Jan. 17, 1967 H. WIRTH ET AL 3,299,158

PRODUCTION OF PURE AROMATIC HYDROCARBONS

Filed Sept. 8, 1964 4 Sheets-Sheet 1

Fig. 1

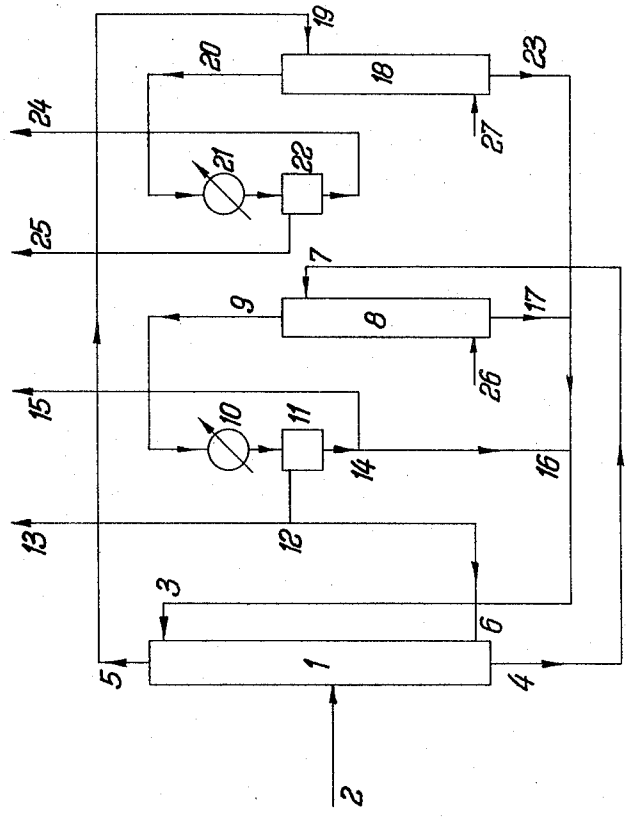

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Fig. 2

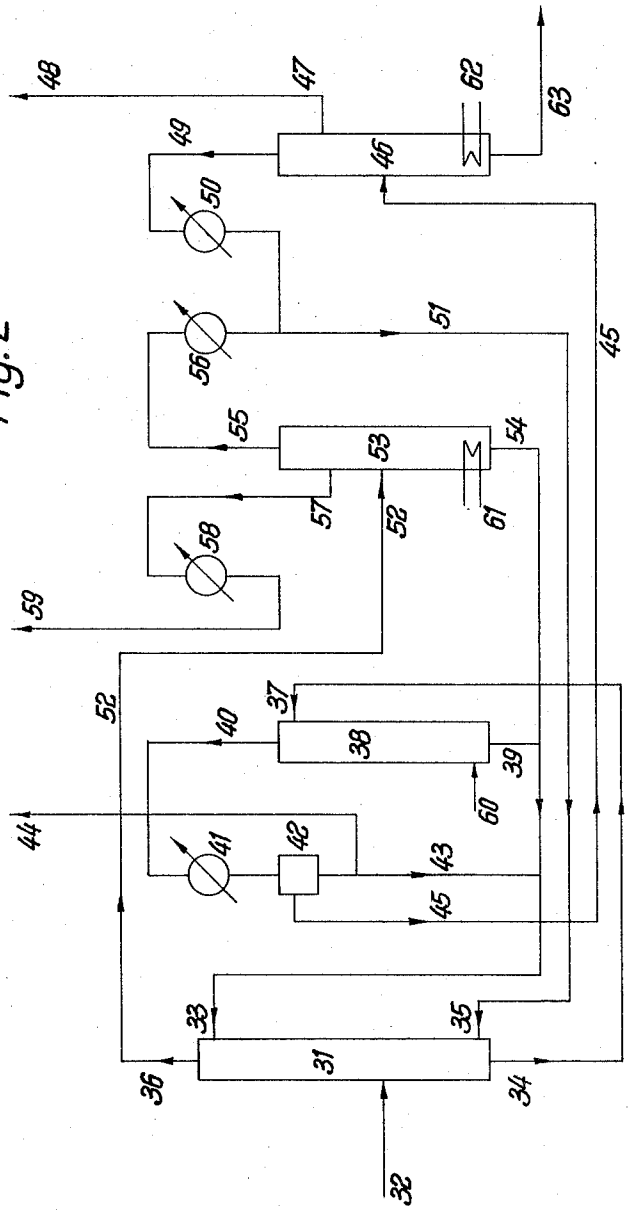

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Fig. 3

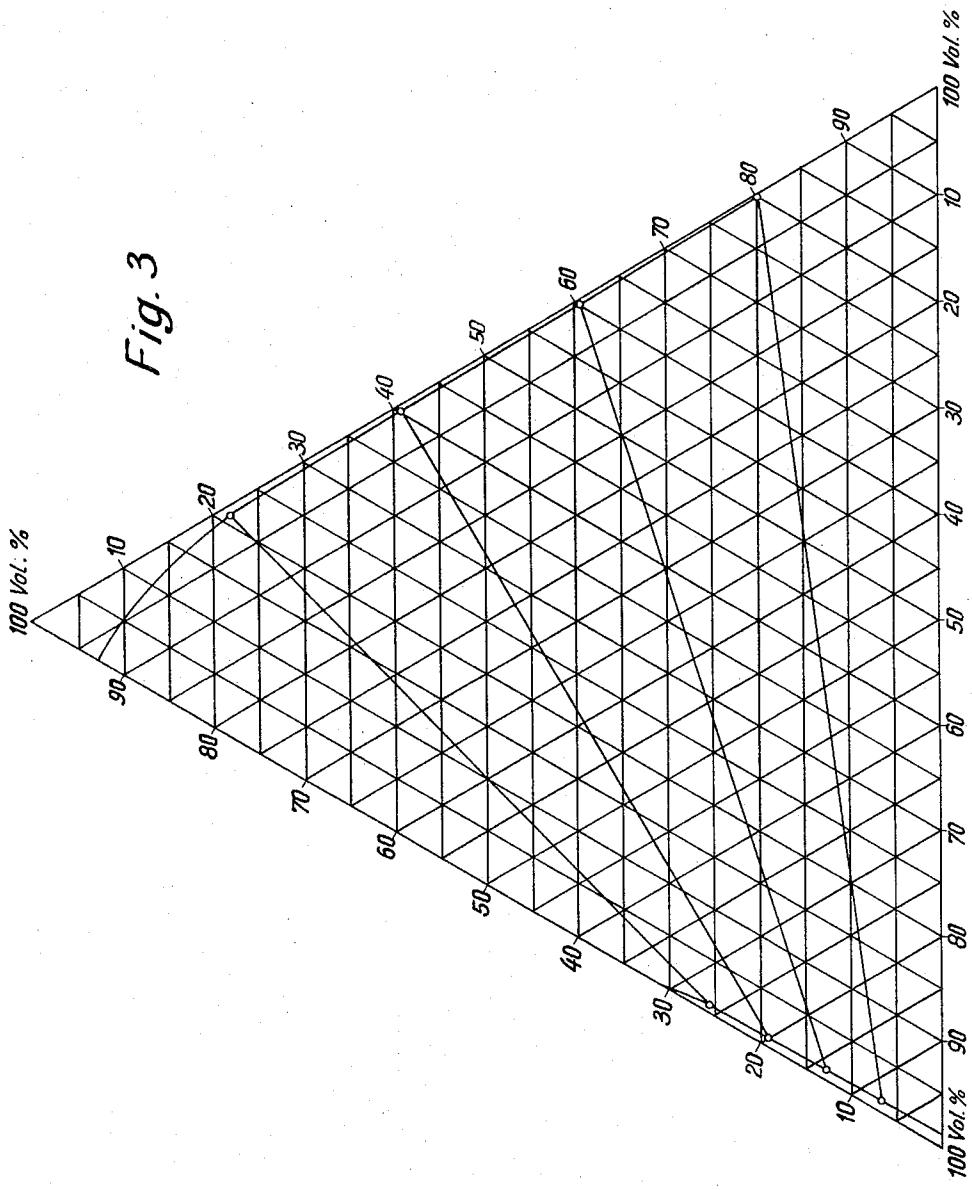

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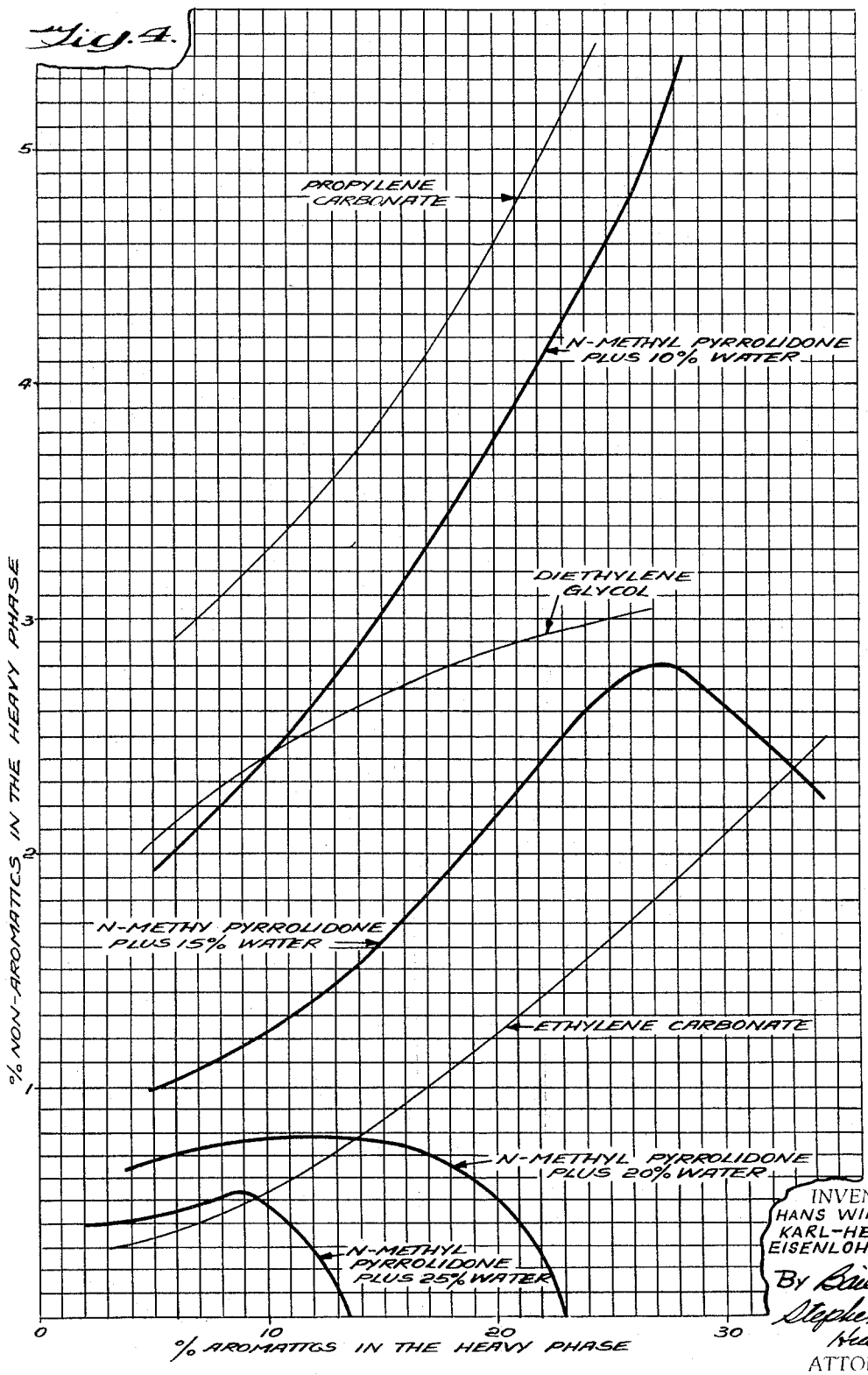
Fig. 4.



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PRODUCTION OF PURE AROMATIC HYDROCARBONS

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Claims priority, application Germany, June 4, 1960, M 45,554
2 Claims. (Cl. 260—674)

This application is a continuation-in-part of copending application Serial No. 115,001, filed June 5, 1961, now abandoned.

The present invention relates to a process of producing pure aromatic hydrocarbons from mixtures containing aromatic and paraffinic hydrocarbons employing a selective solvent, a mixture of N-methyl-pyrrolidone and more than 10% water.

More specifically this invention is directed to obtaining pure aromatic hydrocarbons from hydrocarbon mixtures, especially coke oven benzene, low temperature carbonization benzene, reformates from petroleum products, and cracked benzine resulting from cracking of petroleum fractions, by extraction with a selective solvent consisting of N-methyl-pyrrolidone with more than 10% and as much as up to 40% water, specifically 15–35% water. The starting hydrocarbon mixture may be purified in a preliminary step, for example, by catalytic hydrorefining in which polyunsaturated hydrocarbons are selectively hydrogenated and may be treated with bleaching earth or other known agents.

