerable portion of these oils cannot be completely separated from the toluene by direct fractional distillation because of the closeness of their boiling points to that of toluene or because they form constant boiling mixtures with toluene. Furthermore, while ordinarily toluene is readily separable by direct fractional distillation from light oils produced by the gasification of coal, in some cases the toluene is accompanied by difficultly separable non-aromatic oils of the same general character as described, owing to carbonization conditions, type of coal used or other special circumstances. Also synthetic hydrocarbon gas mixtures produced by various catalytic processes may contain toluene which, when recovered, is accompanied by similar difficultly separable constituents.

By fractional distillation of these oils containing toluene, fractions relatively high in toluene content may be obtained. These toluene fractions, however, will still contain large amounts of the other constituents of the oil having boiling points in the neighborhood of the boiling point of toluene or forming mixtures of constant boiling points in the range of temperatures at which toluene distills from the oil. For example, by distillation of the above described types of oils containing toluene under the most efficient conditions practicable for rectifying the vapors, a fraction containing about 82% to 85% toluene appears to represent a product of maximum toluene concentration obtainable by direct fractional dis-

tillation. Accordingly, recovery of toluene of a relatively high purity from these sources presents a difficult problem of great industrial importance.

For many purposes to which toluene is put, it is desirable to use as pure a material as may be economically available. For example, toluene is largely used for the production of TNT, for which purpose a so-called "nitration grade" of toluene is now preferred. While toluene products containing substantial proportions of certain hydrocarbon oils other than toluene can be nitrated, the mono-nitro compound made from them must be purified prior to complete nitration. This materially increases the cost and complexity of the process for making TNT. Furthermore, even though toluene containing substantial quantities of certain other materials is sometimes used for nitration, this is only because the difficulties of preparing a pure toluene have outweighed the disadvantages of using the impure toluene for the production of explosives. Direct fractional distillation, because of the difficulties pointed out above, will not effect a recovery of pure toluene from oils such as enumerated and in many cases will not give fractions of suitably high toluene content or free from materials which even in small concentrations adversely affect the nitration of the toluene or the nitrated product.

The separation of the toluene from materials distilling from the toluene oil fraction at temperatures substantially higher or lower than the toluene does not present any great technical difficulties. The difficulty in recovering pure toluene from an oil fraction containing it, such as those referred to above, is presented by the problem of separating the toluene from the like-boiling, non-aromatic hydrocarbons; i. e., from those hydrocarbons which by direct fractional distillation processes as commonly operated for the fractional distillation of oils, distill from the toluene fraction within the same temperature range as the toluene distills therefrom.

It is an object of my invention to provide a process whereby toluene of any desired degree of purity may be recovered from oils containing it and other hydrocarbons which distill out over the same temperature range as the toluene.

I have now discovered a relatively pure toluene, e. g. toluene accompanied by no more than 5% of the hydrocarbon impurities of similar boiling range to that of the toluene, can be recovered from many oils containing toluene and other hydrocarbons by an azeotropic distillation of the oil under the conditions hereinafter described.

In using my invention for the treatment of an

oil such as has been described above, containing toluene and other hydrocarbons, particularly when the toluene concentration of the oil is low or the oil is one containing materials of wide boiling range, I prefer first to fractionally distill the oil to recover therefrom an enriched toluene fraction which contains, in addition to toluene, other hydrocarbons which distill at the same temperatures as the toluene. Although toluene fractions having an end boiling point substantially above the boiling point of toluene (e. g. a boiling point up to 118° C.) may be azeotropically distilled in the manner hereinafter described, I prefer the toluene fraction recovered in the preliminary distillation step be one having a maximum boiling point substantially corresponding to the boiling point of pure toluene; i. e., 111° C. Further, for the reasons which will be more specifically pointed out below, I prefer that the toluene fraction recovered by the preliminary distillation of the crude toluene oil be so cut as to exclude therefrom the forerunnings which do not contain substantial proportions of toluene, for example, to exclude any materials distilling below 100° C.

