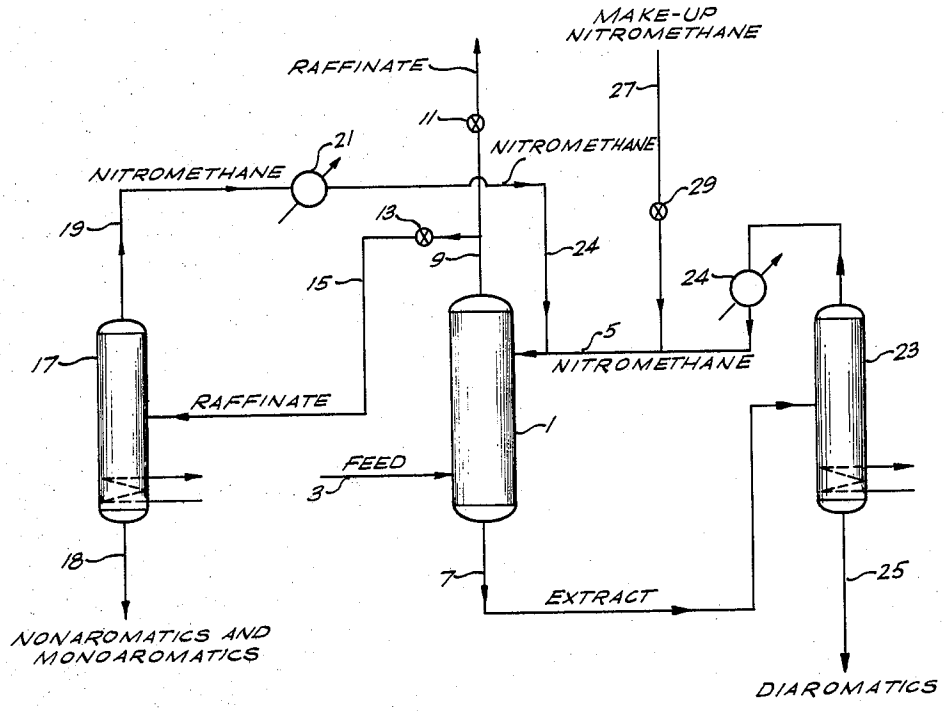
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SOLVENT EXTRACTION PROCESS

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SOLVENT EXTRACTION PROCESS

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This invention relates to a solvent extraction method for separating aromatic hydrocarbons of greater aromaticity from those of lesser aromaticity in admixture therewith. More specifically, the invention relates to such a method in which nitromethane is employed as a selective solvent for said hydrocarbons of greater aromaticity. The invention has particular utility for the recovery of diaromatic hydrocarbons, such as naphthalene or the like, from mixtures thereof with monoaromatic hydrocarbons of substantially equivalent boiling points, such as alkylbenzenes or the like.

There are a number of known solvent extraction procedures for isolating various components of hydrocarbon mixtures and numerous materials have been proposed for use as selective solvents in such procedures. Solvent extraction processes have been attempted with varying degrees of success on mixtures of aromatic and nonaromatic hydrocarbons for purposes of nonselectively extracting all of the aromatics therefrom, but, insofar as I am aware, no effective means of separating aromatic mixtures into fractions of like aromatic components has been openly proposed. However, I have now discovered an improved method of solvent extraction for use on hydrocarbon mixtures which accomplishes such aromatic fractionation, whereby aromatic components of differing degrees of aromaticity can be economically and effectively segregated into fractions of like degree.

There are many hydrocarbon mixtures, as, for example, various petroleum processing fractions, which contain substantial proportions of diaromatic hydrocarbons such as naphthalene and its alkyl and polyalkyl derivatives, and also monoaromatic hydrocarbons, which can be monocyclic, such as alkylbenzenes, and/or bicyclic, such as alkyltetralins, alkylindanes, alkylindenes, and the like, which boil within the same boiling range as the diaromatics. The boiling range of the diaromatics in hydrocarbon mixtures of this type is typically from about 400° to about 450° F. A specific example of such a hydrocarbon mixture is the heavy reformate fraction obtained in the catalytic reforming of naphtha or heavy gasoline fractions. This fraction normally boils above about 400° F. and contains from about 40 to about 80 percent by weight naphthalene and methylnaphthalenes, the remainder being either largely made up of monoaromatic compounds such as alkylbenzenes, tetralins, indanes, indenes, and the like, or of such monoaromatics plus a significant proportion of nonaromatics such as naphthenes, paraffins, etc. Many other fractions obtained in the practice of petroleum fractionating and conversion operations such as catalytic cracking, thermal cracking, catalytic reforming, catalytic cycle oil, etc., operations, also fit the above-described category.

