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SOLVENT EXTRACTION OF NAPHTHALENES

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This invention relates to the fractionation of mixtures of petroleum hydrocarbons containing mononuclear and polynuclear aromatic compounds into a fraction richer in the polynuclear component.

Solvent extraction, wherein is employed a liquid feed stock and a liquid extractor, is a widely used process in petroleum refining. By means of this process crude oil fractions are resolved into various classes of materials which differ from each other by their solubility characteristics. This principle permits solvent refining to be employed in the deasphalting and dewaxing of lubricating oils prepared from crude petroleum oils and also to improve their viscosity index and oxidation resistance by the removal of aromatic and naphthenic constituents, an effect which also reduces the carbon and sludge-forming tendencies of these lubricating oils. Extraction with selective solvents has also been employed for the desulfurization of light petroleum distillates where the concomitant removal of aromatic hydrocarbons from the distillate is not disadvantageous.

The petroleum industry has also been instrumental in the development of a versatile chemical industry which has created a need for a wide variety of raw materials, including various hydrocarbons. Petroleum being a complex homogeneous mixture of a very large number of hydrocarbons plus a small quantity of other materials is an excellent source for hydrocarbons which are to be employed as raw materials and subjected to further processing. However, the separation of relatively pure hydrocarbons or concentrated solutions thereof from petroleum is a difficult task. While fractionation of petroleum mixtures may be effected by distillation, adsorption, absorption, crystallization, and so forth, because of the satisfactory experience in operating the above mentioned solvent refining processes, the petroleum industry has utilized to a great extent the principles of solvent extraction in the recovery of hydrocarbons which are difficult to separate in other types of fractionating processes. In spite of the effectiveness of solvent refining processes as a means for separating hydrocarbon components which have substantially the same volatility, this technique is generally limited to the separation of aliphatic hydrocarbons from cyclic hydrocarbons, or even in the separation of more unsaturated aliphatic hydrocarbons from less saturated aliphatic hydrocarbons. Fractionation of these components by solvent extraction can be carried out rather readily because of the solubility characteristics of the component hydrocarbons involved in relation to the selective solvent employed. The separation of mixtures of aromatic hydrocarbons, however, presents a more difficult problem. Experience has shown that the conventional techniques of distillation, crystallization, and the like are not satisfactory for separating mixtures of mononuclear and polynuclear aromatic hydrocarbons into fractions richer in the polynuclear components. Similarly solvent extraction processes have not been generally employed in this capacity because of their low efficiency. According to this invention, however, it has been found that the principles of solvent refining may be used advantageously to effect this separation.

It is therefore an object of this invention to provide a solvent extraction process which may be employed in the separation of polynuclear aromatic hydrocarbons from admixture with mononuclear aromatic hydrocarbons. It is a more specific objective of this invention to employ the principles of solvent extraction to separate mixtures of naphthalene and alkyl derivatives thereof, and benzene and its alkyl derivatives into a fraction enriched in naphthalene and its alkyl derivatives.

It is well known that aromatic hydrocarbons are more powerful solvents than aliphatic hydrocarbons. Inasmuch as the mechanism of solvent extraction is based upon the miscibility of the solvent in the solution to be extracted, the high solvency powers of aromatic hydrocarbons have prevented general acceptance of solvent extraction in the separation and recovery of aromatic hydrocarbon mixtures. The problem of miscibility of the solvent in the solution is illustrated by Table I which lists a plurality of conventional selective solvents which are completely miscible in mixtures of aromatic hydrocarbons.

TABLE I

SO_2
Acetonitrile
Triethylene glycol and acetonitrile
Furfural
Dichloroethyl ether
Ethylene glylcol diethyl ether
Ethylene glycol monoethyl ether
Dichloroethyl ether-hexane
Nitromethane
Methylacetoacetate
Dimethoxy tetraglycol

Even in the event that immiscible solvents can be obtained, the refiner is faced with the additional problem of inoperativeness of the solvent refining process to effect the separation of aromatic hydrocarbon mixtures. For example, the inoperativeness of solvents conventionally used in the separation of aliphatic hydrocarbons from aromatic hydrocarbons is demonstrated by the data in Table II.