Pure aromatics as employed herein means aromatic hydrocarbons which are usable as starting materials directly in chemical synthesis and conversions which are sensitive to impurities and also means those which comply with the customary purity requirements for these raw materials. The purity requirements for aromatics differ somewhat from country to country and according to the purpose for which the aromatics are to be used. However, certain minimum requirements or standards exist. For pure toluene, a refractive index of at least $n_D^{20}=1.496$ and generally at least 1.4966 is required in comparison with that of chemically pure toluene of 1.49693. Pure C_8 aromatics are frequently not used in the form of single individual components, that is the ortho, meta, and para xylene and ethylbenzene are not separated individually, but rather employed as "pure xylene" or a "C_8 cut." The usual specifications or purity requirements for this "pure xylene" or "C_8 cut " originated at a time when the xylene was recovered from coal tar and therefore was by nature free from non-aromatics. Accordingly, the provision of a boiling range of, for example, 135–145° C. was sufficient to obtain the then desired purity. While "pure xylene" which satisfied these purity requirements could be produced from a starting mixture containing non-aromatics, the starting mixture containing non-aromatics was not sufficient for work up to the individual components, as, for example, ortho xylene for the production of phthalic anhydride, para xylene for the production of terephthalic acid and ethyl benzene for the production of styrene, since the non-aromatic content could not be reduced to about 0.05 to 0.1%.

Numerous processes have been known for a long time for separating hydrocarbon mixtures into a raffinate phase relatively enriched with one or several groups of materials and an extract phase relatively enriched with other groups of materials with the aid of a selective solvent. In many cases, also heterocyclic ring compounds have been used in these separation processes as the selective solvent.

Thus, for example, olefines have been separated from diolefines with good efficiency employing N-methyl-pyrrolidone containing 1–15% water, preferably 3–7% water, as the selective solvent. Lactones, particularly butyrolactone, have been suggested for separating aromatics from hydrocarbon mixtures. It is known, for example, to obtain a relatively high concentration of toluene from a toluene-heptane mixture employing butyrolactone having a water content of 25%, or to recover a concentrated extract containing up to about 98% aromatics from a light hydroformate by means of butyrolactone having a water content of 10%. Also the non-continuous separation of an extract concentrated in aromatics having a refractive index of $n_D^{25}=1.5691$ from a recycle oil having a 25% aromatics content is known by extraction with N-methyl-pyrrolidone containing up to 5% water, just as the production of extracts having relatively high aromatic content, up to 98%, is known with the aid of compounds of the oxazolidone series having a water content of 1–20%.

While these processes in general have as a purpose the enrichment or concentration of aromatics by selective extraction, they do not concern a partial step of a process for the production of the purest aromatics but only of relative enrichment. These processes are completely separate from those which are required for the production of pure aromatics. Even an enrichment or concentration to an aromatic content of 98% corresponding to an impurity content of 2%, that is a content of non-aromatic impurities, is not satisfactory for the purposes of this invention since this impurity content is around 20–200 times higher than permissible for work up to pure hydrocarbons.

It is known that the separation effect of a selective extraction with a given ratio of distribution of aromatics to non-aromatics in a specific solvent can be improved by increase of the number of stages to certain degree that is provided above all by the physical solubility of the non-aromatics. But the separation cannot be improved above this. A further improvement of the separating effect is possible through the use of an anti-solvent, which is separable from the aromatics by distillation, or in many cases by the use of an extract recycle. Both the use of an aromatic recycle and the use of an anti-solvent reduce the output of an apparatus and increase cost of energy and heat. Accordingly it is desirable on the basis of economy to use both means as little as possible.

Likewise it is known that the selectivity of many solvents can be increased by dilution with water, but only at the cost of absorbing capacity, charging capacity or absolute solvent power given, that is the amount of extract which a given amount of solvent can absorb. The disadvantage can be balanced somewhat by an increase in temperature, but an increase in temperature itself provides a series of other disadvantages, such as the necessity of making the apparatus pressure resistant.

These known means have therefore been used only in a few cases in order to achieve the high requirements of purity which are placed on an extract suited for processing to pure aromatics.

In order to achieve the given specifications for the final product, olefines and naphthenes must be kept out of the extract more completely than is possible with most of the usual solvents. Thus the cyclohexane content of benzene, for example, may be no higher than 0.2% if the benzene is not to have a melting point below 5.4° C. If the benzene must have a melting point of 5.5° C, then the cyclohexane content may not even exceed 0.01%. The ratio with the corresponding impurities in toluene

and xylenes is different, but is effected in the same manner.