The expanding use of naphthalene and alkylnaphthalenes for the production of dicarboxylic acids useful in manufacturing synthetic resins and fibers has created considerable interest in the recovery of these naphthalenic hydrocarbons from hydrocarbon mixtures, such as the aforesaid reformate fractions, as a feed source for dealkylation processes. Such dealkylation processes, as those skilled in the art appreciate, are conventionally of either catalytic or thermal type and they are designed to convert alkylnaphthalenes to naphthalene, a highly valuable starting material for the manufacture of phthalic anhydride.

Hydrocarbon mixtures such as reformate fractions or the like are difficult of separation into fractions of similar aromaticity, i.e., fractions substantially limited to diaromatic, monoaromatic, etc., components, by conventional fractionation means, chiefly because of the nearness in boiling point of the principal aromatic components involved. The present invention comprises a method of solvent extraction employing nitromethane as a solvent whereby these separations are readily achieved. In addition to the problem of fractionating aromatics according to degree of aromaticity, there is, in the treatment of typical reformate fractions or the like, a parallel problem of separating aromatics from nonaromatics of similar boiling ranges. Here again my invention provides a simple and practical solution since nitromethane, in addition to being more selective as a solvent toward aromatics of higher degree than those of lower degree, also exhibits such selectivity for aromatic hydrocarbons over nonaromatic hydrocarbons.

It is thus a principal object of this invention to provide an improved solvent extraction method by means of which fractions of differing aromaticity levels can be segregated from mixtures of aromatic compounds of varying degrees of aromaticity.

It is another object of the invention to provide a solvent extraction method for readily and economically separating aromatic compounds from like boiling nonaromatic compounds in admixture therewith.

A more specific object of the invention is to provide a practical solvent extraction method by means of which diaromatic compounds are readily separable from like boiling monoaromatic compounds in admixture therewith. Other objects and advantages of the invention will be apparent from the complete description thereof which follows.

The degrees of aromaticity of organic compounds of roughly equivalent boiling points depend upon the number of aromatic rings (benzene nuclei) in their respective molecules, the higher the number of such rings the greater the aromaticity of a given compound. Thus, diaromatic compounds, those having two aromatic rings per molecule, are considered to have a greater degree of aromaticity than the monoaromatic compounds which have molecular structures containing only one such ring. It makes little difference, insofar as degree of aromaticity is concerned, whether polyaromatic compounds have individual or condensed ring systems. Thus, diaromatics of individual ring systems such as biphenyl, diphenylmethane, etc., are considered to have roughly the same degree of aromaticity as the dinuclear aromatics (diaromatics having condensed ring systems), such as naphthalene, etc., at least insofar as this invention is concerned.

The method of my invention is not limited to the treatment of aromatics of the mono-and diaromatic types, and mixtures containing higher polyaromatic compounds are also amenable to separation thereby. For example, it is within the reach of the invention to subject hydrocarbon mixtures containing triaromatic compounds, such as anthracene and phenanthrene, and diaromatic compounds of roughly the same boiling range to solvent extraction as taught herein, to separate the triaromatics from the diaromatics. Furthermore, it is possible, by means of this invention, to separate aromatic compounds differing less sharply from each other in degree of aromaticity than do the mono- and polyaromatic compounds. Exemplary mixtures of such weakly differing aromatics are those containing, in addition to mono-aromatics or diaromatics of the above-noted types, substituted aromatics with functional groups which have either an additive or subtractive influence on their unsubstituted aromaticities. It will be apparent to those skilled in the art that a wide

variety of feed mixtures can be resolved by the method taugh herein.