TABLE II

Separation of naphthalenes from alkylated benzenes by solvent extraction

Components	Composition of Original Mixture	Composition of Hydrocarbon Phase of Extract Obtained Using Extracting Solvents [1]			
		Propylene Glycol	Polyethylene Glycol		
			"300"	"400"	"600"
Naphthalene, percent	7.1	7.1	5.6	5.3	5.6
1-Me-Naphthalene, percent	21.3	24.9	22.2	24.1	22.0
2-Me-Naphthalene, percent	33.9	37.8	36.4	37.9	36.1
Alkyl Benzenes, percent	37.7	30.2	35.8	32.7	36.3
Yield of Material Extracted, Vol. percent	----------	3	44.5	49.0	63.0

[1] Solvent to hydrocarbon ratio 1:1.

However, according to this invention, it has been found that the condensation products prepared by reacting the monoethanoid nitrile, acrylonitrile, with either water, hydrogen sulfide or ammonia in the presence of a suitable condensation catalyst may satisfactorily be employed in the separation of hydrocarbon mixtures containing mononuclear and polynuclear aromatic hydrocarbons to produce a fraction enriched in the polynuclear constituent.

Specific examples of such condensation products which may be used as solvents in the instant invention are

β,β'-Thiodipropionitrile
β,β'-Oxydipropionitrile
β,β'-Iminodipropionitrile

To illustrate the instant invention, the foregoing components were separately employed as solvents in a single stage extraction process using a solvent ratio of 1:1. The charge was an aromatic hydrocarbon-containing fraction obtained from the polymers produced in a conventional hydroforming process and containing 42% naphthalenes and 58% alkyl benzenes. A tabular summary of the results of these extractions is shown in Table III.

TABLE III

Effectiveness of oxy-, thio-, and iminodipropionitriles as selective solvents for naphthalenes

Solvent	Solvent Ratio	Phase	Naphthalenes, Vol. Percent	Yield, Vol. Percent	Percent Enrichment
Oxy	1:1	Extract	62.3	25	48
Thio	1:1	do	61.4	20	46
Imino	1:1	do	59.0	29	40

It is thus seen that the solvent extraction process of this invention has the ability to extract naphthalenes from benzenes, a system very difficult to process by means of solvent extraction. In general, the solvents employed in the instant invention were able to effect a concentration of the naphthalenes in the extract phase by enriching the naphthalene concentration from 42% to 60% in a single stage extraction, each of the solvents employed evincing substantially equivalent selectivity. Although the substantial equivalency of each solvent, with regard to selectivity, is shown, consideration of the process conditions may make it more desirable to use the oxy-derivative because of its physical properties. In the use of this particular composition, the recovery of the enriched aromatic hydrocarbon mixture and solvent from the extract phase is facilitated because the use of steam distillation may be expeditiously employed to recover the aromatic hydrocarbons separated in the extract phase. With the separation of the aromatic hydrocarbons there results the production of a water-rich phase and a solvent-rich phase. Upon cooling, these phases can be readily separated, the water-rich phase being recycled to the steam distillation step and the solvent-rich phase being recycled for further use in the extraction step of the process. The imino- and thio-derivatives, however, can not be employed as effectively in this manner, inasmuch as the recovery of the imino compound is complicated due to its complete miscibility with water at normal temperatures. Although the thio compound is not completely miscible with water at the temperature at which a normal steam distillation step would be carried out, elevated pressures would be necessary to effect an efficient separation of aromatics from the solvent by steam distillation.