The solvent employed for extraction must therefore be extremely selective with regard to the separation of benzene and cyclohexane in order to obtain an extract substantially completely free of cyclohexane since subsequent separation of benzene through rectification is extremely expensive due to the very close vapor pressures of these two components. Thus, for example, to lower the cyclohexane content of an impure benzene from 1% to 0.01% a column having 60 theoretical plates and a reflux of 150 times is necessary calculated on removal of the desired compounds as an azeotrope which must be removed in an amount of about 2.5%. The recovery of an extract which is only enriched in aromatics from a mixture of aromatics and non-aromatic hydrocarbons by solvent extraction is basically different from recovery of an extract useful for processing to pure aromatics in that in this instance the extract must be practically free of all non-aromatics, that is, also of such compounds whose solubility in most solvents which are used normally for solvent extraction is very similar to the solubility of singly or at least normally separated aliphatics.

It is of especial significance in this connection that the viscosity of the solvent be as low as possible. If the viscosity is too high then the exchange of materials occurring in the extraction column, as, for example, in a column filled with screen bodies, a column having rotating disk contactors, a spray column or the like, is considerably reduced. In order to force this a battery of special mixer-separators is necessary. In such a case separation of the two phases into individual compounds presents practically insurmountable difficulties. Therefore the use of a solvent having a viscosity which is too high must be offset by an increase in temperature which brings with it other difficulties such as the lowering of selectivity, increasing of decomposition and corrosion processes and the necessity of using pressure resistant apparatus.

Only a few of the numerous known selective solvents can be used for recovery of pure aromatics from mixtures containing non-aromatics, while all other solvents are unusable on various grounds of technical and economic difficulties. Thus, for example, alkane dinitriles, γ-butyrolactone and cyanoether of diethylene glycol are unsuitable due to lack of chemical and thermal stability.

Many of the suggested compounds or compositions such as, for example, dimethyl hydantoin also precipitate and are therefore not even considered technically. Several others, as, for example, furfurol, phenol and cresol have very little selectivity which cannot be brought up to the required degree by addition of water.

The one group of solvents which was used with some success heretofore for recovery of an extract suited for further processing to pure aromatics from aromatic rich hydrocarbon mixtures is the lower polyethylene glycols, especially di-, tri- and tetraethylene glycol. These have suitable selectivity for aromatics and against olefines and naphthenes in order to achieve an adequately pure extract in the usual number of stages.

However, their absolute solvent power is small and their viscosity high so that it is necessary to adapt the extraction apparatus to essentially higher temperatures, especially about 130° C., in order to bring the charge and viscosity within a range in which the solvent ratio is operable to some degree and the dimensions of the extractor are technically suitable. Moreover, with this solvent it is necessary to have a solvent ratio of about 20 parts by weight of solvent for each part by weight of aromatic solvent in the starting mixture.

It is accordingly an object of this invention to provide a selective solvent composition and a selective extraction process which is very selective in removal of aromatics from hydrocarbon mixtures containing both aromatics and non-aromatics and which does not have the disadvantages set out above.

It was found according to the invention that the selectivity of N-methyl-pyrrolidone, herein referred to as NMP, heretofore suggested as a selective solvent, and its ability to separate impurities from hydrocarbon mixtures, such as olefines and naphthenes, can be increased by diluting it with a precise determined amount of water. The resulting mixture of NMP and water has a selectivity which is at least equivalent to an if desired exceeds that of polyethylene glycols. However, the viscosity is lower and the absolute chargeability, that is the amount of aromatics able to be dissolved in the solvent mixture of the invention, is higher than that of polyethylene glycols. For example, according to the invention a mixture of NMP and 15% water at 20° C. has a viscosity of 4.2 cs. contrasted to 43.5 cs. for tetraethylene glycol at the same temperature. Therefore with a mixture of NMP and 15% water as the extraction agent, for example, 2.5% cyclohexane can be separated from a mixture containing 25% benzene, 25% toluene, 10% xylene and 40% non-aromatics, that is a cyclohexane content corresponding to 10% of the benzene content, using an extraction apparatus having 22 theoretical plates.