Attention is now directed to the accompanying drawing which schematically illustrates, as a preferred method for the practice of my invention, a continuous countercurrent solvent extraction process employing nitromethane as the solvent. A feed stream containing both aromatic and nonaromatic hydrocarbons of like boiling ranges such as a heavy reformate petroleum fraction containing diaromatics (naphthalene, alkylated naphthalenes, etc.); monoaromatics (alkylbenzenes, alkyltetralins, alkylindanes, etc.); and nonaromatics (naphthenes and paraffins), is continuously fed into the bottom of a countercurrent solvent extraction column 1 through line 3 as shown. Simultaneously, nitromethane is recycled into the top of column 1 through line 5, from a source hereinafter disclosed. Solvent extraction column 1 is so designed and the conditions of operation so fixed and controlled as a result in the extraction of substantially all of the diaromatic components from the feedstock as it circulates upward in countercurrent contact with the nitromethane in the column.

Solvent extraction column 1 is effectively operative on systems of the type normally encountered when maintained at atmospheric pressure and within an operating temperature range of from about 20° to about 100° C., the preferred temperature range being from about 30° to about 60° C. The yield and purity of the raffinate and extract products from column 1 are partially dependent upon the number of extraction stages in said column. Column 1 is particularly effective for typical purposes of my invention when it has from about 2 to about 15, and preferably from 7 to 11, stages.

Referring again to the drawing, an extract phase is withdrawn from the bottom of solvent extraction column 1 through line 7 and a raffinate phase is withdrawn from the top of the column through line 9 as shown. When column 1 is designed and operated in accordance with the preferred operating conditions set forth above, diaromatic hydrocarbon yields of from about 80 to about 90 percent and purities of from about 90 to about 95 percent (all percentages being on a weight basis) are attainable in the extract phase. The extract phase contains most of the nitromethane leaving column 1, in addition to that portion of the feedstock which it has extracted in passing through the column. The raffinate phase from column 1, under optimum operating conditions, typically contains between about 80 and about 90 percent by weight nonaromatic and monoaromatic hydrocarbons, the remaining portion of the raffinate being nitromethane.

As the drawing shows, there is an alternate choice of disposition of the raffinate from column 1. Thus, it can be withdrawn from the process through valve 11, with valve 13 closed, without further treatment, or it can be circulated to distillation column 17 through line 15, as shown on the drawing, to effectuate the recovery of nitromethane therefrom. Obviously, valve 13 is kept open and valve 11 closed in the latter event.

While, for reasons previously given, my solvent extraction process is of particular utility for the purpose of extracting naphthalenic diaromatics (as dealkylation process feeds) from hydrocarbon mixtures containing monoaromatics, for which purpose the schematic arrangement of the drawing is ideally suited, the process is readily adaptable for use in recovering various other aromatic fractions as well. For example, the process of the drawing can be adapted to make a straightforward aromatics-nonaromatics separation of a feed material such as a heavy reformate petroleum fraction merely by assuring the proper number of stages in column 1 and the proper operating conditions for the purpose.

The determination of optimum plate plurality and operating conditions to achieve a desired result is a relatively simple matter, in the light of the present teachings, to those skilled in the solvent extraction art, requiring at most a minimum amount of routine experimentation. Primarily, the achievement of maxium separating efficacy among compounds of varying degrees of aromaticity is a matter of having the optimum number of extraction stages in column 1. In this respect, it is pointed out that more stages are required for such selective extraction, all other things being equal, than for mere separation of a mixture into aromatic and nonaromatic fractions.

If it is desired to obtain two or more aromatic fractions from a mixture containing both aromatics of differing aromaticities and nonaromatics, the process illustrated on the drawing can be relatively simple modification be made to achieve this purpose. One way of so modifying the process is to add at least one additional solvent extraction column similar to column 1 to the process, with appropriate lines, fittings and other equipment, where needed, to handle the various material streams thereby involved. For example, if it is desired to separate a diaromatic fraction and a monoaromatic fraction from a feedstock containing diaromatics, monoaromatics and nonaromatics, this can be done by incorporating an additional solvent extraction column in series with column 1; using column 1 to extract the diaromatics from the feedstock; and utilizing the additional column to separate the monoaromatics from the nonaromatics in the raffinate phase from column 1.