A toluene fraction such as may be obtained by this preliminary distillation, which may contain paraffins, naphthenes, or olefins, is subjected to a second distillation in the presence of an azeotropic agent. An important factor in this azeotropic distillation of the toluene fractions is the provision of an azeotropic agent which sharply separates the toluene and the like-boiling, non-aromatic hydrocarbons so that a high yield of toluene of a desired purity may be obtained in distilling the toluene fraction. It is highly desirable, from an economic standpoint, that the azeotropic agent, in addition to its ability to separate the toluene and like-boiling hydrocarbons sharply, also should have a high capacity for carrying over as distillate the non-aromatic hydrocarbons; i. e., an agent which forms with these hydrocarbons azeotropes having a high ratio of hydrocarbons to azeotropic agent. According, it is an object of this invention to provide a process for azeotropically distilling a toluene oil in the presence of an azeotropic agent which is particularly effective for separating the toluene from like-boiling, non-aromatic hydrocarbons contained in the toluene oil.

I have discovered that p-dioxane (para-dioxane) is particularly effective when used for the azeotropic distillation of toluene fractions to separate the toluene from the like-boiling, non-aromatic hydrocarbons. Accordingly, my invention broadly comprises fractionally distilling a toluene oil containing like-boiling, non-aromatic hydrocarbons in the presence of p-dioxane.

I have found that commercial dioxane now available, consisting almost entirely of p-dioxane, is a suitable azeotropic agent. While this material is sold with a wide boiling range specification, e. g. 95° to 103° C., actually its boiling range is usually much less, e. g. within 4° C., the major portion distilling over within 1° C. It appears p-dioxane forms a low boiling azeotrope with toluene. I have discovered, however, p-dioxane forms with the non-aromatic hydrocarbons low boiling azeotropes which may be separated by fractional distillation from the toluene or any azeotropes which may be formed by the toluene and p-dioxane. There is a relatively wide spread between the boiling points of the azeotropes of the like-boiling, non-aromatic hydrocarbons and of toluene or any azeotrope of toluene and dioxane which facilitates the separation of these materials by

fractional distillation. In addition, the ratio of p-dioxane to hydrocarbons in the distillates is unusually favorable. The ratio of p-dioxane to non-toluene hydrocarbons varies from about 55 to 45 at the start of a distillation of toluene fraction with p-dioxane to about 65 to 35 when the non-toluene hydrocarbons have been practically exhausted from the material being distilled. These ratios are reasonably economical, entailing handling of not too great a volume of azeotropic distillates. The ratio of p-dioxane to toluene vaporized in the distillation is far higher, i. e. close to 93 to 7. Such a mixture is highly effective as a scrubbing medium for the toluene vapors. Yet such a mixture, which would be more uneconomical to distill, does not go over as distillate until the objective of the process of this invention is accomplished; i. e., until the non-toluene hydrocarbons have been distilled over and separated from the toluene which remains in the residue at this point in the distillation. These characteristics of the p-dioxane contribute materially to its effectiveness as an azeotropic agent in the distillation of toluene oil fractions.

In its more specific aspects my invention comprises azeotropically distilling a toluene fraction containing like-boiling, non-aromatic hydrocarbons with rectification of the evolved vapors in the presence of p-dioxane while maintaining at a point in the rectification of the vapors a temperature not above substantially 102° C. under substantially anhydrous conditions and not above substantially 85° C. in the presence of water until the unvaporized residue contains at least 95 parts by weight toluene for every 5 parts by weight of said like-boiling hydrocarbons. These temperatures are hereinafter referred to as a "control temperature."

Regulation of the temperature in the rectification of the vapors to meet the conditions set forth above is accomplished by maintaining an adequate quantity of the azeotropic agent present in the still and/or rectification column during the distillation of the toluene fraction to selectively carry over through the rectification treatment the vapors of the hydrocarbons to be removed from the toluene. Some of the toluene may also be carried over, but so long as the control temperature is not exceeded, the undistilled residue will be enriched in toluene and by continuing the distillation, separation of the toluene from the hydrocarbons of similar boiling range will be accomplished.