A pure benzene, that is one having a melting point of at least 5.5° C. corresponding to a purity of at least 99.99% can be obtained from the resulting mixture directly by a simple distillation. This high purity according to the invention is however not obtained by increasing costs or significant reduction of yield because benzene having the above purity can be obtained in yields of 99.5% based on the benzene content of the starting mixture. Since NMP is not corrosive and is thermally and chemically stable and can be produced on a large scale at a practical price, all the disadvantages of extraction solvents employed heretofore are overcome by the solvent mixture of the invention. Also the essentially higher boiling point of 204° C. as compared to that of the pure aromatics to be recovered not only permits the aromatic extract to be recovered overhead by distillation of the extract phase and the solvent to be recovered as the pot product, which provides advantages in heat efficiency, but also permits the composition to be carried out with fewer plates (about 5 to 10 plates according to the composition of the extract) and lower reflux ratio.

The limits of dilution of the NMP according to the invention lie between a water content of over 10% and up to a maximum of 40%. NMP having a water content up to about 10% has the disadvantages of all other known extraction solvents in that, with increased charge in aromatics from a mixture containing non-aromatics the non-aromatics are taken up equally as well as the non-aromatics whereby the charge may be increased in non-aromatics even more strongly in aromatics. However, it was found that just the opopsite of this well known phenomena occurs if NMP with a water content of more than 10% is used as a solvent. The change in the separation into the counterparts occurs initially above a water content of 10%, that is, after exceeding a critical aromatic content of the extract phase decreasing amounts of non-aromatics are absorbed, if the charge of the extract phase with aromatics is increased. The limits of the water content of the solvent and the aromatic content of the extract, where this sudden reversal in absorbing properties occurs, depends on several factors, such as the exact composition of the aromatic and non-aromatic constituents in the starting mixture and above all the operating temperature. By exceeding the lower limits of the water content, i.e., above 10% water, in each case there is assurance that the separation will occur for practically every combination in the starting mixture at temperatures corresponding temporarily to at least the surrounding temperatures and therefore can be maintained without artificial cooling.

The selectivity for aromatics over non-aromatics and

also over cycloparaffins and olefins increases further by increasing the addition of water while the capacity of the selective mixture according to the invention decreases only slightly. The first strong decrease in capacity or chargeability occurs when the water content exceeds 40%. On this basis the critical limits of the water content of selective solvent according to the invention are above 10% and up to 40%, specifically about 15 to 35%.

The increase in selectivity achieved in this manner while maintaining solvent capacity is mostly sufficient alone in order to recover an extract directly from a starting mixture available from an industrial process with a technically efficient number of steps which extract satisfies the high purity requirements in order to use it for further processing to pure aromatics. Nevertheless, this selectivity is sufficient to permit recovery of an extract having the required purity in a single step by using the extract recycle and/or the countercurrent flow of an anti-solvent, both known per se and in other combinations. According to the invention low boiling hydrocarbons are used as an anti-solvent, that is, hydrocarbons which boil below the boiling range of the aromatic fraction to be recovered, preferably pentane.

Usable starting mixtures are all hydrocarbons stemming from the purification of solid and volatile combustible materials, especially coke oven benzene and low temperature carbonization benzine, as well as reformates of petroleum products and cracked benzines resulting from cracking of petroleum fractions to produce olefines. The starting material can also be purified in known ways, for example, by catalytic hydrorefining and treated with bleaching earth or other known agents.

The process of the invention is hereinafter described by way of illustration with reference to the accompanying drawings wherein:

FIGURE 1 is a schematic diagram of an apparatus suitable for separating aromatic hydrocarbons from a hydrocarbon mixture containing aromatic and non-aromatics;

FIGURE 2 is a schematic diagram of an apparatus suitable for separating aromatic hydrocarbons according to the invention wherein an anti-solvent is employed to increase the selectivity of the solvent mixture;

FIGURE 3 is a three component diagram for a mixture of benzene, hexane and N-methyl pyrrolidone containing 25% water at 20° C. showing the results of tests for equilibrium; and

FIGURE 4 is a graph showing a comparison of known solvents with solvent mixtures according to the invention.

The process of the invention comprises feeding the starting hydrocarbon mixture into a multistage extractor, for example, into about the middle of an extraction column, feeding NMP containing more than 10% and up to about 40% water as the selective solvent into one end of the extractor and part of the resulting extract into the other end of the extractor. The raffinate phase, freed extensively of aromatics, is removed from the extractor at the end into which the selective solvent is fed and the extract phase, practically free of non-aromatics, from the end into which the extract recycle or the anti-solvent is fed.