While my method is preferably practiced as a continuous or flow process, as indicated by the drawing and description thereof which illustrate that aspect of operation, it functions equally well as a batch process or a process partaking of both batch and flow characteristics.

To continue with the detailed description of the drawing, in the event the raffinate phase from column 1 is routed to distillation column 17, it is there fractionated into an overhead product of substantially pure nitromethane, which is passed through line 19 into cooler 21, wherein it is condensed, and from thence through line 24 to juncture with line 5 and admixture with the solvent feed to column 1; and a bottoms product of nonaromatic and monoaromatic raffinate hydrocarbons which is withdrawn to storage or other disposition through line 18.

The extract phase from solvent extraction column 1, normally containing from about 10 to about 40 percent diaromatic hydrocarbons and from about 60 to about 90 percent nitromethane, is passed through line 7 and into distillation column 23 wherein it is separated into nitromethane (overhead) and diaromatic hydrocarbon (bottoms) fractions, the former being recirculated to solvent extraction column 1 through condenser 24 and line 5 as shown on the drawing, and the latter (bottoms) being withdrawn through line 25. None of the components of the extract phase from column 1 decompose at or near their normal boiling points. Furthermore, the boiling points of the extract components are typically of such magnitude and disposition as to permit distillation of the extract phase at atmospheric pressure and, accordingly, distillation column 23 is preferably operated at about that pressure level. At atmospheric pressure, the most effective temperature range for operation of column 23 is, in most instances, from about 200° to about 250° C., the preferred range being from about 210° to about 220° C.

Under certain circumstances, there may be minor quantities of contaminating hydrocarbons present in the extract phase from column 1, the exact amounts of such contaminants depending upon, inter alia, the operating temperature and pressure, and the number of stages, in the column. Where such is the case, it is conceivable that the contaminants will, at least to some extent, accompany the nitromethane solvent overhead from column 23, possibly in the form of minimum boiling azeotropes therewith. While the likelihood of nitromethane contamination by an occurrence of this type is perhaps

remote, it is readily cured by inserting a phase separator in line 5 between condenser 24 and column 1 and routing the nitromethane phase therefrom to column 1. Bottoms product from column 23 is recovered as the final extract product from the process, or it can be circulated to further treatment, not shown, such as some form of purification treatment to remove traces of nitromethane and/or other contaminant(s) possibly present. Makeup nitromethane is introduced into the system through line 27 and valve 29 as needed.

A "fringe benefit" advantage of the use of nitromethane as a selective solvent in the present process is its low corrosivity toward materials vulnerable to acid attack. This is obviously of major importance from the standpoint of equipment economy and simplicity of maintenance. In addition to being highly selective toward aromatic hydrocarbons, nitromethane exhibits high solvent power, that is, relatively small quantities of nitromethane dissolve relatively large quantities of aromatics. More specifically, nitromethane proportions of from about 0.25 to about 3.0 parts of solvent (my preferred proportions) to about 1 part of hydrocarbon feedstock, on a weight basis, will normally manifest a solvent power of from about 5 to about 35. The method of calculating solvent power values for purposes of this invention is set forth in Example I following.

An important factor in arriving at optimum conditions of operation in solvent extraction processes is the rapidity with which the raffinate phase separates from the extract phase under various circumstances. By using nitromethane as a solvent in the method of my invention, exceptionally rapid separation takes place between the phases at room temperature. At higher temperatures phase separation is faster and the solvent power of nitromethane is greater, but temperature increases have an adverse effect on the selectivity of nitromethane towards aromatics. The previously recommended temperature ranges for the practice of my invention (about 20° to about 100° C., preferably from about 30° to about 60° C.) were arrived at by taking the aforesaid factors into consideration. The relatively fast phase separation achievable with nitromethane as a solvent is thought to be attributable, at least in part, to the fact that it has a density in excess of 1 (specific gravity: 1.138 20°/20), which is relatively high compared to the densities of hydrocarbon oils. While the above recommended operating temperatures are completely adequate for most purposes, in special cases where exceptionally pure products such as for example 99+ percent purity diaromatics are desired, lower temperatures might be required. In these cases refrigeration means would be a desirable adjunct to the process.