After the distillation has been carried to the point at which the residue containing toluene has the desired purity with respect to hydrocarbons of similar boiling range to toluene, the distillation may be stopped and the residue withdrawn from the still. This residue ordinarily will contain toluene and other hydrocarbons in the proportion of 95 or more parts toluene to 5 or less parts of total hydrocarbons other than toluene. It may be purified further, as desired, to remove any azeotropic agent it contains and to remove any other impurities present. When the distillation has been carried to the point at which the hydrocarbon portion of the residue has a toluene content of 99% or more, the residue, after removal of residual azeotropic agent (if any), and if necessary after a conventional refining treatment such as a sulfuric acid treatment followed by redistillation, is suitable for marketing as a nitration grade toluene of particularly high purity.

Instead of withdrawing the toluene residue

from the still, the distillation may be continued and the toluene distilled over and separately collected from the distillate containing the hydrocarbons from which the toluene residue previously has been separated by azeotropic distillation. If p-dioxane is present during the distillation and collection of the toluene, an azeotrope of p-dioxane and toluene may be distilled out. The toluene may be separated from the distillate in any suitable manner, for example by extraction with a liquid which will form separate layers, one containing the toluene and the other containing the dioxane. Water is a suitable liquid for effecting this separation. In the absence of the dioxane, in distilling out the toluene the temperature in the rectification column may rise to the boiling point of toluene under the conditions prevailing as to pressure, etc.

The toluene fraction treated in accordance with my invention preferably will contain little, if any, hydrocarbons distilling from the hydrocarbon-toluene fraction at temperatures materially above those at which toluene distills therefrom. On the other hand, high boiling materials may be left with the toluene residue at the conclusion of the azeotropic distillation of the toluene fraction under the conditions set forth above to separate the toluene from the hydrocarbons of similar boiling range. Once this separation has been effected, the toluene may be separated from the high boiling hydrocarbons by fractional distillation in the absence of an azeotropic agent. Whether or not high boiling constituents should be left in the toluene fraction to be azeotropically distilled or whether, if left in the toluene fraction, they will remain in the residue after azeotropic distillation, depends upon a number of factors, among which their boiling range and chemical characteristics are important. If the constituents form azeotropes with the dioxane which have boiling points close to the above control temperatures of 102° C. and 85° C. for anhydrous conditions and in the presence of water, respectively, it is preferable to separate them by a direct fractional distillation before azeotropically distilling the toluene fraction. If they do not form azeotropes having boiling points close to the foregoing temperatures or if their amount is small, this procedure is not so important.

It is preferred that the toluene fraction subjected to azeotropic distillation in accordance with my invention be a fraction boiling in the range of 100° C. to 111° C. Such a fraction may be azeotropically distilled by my process and pure toluene obtained with a relatively small quantity of azeotropic agent present during the distillation. Pure toluene may be obtained by distilling with p-dioxane a toluene fraction boiling, for example, from 95° C. to 118° C. but the quantity of the dioxane present in the distillation of the toluene fraction of wider boiling range must be substantially increased as compared with the quantity which suffices for distilling the fraction of the narrower boiling range.

My invention will be more particularly illustrated and described in conjunction with the following examples.

The accompanying drawing diagrammatically illustrates an apparatus suitable for carrying out the processes of these examples.

The apparatus of the drawing comprises a still 1 provided with a heater 2 and connected with a rectification column 3 and a condenser 4 for the vapors leaving the top of the column. By means of valves 5 and 6, condensate flowing from

condenser 4 is divided in controlled proportions. One part of the condensate is returned through pipe 7 to the top of column 3 and refluxed in contact with the vapors rising in the column. The other portion of the condensate is withdrawn through pipe 8. Two receivers 9 and 10 are connected to pipe 8 through valve-controlled branch pipes 11 and 12 so that the condensate drawn off through pipe 8 may be divided and distributed as described below to the two receivers.

Receiver 10 is connected by a pipe 13 controlled by valve 14 with a second still 15. Still 15, like still 1, is provided with a heater 16, a rectification column 17, a condenser 18 and pipes 19 and 20 controlled by valves 21 and 22 for return of determined proportions of condensate from condenser 18 to the top of column 17 and withdrawal of another portion of the condensate through pipe 20. Pipe 20 leads to a separator 23 into which water may be introduced from a pipe 24.