It is especially advantageous if an anti-solvent is passed through the extractor countercurrent to the flow of the selective solvent at the same time and an extract recycle is employed since thereby the charge of the solvent with aromatics is shifted in the area in which the absorption capability for non-aromatics surprisingly declines again. The simultaneous use of an anti-solvent and an extract recycle makes is possible to employ both supplemental materials together in smaller amounts than was necessary with each alone. This special feature of the invention permits use of an essentially lower solvent ratio in comparison to other processes and also processing to the highest purity of aromatics under that with other processes. Thus, for example, the purest benzene having a melting point of 5.5° C. is recovered according to the invention using a solvent ratio of only 5–7 parts by weight solvent for each part by weight of aromatics contained in the starting mixture. This preferred embodiment of the invention is effected simply by introducing the extract recycle along with the anti-solvent into the extractor at the end from which the extract phase is removed. In this case it is advantageous to strip the extract phase by distillation such that the extract results which is practically free of anti-solvent but an anti-solvent is produced still containing essential amounts of extract.

The favorable aspects of the balance of constituents is demonstrated in the following Table 1 which gives the results of two tests using mixtures of benzene and hexane. Test 1 was carried out using a mixture of 70% by volume benzene and 30% by volume n-hexane while Test 2 was carried out employing a prepared mixture of 92% by volume benzene and 8% by volume n-hexane. NMP containing 25% by volume water served as the selective solvent and was introduced in an amount of 1 part by volume selective solvent, i.e., NMP containing 25% water, to each part. The concentration data is based on the solvent free mixture.

TABLE 1

Mixture	10 parts by volume of N-methyl-pyrrolidone plus 3.3 parts by volume of water.
Solubility of pure benzene in this mixture at 20° C.	6 parts by volume.

	Test 1	Test 2
Composition of the refining phase:		
Percent by volume of benzene	59.8	87.4
Percent by volume of hexane	40.2	12.6
Composition of the extracting phase:		
Percent by volume of benzene	95.5	98.4
Percent by volume of hexane	4.5	1.6

The high selectivity of solvents containing N-methyl-pyrrolidone makes it possible to separate by extraction those fractions which have a very wide boiling range. Thus, it is not necessary, for example, in order to obtain aromatic substances from the starting product by the use of solvents containing N-methyl-pyrrolidone, to distill the C_5-fractions and lower boiling fractions or a portion of the C_6-hydrocarbons in the manner generally required in several known extractive processes.

The process of the invention is further described in the following examples with reference to the accompanying drawings.

Example 1

The hydrocarbon mixture which was separated consisted of 50% non-aromatics having a boiling range of from 50 to 160° C., 23% benzene, 15% toluene, 18% xylene and 4% higher aromatic substances. The solvent mixture used in the separating process consisted of 78.5% of N-methyl-pyrrolidone and 21.5% of water.

Referring to FIGURE 1, extraction column **1** has an efficiency of 20 theoretical stages. The hydrocarbon mixture to be separated was introduced through supply line **2** to a central stage of column **1**. The solvent was introduced into column **1** at the upper end thereof through the solvent supply line **3** and was enriched with aromatic substances as it proceeded downwardly through the column. 300 parts of the solvent were added for each 100 parts of starting mixture.

The solvent which contained dissolved aromatics free from non-aromatic hydrocarbons was discharged through line **4** at the lower end of column **1**. The non-aromatic hydrocarbons were discharged from the top of column **1** through line **5**. An extract recycle including aromatics separated from the solvent was reconducted into the column through line **6**. 40 parts of the extract recycle were used for each 100 parts of the starting mixture.

The solvent which contained dissolved aromatics passed through line **4** and was introduced at **7** into stripper col-

umn 8. In this column the aromatics were separated from the solvent by a direct flow of steam which entered the column through line 26. A mixture of aromatics and water vapor was discharged from the stripper column at 9. This mixture was then condensed in the cooler 10 and flowed into the separator 11 within which it was separated into water and an aromatic phase. The resulting aromatic substances which were discharged from the separator 11 through line 11A were taken off at the point 12 and discharged through line 13. These aromatic substances resulting were separated by means of a simple distillation into the pure aromatic constituents consisting of benzene, toluene and xylene.

A portion of the aromatic substances which were discharged from separator 11 were recirculated into column 1 through line 6.

Water was withdrawn from separator 11 through line 14 and a portion of this water was discharged through line 15.

The remaining portion of the water was passed through line 16 and introduced into the regenerated solvent from lines 17 and 23.

The solvent which was free from aromatic substances was discharged from column 8 through line 17. The water content of this solvent was then increased to the necessary amount by water introduced through line 16 and the solvent was then introduced into column 1 through line 3.