Nitromethane is relatively non-toxic at standard, as well as operating, conditions. Also, it is miscible with water to some extent (9.5 parts per 100 parts of water at 20° C.) thus making it possible to recover the nitromethane from extract phases by water extraction, for recycling or other purpose. This would not be a preferred method of recovery, however, because of the relatively low solubility of the nitromethane. Nitromethane is stable at its boiling point (101.5° C.) and unreactive with feedstock components at that temperature, as well as other temperatures to which it is exposed in service.

The solvent extraction process of my invention can be carried out in various ways, the most common mode of operation comprising the use of a spray, packed or bubble plate tower, wherein the hydrocarbon feed mixture is contacted by the stream of nitromethane flowing, usually countercurrently, therethrough. It has been found desirable, in certain instances, to add a minor amount of a lower glycol to nitromethane before employing it as a solvent in my process and this expedient is within the scope of my invention. The glycol can be incorporated in the nitromethane either prior to or during the solvent extraction operation and its purpose is to facilitate the rapid and distinct formation of two liquid phases therein. Examples of suitable lower glycols for this purpose are ethylene glycol, propylene glycol, 1,2-butanediol, etc.; mixtures of such glycols can be employed if desired. When glycols are used in the manner and for the purpose above indicated, the proportions should normally not exceed about 20 percent of the weight of the nitromethane and preferably fall within the range from about 2 to about 5 percent of the nitromethane weight.

Still another way in which my process can be carried out is to employ an antisolvent in conjunction with the nitromethane in any manner known to those skilled in the art. The use of such antisolvents in hydrocarbon solvent extraction processes is well known and need not be considered in detail here. Typical antisolvents for purposes of this invention are paraffins such as pentane, heptane, octane, isooctane, and the like.

Following are examples included for purposes of illustrating the invention. It is emphasized that these examples are to be considered as illustrative only and not limitative of the scope of the invention.

Example I

This example illustrates the selectivity of nitromethane for diaromatic hydrocarbons in the presence of monoaromatic hydrocarbons.

A 133 ml. quantity of nitromethane was admixed with 100 ml. of a hydrocarbon fraction having a boiling range of 430°–520° F. The hydrocarbon fraction was distilled from a mixture of FCC and TCC cycle oils, and was composed of 58.3 percent monoaromatics and diaromatics, including naphthalene, methyl- and dimethylnaphthalenes, alkylindanes, alkylindenes, alkyltetralins, and the like. The balance of the hydrocarbon fraction (41.7%) was composed of paraffins and naphthenes. The ratio of diaromatics to monoaromatics in the hydrocarbon fraction was 1.73 to 1.

The mixture of nitromethane and hydrocarbon fraction was moderately agitated at 25° C. and allowed to settle into a raffinate and extract phase. The extract phase after analysis showed an aromatic concentration of 93.3 percent which was found to be 68.9 percent diaromatics such as naphthalene, and methyl- and dimethylnaphthalenes, the balance being composed of monoaromatics such as those named above. Thus, it can be determined that the ratio of diaromatics to monoaromatics increased from 1.73 in the feed to 2.83 in the extract.

The above results clearly show that there was substantially greater selectivity of the nitromethane solvent for the diaromatics than for the monoaromatics present in the system. The selectivity factor for the present example was calculated to be 10.8. This selectivity factor or β, as it is sometimes called, was determined in accordance with the method set forth on page 39 of Cyanamid's "New Product Bulletin," collective volume II (December 1950). The selectivity factor is, as the term implies, a measure of the selectivity of a solvent, the higher the value the better the selectivity. As those skilled in the art will appreciate, the value of 10.8 is indicative of very good selectivity.

The solvent power of the nitromethane was calculated from the results of this example to be 17.9, an exceptionally high value, indicative of a good performance capability as a solvent for purposes of this invention. The solvent power excellence of the nitromethane is accented by the rather low ratio of nitromethane to feed in the described procedure. I calculated the foregoing solvent power value by the formula: percent removal of bicyclics x percent improvement in bicyclics concentration $\times 10^{-2}$. All percentage values representing or derived from component concentrations in this example are based on weight concentrations.

Example II

This is an example of a laboratory scale solvent extraction of methylnaphthalene from a mixture of methylnaphthalene (a diaromatic), and dodecane (a paraffin), using nitromethane as a solvent.