Example 1.—In carrying out one embodiment of my invention in the apparatus described above, a liquid hydrocarbon mixture containing about 20% toluene by volume, the remainder substantially consisting of other aromatic hydrocarbons and aliphatic and naphthenic hydrocarbons with only traces of olefines, was introduced into still 1. This crude toluene material was produced by catalytic treatment of a petroleum distillate in the presence of hydrogen. It had a specific gravity of 0.757 at 15.5° C. and distilled over a range of from 53° C. to 156° C.

The charge of this hydrocarbon mixture introduced into still 1 was boiled in the still and the evolved vapors were countercurrently contacted in column 3 with reflux from condenser 4, in which the vapors leaving the top of the column were substantially entirely condensed. Most of the condensate from condenser 4 was returned through valve 5 and pipe 7 to the top of the column to furnish the reflux for the column, the remaining small portion of the condensate being continuously withdrawn through valve 6 and pipe 8 and passed into collecting vessel 9. The distillation was conducted under substantially atmospheric pressure; i. e., the pressure in condenser 4 and at the top of column 3 was substantially atmospheric and the pressure in still 1 was only enough higher to force the vapor through the rectification column to the condenser.

When the vapor temperature in the top of column 3 reaches 109.5° C., the condensate passing through pipe 8 is diverted to vessel 10. The cut taken in vessel 10 includes the distillate coming over up to and at a temperature of 110.5° C. at the top of the column. With efficient rectification of the vapors in column 3 during the fractional distillation of the crude toluene oil, the cut collected in vessel 10 contains about 76% by volume of toluene, as determined by the specific dispersion method for analyzing hydrocarbon oils described in *Industrial & Engineering Chemistry, Analytical edition*, vol. 11, page 614, November 15, 1939.

The toluene fraction collected in vessel 10 is subjected to azeotropic distillation, which represents the second stage of this example. For this purpose the toluene fraction containing 76% toluene was introduced into still 15 together with p-dioxane in the proportions of 150 volumes of p-dioxane for every 100 volumes of the toluene fraction. The p-dioxane used was a commercial product having a boiling range of 97.5–103.2° C. and a freezing point of 10.1° C. Ninety per cent of this material distilled between 100° and 102°

C. The quantity of p-dioxane used in this example is a liberal excess over that required for complete removal of non-toluene hydrocarbons from the toluene fraction. In general at least 1.5 volume parts of p-dioxane are required for the removal of one part of non-toluene hydrocarbons present in the still charge. A larger ratio of p-dioxane to non-toluene hydrocarbons should be used, the ratio depending on the effectiveness of the fractionating column, and its mechanical construction, which determine the quantity of p-dioxane required to provide vapor-liquid equilibria throughout the column under actual operating conditions. The mixture of p-dioxane and toluene fraction was distilled with rectification of the vapors in column 17 and condensation of the vapors leaving the top of the column in condenser 18. Most of the condensate was returned through pipe 19 to the top of column 17 while the remainder was withdrawn through pipe 20 to separator 23.

With adequate p-dioxane present to effect the desired separation, the major part of the non-toluene hydrocarbons appears in the early distillate fractions accompanied by very little toluene; in this stage the vapor temperature at the top of the column is below 100° C. The toluene content of the distillate then gradually increases and the vapor temperature rises and finally, when nearly pure toluene distills over with the p-dioxane, the vapor temperature stands at approximately 102° C. Azeotropes formed with the p-dioxane by the hydrocarbons other than toluene present in the toluene fraction introduced into still 15 have boiling points sufficiently below that at which the toluene distills for them to be preferentially vaporized and by rectification in column 17 to be largely separated from the toluene and any toluene-p-dioxane azeotrope which is vaporized in still 15 and enters column 17 so long as there is sufficient p-dioxane present in the vapor and liquid phases in the rectification column. As pointed out above, the requisite quantity of p-dioxane to be supplied is that which will maintain the temperature at a point in the rectification column, preferably at the top of the column, not above substantially 102° C. under the substantially anhydrous conditions of this example. p-Dioxane is vaporized from the still, enters the rectification column as vapor and in part is returned to the column as liquid in the condensate from condenser 18. If insufficient p-dioxane is initially introduced in the charge to the still, additional p-dioxane, sufficient to maintain the requisite temperature in the rectification column, may be supplied as the distillation progresses. This p-dioxane may be introduced either into the still or into the rectification column itself. The toluene is in large part returned down the rectification column and retained in the still, while the azeotropes of the p-dioxane with the other hydrocarbons are distilled out and are collected in separator 23. The loss of toluene from the still to the condensate drawn off through pipe 20 will depend upon the efficiency with which the vapors are rectified. Efficient rectification is employed in order to keep down this loss of toluene.