The non-aromatic substances which were discharged through line 5 from column 1 contained a small quantity of solvent. This solvent was separated from the non-aromatic substances in column 18 by a flow of steam introduced through line 27. The non-aromatic substances were introduced into column 18 through line 19 and were discharged from the column through line 20, which conveyed them to cooler 21 and separator 22 wherein the substances were separated from water. The non-aromatic substances were then discharged through line 25. Small quantities of water were discharged from separator 22 through line 24. The solvent free from non-aromatic substances was discharged from column 18 through line 23 and recirculated through column 1 together with the solvent withdrawn from column 8 through line 17.

In an extraction conducted according to the above process, pure benzene having a crystallization point of 5.5° C. was obtained, as well as hexane and toluene, having a purity greater than 99.8%.

Example 2

The same starting mixture as employed in Example 1 was processed in the apparatus as described in FIGURE 2 with a solvent consisting of 85% NMP and 17% water. The apparatus employed in the example consisted of a 20-stage extractor 31 into which the starting mixture was introduced at one of the central stages through line 32. The solvent comprising NMP and water was introduced through line 33 in the ratio of 360 parts of solvent per 100 parts of starting mixture. The solvent was discharged from the column through line 34 together with aromatic substances. A hydrocarbon mixture having a boiling point below 50° C. and comprising primarily pentane was introduced as an anti-solvent into the extractor 31 through line 35. The pentane passed upwardly through column 31 countercurrent to the flow of NMP and was discharged from the column through line 36 together with non-aromatic substances carried along therewith.

The NMP and aromatic substances withdrawn through line 34 were introduced into stripper column 38 through line 37. In this column a direct flow of steam was employed to separate the dissolved aromatic substances from the NMP. The solvent was then recirculated through lines 39 and 33 into column 31.

The aromatic substances and water were discharged from column 38 through line 40, subsequently condensed in cooler 41 and separated into an aqueous phase and a hydrocarbon phase in separator 42. The required amount of water was introduced into the solvent through line 43 and the remaining water was discharged through line 44. The aromatic substances were then discharged through line 45 into distillation column 46 in the upper part of which pure benzene was obtained at 47. The pure benzene was discharged through line 48.

The solvent withdrawn from column 31 still contained small quantities of pentane with which it was in contact in the column. The pentane was distilled in and removed from the top of column 46 through line 49 and recirculated into column 31 through cooler 50 and line 51. The major portion of the anti-solvent was discharged from the extractor column at 36 together with some non-aromatic substances and was passed through line 52 into distillation column 53. The small quantity of NMP which was carried along with these non-aromatic substances was withdrawn from column 53 through line 54 and introduced into the recycled solvent through line 33.

The pentane was distilled and removed from column 52 through line 55, condensed in cooler 56 and recirculated through lines 51 and 35.

Any non-aromatic substances remaining in column 53 were tapped therefrom through outlet 57, condensed in cooler 58 and discharged through line 59.

Stripping steam was introduced into the column 38 through line 60. In column 53, however, the substances therein were heated by means of a heater coil 61 within which steam was circulated. The column 46 was similarly indirectly heated by a heater coil 62.

The residue resulting from column 46 consisted of toluene, xylene and higher aromatic substances and was discharged therefrom at 63. This residue can be introduced into another system of columns not shown in order to obtain the individual constituents in their pure condition.

The process and system as described in this example produced a yield of 99.5% benzene having a crystallization point of 5.5° C.

Our description in specific detail of the selected embodiments of the invention will suggest various changes, substitutions and other departures from our disclosure within the spirit and scope of the appended claims.

We claim:

1. A process for separating pure aromatic hydrocarbons boiling at about 80 to 160° C. from a starting hydrocarbon mixture consisting essentially of aromatic and non-aromatic hydrocarbons comprising intimately contacting the said hydrocarbon mixture with a selective solvent consisting essentially of N-methyl-pyrrolidone with more than 10% by weight and up to 40% by weight water whereby the aromatic hydrocarbons are dissolved in the selective solvent to form an extract, and passing a mixture consisting essentially of a non-aromatic hydrocarbon anti-solvent boiling below the aromatic hydrocarbons in combination with recycled extracted aromatics countercurrently through the resulting extract and recovering the aromatic hydrocarbons dissolved in the extract in pure form.

2. A process as in claim 1 wherein pure benzene having a crystallization point over 5.5° C. is recovered.

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