A single stage solvent extraction is carried out at 25° C. by treating a mixture of 14 ml. of dodecane and 6 ml. of methylnaphthalene with 16 ml. of nitromethane. The weight ratio of nitromethane to hydrocarbon feed mixture is approximately 2 to 1. The nitromethane-hydrocarbon mass is moderately agitated and a nitromethane rich phase separated therefrom. It is determined that approximately 25 percent of the volume of the nitromethane rich phase is methylnaphthalene whereas only about 12 percent of the volume of the dodecane rich phase is methylnaphthalene. Comparison of the latter figure with the volume percentage of the methylnaphthalene in the feed mixture (about 30%) clearly points up the selectivity of the nitromethane solvent for that hydrocarbon under the conditions set forth.

Example III

This example illustrates the selective extraction of monoaromatic hydrocarbons from a mixture thereof with nonaromatic hydrocarbons according to the method of this invention.

100 grams of nitromethane is admixed at 25° C. with a hydrocarbon fraction composed of 20 percent benzene, toluene and xylene and 80 percent paraffins and naphthenes as the result of which an extract phase rich in the monoaromatic hydrocarbons is recovered. The extract phase is composed of about 15 percent monoaromatic hydrocarbons and 85 percent nitromethane and nonaromatic hydrocarbons and contains about 75 percent of the monoaromatic hydrocarbon content of the feedstock mixture. The yield and purity of the extract product would be greatly increased by an increase in the number of solvent extraction stages.

It will be apparent that many modifications of my process can be practiced simply by varying the permissible solvent components, feed materials and operating techniques within the limits taught herein. As previously indicated, the present process is particularly well adapted to the preparation of feedstocks for dealkylation processes. Thus, a heavy reformate fraction containing alkylnaphthalenes and nonnaphthalenic materials can be treated in accordance with the invention to obtain an alkylnaphthalene concentrate which is thereafter dealkylated to form naphthalene by any of the conventional catalytic or thermal dealkylation processes.

I claim:

1. A method of extracting diaromatic hydrocarbons from a mixture thereof with monoaromatic and nonaromatic hydrocarbons are difficult to separate from said mixture with nitromethane to form a raffinate phase and a nitromethane extract phase in which the ratio of diaromatic hydrocarbons to monoaromatic and nonaromatic hydrocarbons is substantially greater than the ratio thereof in said mixture.

2. A method as defined in claim 1 wherein said diaromatic hydrocarbons are difficult to separate from said hydrocarbon mixture by fractional distillation.

3. A method as defined in claim 1 wherein substantially all of the diaromatic hydrocarbons are recovered from said extract phase.

4. A method of extracting diaromatic hydrocarbons from a feedstock containing diaromatic, monoaromatic and nonaromatic hydrocarbons comprising: (1) continuously contacting said feedstock, in countercurrent relationship, with nitromethane as a solvent, whereby a nitromethane-rich extract phase in which the ratio of diaromatic hydrocarbons to monoaromatic hydrocarbons is substantially greater than the ratio thereof in said feedstock, and a raffinate phase containing substantially all of the remaining portion of the feedstock and a minor amount of nitromethane, are obtained; (2) subjecting said extract phase from step (1) to fractional distillation to from an overhead product of substantially pure nitromethane and a hydrocarbon bottoms product enriched in diaromatic hydrocarbons; (3) condensing the overhead nitromethane product from step (2); and (4) recycling the condensed nitromethane from step (3) to step (1).

5. The method of claim 4 in which step (1) is conducted at atmospheric pressure and at a temperature within the range from about 20° to about 100° C.

6. The method of claim 4 in which the ratio of nitromethane to hydrocarbon feedstock in step (1) is from about 0.25 to about 3.0 parts by weight of the former to 1 part by weight of the latter.

7. The method of claim 4 in which the raffinate phase from step (1) is subjected to fractional distillation to remove nitromethane therefrom as an overhead product and to obtain a substantially nitromethane-free hydrocarbon bottoms product.

8. The method of claim 4 in which step (1) is conducted at atmopheric pressure and at a temperature within the range from about 30° to about 60° C.

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