In carrying out the process of this example, as the distillation continued the temperature of the vapors at the top of column 17 rose from about 96° C. to 101.6° C. The toluene content of the oil obtained from the condensate withdrawn through pipe 20 by washing the condensate with water to free it of p-dioxane increased from 3%

to 100%. At this point the distillation was discontinued. The residue left in still 15 may be washed with water to remove p-dioxane. The oil layer which separates from a water-p-dioxane layer contains 100% toluene. The quantity of 100% toluene isolated in this manner represented 92% of the toluene originally present in the still charge.

Almost all of the remaining 8% may be recovered in subsequent operations by collecting separately the last distillate fractions, relatively rich in toluene, and re-using this material directly in a subsequent azeotropic fractionation of a toluene fraction, the p-dioxane serving as a source of azeotropic component in the fractionation.

By agitating the distillate collected in separator 23 with water and allowing the liquid to remain quiescent for a short time, it will separate into two layers. The upper layer is an oil containing the non-toluene constituents of the toluene fraction originally supplied to still 15 and the portion of the toluene carried over in the distillation. This oil may be treated or used as desired. The aqueous p-dioxane layer separated in treating the distillate with water may be treated in any of the well known manners to recover p-dioxane therefrom for use in distilling a subsequent batch of toluene fraction.

Example II.—The procedure of Example I may be modified to use p-dioxane in the azeotropic distillation of a toluene fraction obtained by distilling in still 1 and column 3 an oil containing about 20% toluene, 20% of other aromatic hydrocarbons and the remainder substantially consisting of aliphatic and naphthenic hydrocarbons and traces of olefines. This crude toluene material was produced by catalytic treatment of a petroleum distillate in the presence of hydrogen. It had a specific gravity of 0.760 at 15.5 C. and distilled over a range of from 56° C. to 161° C. In distilling this crude toluene material a cut boiling over the range of 109.5° C. to 110.8° C. was taken off in vessel 10 of the apparatus of the drawing. This cut or toluene fraction may contain 76% by volume of toluene. A mixture of 200 volumes of p-dioxane for every 100 volumes of this toluene fraction is distilled in still 15 and rectification column 17 as described in Example I, above. A temperature not above 102° C. is maintained at a point in the rectification of the vapors from the still. As the distillation proceeds the temperature at the top of the rectification column rises to 102° C. from an initial temperature of about 98° C. and the hydrocarbon oil in the distillate coming over from the top of the column contains about 98% toluene. After washing the residue which remains in the still with water, a hydrocarbon oil containing about 98% toluene is obtained. The distillate may be extracted with water to separately recover the oil and p-dioxane it contains.

Numerous changes and modifications may be made in the above described processes without departing from my invention. While in the first distillation step of the crude toluene oil it is preferred to take off a toluene fraction having an end boiling point of substantially 111° C. and fractions with a higher end boiling point, such as 118° C., may be successfully distilled azeotropically to obtain pure toluene, even a larger leeway is permitted in the temperature at which the toluene fraction starts to be taken off; i. e., in the initial boiling point of the toluene fraction. Nevertheless, it is preferred the toluene fraction subjected to azeotropic distillation be one boiling in the

range of 100° C. to 111° C. Such a fraction may be distilled in the azeotropic distillation step of my process and pure toluene obtained with a relatively small quantity of azeotropic agent present during the distillation. Pure toluene may be obtained by distilling with the azeotropic agent a toluene fraction boiling, for example, from 95° C. to 118° C., but the quantity of azeotropic agent present in the distillation of the toluene fraction of wider boiling range must be substantially increased as compared with the quantity which suffices for distilling the fraction of the narrower boiling range.

While I have described my process in conjunction with examples in which the two distillation steps are batch procedures, either or both of these distillations advantageously may be carried out continuously by well known continuous distillation procedures suitable for the fractional distillation of mixtures of two or more liquids.