It may also be desirable to carry out the solvent refining process of this invention by adding small amounts of water to the selective solvents employed therein. It has been found that the efficacy of this extraction process may be enhanced by carrying out the process employing solvents containing small amounts of water. The amount of water employed will depend upon the solvent employed, the composition of the feed stock, as well as other variables and is best determined experimentally to obtain maximum effectiveness. Generally amounts less than about 5 volume percent should be employed and preferably quantities from about 1 to 2 volume percent. This effect is shown in Table IV in which is compiled the results of extracting a mixture containing 38% of alkyl benzenes and 62% of naphthalene and alkyl derivatives thereof in a single stage extraction process employing β,β'-oxydipropionitrile as the selective solvent. In one instance a substantially anhydrous solvent was used, while the other illustrative extraction was carried out using a solvent containing 1% by volume of water.

TABLE IV

Separation of naphthalenes from benzenes employing β,β'-oxydipropionitrile

Run No	1	2
Water Content of Solvent, Vol. Percent	0.0	1.0
Solvent-Hydrocarbon Ratio	1:1	1:1
Composition of Extract:		
Alkyl Benzenes	25.1	20.7
Naphthalenes	74.9	79.3

Although the foregoing data illustrating the several features of the instant invention were obtained employing a single stage extraction, it is to be understood that the foregoing examples were presented merely as illustrative and non-limiting demonstrations of the instant invention. The solvent extraction process of this invention may be carried out employing several countercurrent extraction stages to improve the separation. In addition, the solvent to hydrocarbon feed ratio may be varied from that employed in the illustrative examples. Inasmuch as the solvents employed in this invention are not sensitive to temperature and their efficiency is not appreciably affected thereby, the process may be operated over a relatively broad temperature range, although preferably at atmospheric temperature. Similarly, other modifications of conventional solvent refining techniques may be employed in carrying out the instant invention and are to be considered within the scope of the invention described in the appended claims.

What is claimed is:

1. A process for separating a polymer mixture produced in a conventional hydroforming process consisting essentially of naphthalene and alkyl derivatives thereof and alkyl benzenes into an extract fraction enriched in the naphthalene constituents which comprises solvent extracting the hydrocarbon mixture with a solvent consisting of a dialkylnitrile derivative selected from the group consisting of β,β'-thiodipropionitrile, β,β'-oxydipropionitrile, β,β'-iminodipropionitrile, and a water-containing mixture thereof containing 1–5 vol. percent of water, and recovering a fraction of the polymer mixture enriched in the naphthalene constituents in the extract phase.

2. A process for separating a polymer mixture produced in a conventional hydroforming process consisting essentially of naphthalene and alkyl derivatives thereof, and alkyl benzenes into an extract fraction enriched in the said naphthalene constituents which comprises solvent extracting said mixture with a solvent consisting of β,β'-oxydipropionitrile to produce a raffinate phase and an extract phase, steam distilling said extract phase to recover therefrom said fraction enriched in the naphthalene constituents, separating the remaining mixture of β,β'-oxydipropionitrile and water into a water phase and a solvent phase, separating the solvent phase and recycling it to be further employed in said solvent extracting.

3. A process for separating a polymer mixture produced in a conventional hydroforming process consisting essentially of naphthalene and alkyl derivatives thereof, and alkyl benzenes into an extract fraction enriched in the naphthalene aromatic constituents which comprises solvent extracting the hydrocarbon mixture with a solvent consisting of an admixture of a dialkylnitrile derivative

selected from the group consisting of β,β'-thiodipropionitrile, β,β'- oxydipropionitrile and β,β'-iminodipropionitrile, and 1–5 vol. percent of water and recovering the fraction of the hydrocarbon mixture enriched in the polynuclear constituents in the extract phase.

4. A process in accordance with claim 3 in which a solvent:hydrocarbon mixture ratio of 1:1 is employed.

5. A process in accordance with claim 4 in which said solvent consists of an admixture of β,β'-oxydipropionitrile and 1–2 vol. percent of water.

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