The minimum ratio of azeotropic agent to the toluene fraction which is suitable for carrying out my invention will vary with the amount and nature of the hydrocarbon impurities in the toluene fraction, the purity desired in the toluene residue from the distillation, the proportion of toluene in the original toluene fraction which is to be recovered in the residue from the distillation, and the procedure used for the azeotropic distillation. The ratios of the above examples are suitable for a batch process carried out according to the procedures of the examples. Irrespective of the particular batch or continuous procedure used, the quantity of p-dioxane used in the distillation of hydrocarbons from a given quantity of toluene fraction should be in excess of that which will form azeotropic mixtures with the non-toluene hydrocarbons which are to be vaporized and taken over into the distillate. This quantity of azeotropic agent includes fresh agent introduced into the material being distilled and also any of the azeotropic agent which may be separated from the distillate and returned continuously or periodically to the still or rectification column while the distillation of the toluene fraction is progressing. Temperature readings are taken of the vapor at the top of the rectification column and, by supplying additional p-dioxane when required to prevent this temperature from rising above the above described control temperatures, an adequate amount of p-dioxane will be present during the separation of the non-toluene hydrocarbons from the toluene fraction. It is not necessary that this point of control temperature be at the top of the column, although this is a satisfactory point for determining this temperature in the equipment used for fractionating the vapors and condensing the fractionated vapors in the above examples for effective use of the rectification column. One skilled in the distillation art will recognize suitable points for maintaining this control temperature in any other specific apparatus according to well known distillation principles.

Water appears to form complex azeotropes with p-dioxane and toluene and like-boiling, non-aromatic hydrocarbons. The spread between the boiling points of the complex azeotropes of water-dioxane-toluene and water-dioxane like-boiling, non-aromatic hydrocarbons is smaller than the spread between the simple azeotropes of the dioxane with like-boiling, non-aromatic hydrocarbons and toluene or its azeotrope with p-dioxane. Accordingly, the presence of water in azeotropically distilling a toluene frac-

tion by the process of this invention reduces the effectiveness with which the toluene is separated from the like-boiling, non-aromatic hydrocarbons and reduces the yield of toluene recovered. The complex azeotropes containing water have lower boiling points than the simple azeotropes not containing water. Thus, in distilling a mixture containing 100 volumes of the 76% toluene fraction and 30 volumes of the p-dioxane of Example I, and also containing 10 volumes of water, the non-toluene hydrocarbons started distilling over below 83° C. and when the temperature had risen to 84.5° C., the hydrocarbons in the distillate were 99% toluene. Although pure toluene may be recovered with sufficient water present in the distillation to form complex azeotropes with the hydrocarbons taken off as distillate, in order to obtain high yields of toluene without having to fractionate the vapors being distilled to an unduly high degree, water is preferably excluded from the materials in the azeotropic distillation of the toluene fraction with p-dioxane.

It is, of course, obvious that preliminary distillation of a crude toluene oil to obtain a toluene fraction suitable for recovery of toluene therefrom by the azeotropic distillation need not be carried out in immediate conjunction with the azeotropic distillation. The toluene fraction may be produced in one plant, transported to and submitted to azeotropic distillation in another plant. Nor is my invention limited to any particular procedure for the production of the toluene fraction. My invention contemplates distilling with p-dioxane any oil containing toluene together with other hydrocarbons which, when the oil is distilled, vaporize therefrom in the same temperature range as the toluene and, therefore, are not separable from the toluene by direct fractional distillation. As used in this specification and the appended claims, the term "toluene fraction" refers to all such toluene-containing oils, whether produced by fractional distillation of toluene-containing materials or by any other means.

In this specification I have described the azeotropic distillation of toluene fractions as carried out under substantially atmospheric pressure. It is, of course, possible to azeotropically distill the toluene fraction under pressures above or below atmospheric. In that case the particular temperatures used as a control for the amount of azeotropic agent present in the distillation will correspond to the change in the boiling points of the p-dioxane and hydrocarbon mixtures with change in pressure. The temperatures as given in this specification and in the appended claims are corrected temperatures for one atmosphere pressure (760 mm. of Hg).

This application is a continuation-in-part of my copending application Serial No. 343,499, filed July 1, 1940, and the process disclosed herein of fractionally distilling an oil mixture containing toluene, collecting a fraction of said oil containing not more than 83-85% toluene and, specifically, collecting a toluene fraction distilling over a range of distillation temperatures of more than 10 centigrade degrees extending from below to at least as high as the boiling point of toluene, and azeotropically distilling the toluene fraction in the presence of a material forming a low boiling azeotrope with toluene, is claimed in said copending application Serial No. 343,499.

In my copending application Serial No. 347,993 I disclose and specifically claim processes for dis-

tilling a toluene fraction in the presence both of para-dioxane and of water.

I claim:

1. The process for the recovery of toluene from a toluene fraction containing the same and containing like-boiling, non-aromatic hydrocarbons which comprises distilling said toluene fraction and rectifying the distilled vapors in the presence of p-dioxane in an amount which selectively carries over as distillate with p-dioxane said like-boiling, non-aromatic hydrocarbons and leaves a hydrocarbon residue of the distillation enriched in toluene.

2. The process for the recovery of toluene from a toluene fraction containing the same and containing like-boiling, non-aromatic hydrocarbons which comprises distilling said toluene fraction and rectifying the distilled vapors in the presence of substantially water-free p-dioxane in an amount which selectively carries over as distillate with p-dioxane said like-boiling, non-aromatic hydrocarbons and leaves a hydrocarbon residue of the distillation enriched in toluene.

3. The process for the recovery of toluene which comprises distilling an oil fraction containing toluene and like-boiling non-aromatic hydrocarbons which boils within the range 95° C. to 118° C. and rectifying the distilled vapors in the presence of a quantity of p-dioxane which selectively carries over as distillate with p-dioxane said like-boiling, non-aromatic hydrocarbons and leaves a hydrocarbon residue of the distillation enriched in toluene.

4. The process for the treatment of a toluene fraction to separate the toluene from other hydrocarbons contained therein which distill from the toluene fraction in the same temperature range as the toluene distills therefrom, which comprises distilling said toluene fraction and rectifying the vapors evolved therefrom in the presence of p-dioxane in amount such that at a point in the rectification of the vapors a temperature not above substantially 102° C. is maintained until the unvaporized residue of the distillation contains at least 95 parts by weight of toluene to every 5 parts by weight of other hydrocarbons which distill from a mixture consisting of the toluene and hydrocarbons in the same temperature range as the toluene, and thereby vaporizing and removing from said toluene fraction, as

distillate with p-dioxane hydrocarbons present therein which distill therefrom, in the absence of said p-dioxane, in the same temperature range as toluene contained therein.

5. The process for the treatment of a toluene fraction having an end boiling point not above 118° C. and containing paraffinic hydrocarbons, and which may also contain naphthenic and olefinic hydrocarbons, the aforesaid hydrocarbons distilling from the toluene fraction in the same temperature range as the toluene boils therefrom, which comprises distilling said toluene fraction and rectifying the vapors evolved therefrom in the presence of p-dioxane in amount such that at a point in the rectification of the vapors a temperature not above substantially 102° C. is maintained until the unvaporized residue of the distillation contains at least 95 parts by weight of toluene to every 5 parts by weight of other hydrocarbons, and thereby vaporizing and removing from said toluene fraction as distillate with p-dioxane hydrocarbons present which distill therefrom, in the absence of said p-dioxane, in the same temperature range as toluene contained therein.

6. The process for the recovery of toluene from a crude toluene oil produced by catalysis of a petroleum fraction in the presence of hydrogen which comprises recovering from said crude oil a toluene fraction having an end boiling point of 111° C. containing paraffinic and naphthenic hydrocarbons, and which may also contain olefinic hydrocarbons, which hydrocarbons distill from said toluene fraction in the same temperature range as the toluene distills therefrom, distilling said toluene fraction and rectifying the vapors evolved therefrom in the presence of p-dioxane in amount such that a point in the rectification of the vapors a temperature not above substantially 102° C. is maintained until the unvaporized residue of the distillation contains toluene substantially completely separated from the paraffinic and naphthene and from any olefinic hydrocarbons which were present in said toluene fraction, said last mentioned hydrocarbons being carried over as a distillate with p-dioxane and thus separated from said residue containing toluene.

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