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SOLVENT EXTRACTION PROCESS

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The present invention relates to a method of treating hydrocarbon mixtures containing saturated and unsaturated hydrocarbons to separate a relatively saturated extract and a relatively unsaturated raffinate, and more particularly, to a method of selectively dissolving and removing a minor relatively saturated hydrocarbon fraction from a petroleum distillate comprising a minor proportion of relatively saturated hydrocarbons and a major proportion of relatively unsaturated hydrocarbons.

The solvent extraction processes now in commercial use provide a means for separating minor proportions of unsaturated hydrocarbons such as aromatics and olefins from hydrocarbon mixtures consisting predominantly of more saturated hydrocarbons such as paraffins and naphthenes. These processes are not well adapted to the separation of hydrocarbon mixtures containing only minor proportions of relatively saturated hydrocarbons and a major proportion of unsaturated hydrocarbons. The solvents employed in the known processes are selective for the unsaturated components of a hydrocarbon mixture and if these components predominate in the mixture to be separated, the volume of solvent required to be contacted with the mixture to selectively dissolve the predominating quantity of unsaturates is extremely large. The recovery and recirculation of the solvent presents an economic obstacle to commercial separation of a stock of this character by these processes.

It has now been discovered that the perfluorocarbons, that is, hydrocarbons in which the hydrogen has been completely replaced by fluorine, are selective for the relatively saturated hydrocarbons as opposed to the relatively unsaturated hydrocarbons. For instance, if a mixture of aromatic and paraffinic hydrocarbons is contacted with a perfluorocarbon, the paraffinic hydrocarbons are selectively dissolved in the perfluorocarbon, a lower extract phase which comprises perfluorocarbon and dissolved paraffinic hydrocarbons is formed, and an upper raffinate phase comprising aromatic hydrocarbons is formed. The phases may be separated and a paraffin-rich extract and an aromatic-rich raffinate may be recovered.

The critical solution temperatures of several typical perfluorocarbons with a number of hydrocarbons have been determined. These temperatures are determined as an aniline point is determined, the perfluorocarbon and the hydrocarbon being mixed, usually in approximately equal volumes, at a temperature sufficiently low that two

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phases exist. The temperature is then gradually raised until the critical solution temperature, indicated by the formation of a single homogeneous phase, is reached. The following Table 1 shows the critical solution temperatures of several perfluorocarbons with a number of hydrocarbons, temperatures being recorded in degrees Fahrenheit.

TABLE 1
Critical Solution Temperatures

Hydrocarbon	Solvent		
	Perfluoro-Methyl Cyclohexane	Perfluoro-Dimethyl Cyclohexane	Perfluoro-n-heptane
o-Xylene	228		
m-Xylene	205		
p-Xylene	201		
Toluene	194		
Benzene	181	183	234
Cyclohexane	122		
Methyl Cyclohexane	111	119	161
Octene-1	113		
Heptene-1	83		
Hexene-1	52	61	95
Pentene-2	32		
Pentene-1	22		
n-Octane	106		
n-Heptane	77	88	121
n-Hexane	48	55	86
2-2,4 Trimethyl Pentane	36	46	75
n-Pentane	15		

Differences in critical solution temperatures are a measure of the selectivity of the perfluorocarbon solvents for the several hydrocarbons and hydrocarbon types shown in Table 1, the perfluorocarbon being more selective for those hydrocarbons with which it shows the lowest critical solution temperatures. It may be seen from the table that the fluorocarbons are more selective for paraffins, olefins and naphthenes than for aromatics. It may also be seen that within a narrow molecular weight range, for instance, the range of the C₇ hydrocarbons, the critical solution temperature is lowest for normal heptane and successively higher miscibility temperatures are shown for heptene-1, methyl cyclohexane, and toluene. Thus, the selectivity of the perfluorocarbons is greatest for the paraffins, somewhat lower for the olefins, still lower for the naphthenes and least for the aromatics.

The following Table 2 shows representative average selectivities, as measured by difference of critical solution temperatures, of several perfluorocarbons for several mixtures of two hydrocarbon types. The temperature differences are recorded in degrees Fahrenheit and the values

given are for mixtures in which the representatives of the hydrocarbon types boil within a narrow range, the difference in their boiling points being usually less than 10° F. The hydrocarbon for which the perfluorocarbons are selective, i. e., have the lowest critical solution temperatures, is written first in the left-hand column of Table 2.

TABLE 2

Selectivities of perfluorocarbons for hydrocarbons critical solution temperature differences

	Perfluoro-Methyl Cyclohexane	Perfluoro-Dimethyl Cyclohexane	Perfluoro-n-Heptane
Branched Chain Paraffin—Normal Paraffin.....	40	40	45
Normal Paraffin—Olefin.....	5	5	10
Normal Paraffin—Naphthene.....	35	30	40
Naphthene—Aromatic.....	85	65	75

Selectivities of perfluorocarbons for a particular hydrocarbon in a binary mixture not shown may be obtained by adding the tabulated values. For example, the selectivity of perfluoromethyl cyclohexane for a branched-chain paraffin from a mixture of that compound with an aromatic will be indicated by the sum of 40, 35 and 85, that is, by a critical solution temperature difference of 160° F.

From the tables it is seen that the perfluorocarbons may be advantageously employed as extractive solvents to remove minor amounts of paraffinic, olefinic and/or naphthenic hydrocarbons from a stock consisting predominantly of aromatic hydrocarbons. For example, the extract obtained by sulfur dioxide extraction of naphtha or kerosene contains minor amounts of non-aromatic hydrocarbons which may be removed from such extracts by a further extraction of the sulfur dioxide extract with a perfluorocarbon. Various highly aromatic cuts are separated from petroleum distillates for use as thinners or solvents or as base stocks in chemical synthesis. These aromatic cuts may be purified and their value for the intended use enhanced by extraction with a perfluorocarbon to remove non-aromatic constituents and separate a highly aromatic raffinate. For example, a highly aromatic xylene cut is separated from catalytically reformed naphtha to serve as a source of ortho xylene for oxidation to phthalic anhydride. The presence of minor quantities of non-aromatic hydrocarbons in this cut is undesirable and they may be extracted with perfluorocarbons. As a further example, a highly aromatic toluene cut may be separated from catalytically reformed naphtha. The minor proportion of non-aromatic hydrocarbons contained in the toluene cut may be extracted with a perfluorocarbon and a nitration grade toluene raffinate can be recovered.

Perfluorocarbons may be employed to separate diverse hydrocarbon mixtures such as petroleum fractions, shale oil fractions, or Fischer-Tropsch synthesis fractions, which have broad boiling ranges such as those of naphtha, gasoline, or kerosene, into a relatively saturated extract and a relatively unsaturated raffinate. In such cases a more complete separation may be obtained by distilling the petroleum fraction and separating a plurality of relatively narrow boiling cuts having a boiling range spread on the order of about 20—70° F. These cuts are then separately extracted with a perfluorocarbon solvent to sepa-

rate extracts soluble in the perfluorocarbon and raffinates insoluble therein. The extracts may be combined to constitute a relatively saturated overall extract and the raffinates may be combined to constitute a relatively unsaturated overall raffinate. Branched-chain paraffins are most readily removed from such cuts by the perfluorocarbon. A first extract fraction may be separated which comprises branched-chain paraffins. From the raffinate of the first extraction a second extraction may be made to separate a second extract fraction comprising normal paraffins and olefins, no attempt being made to separate these latter types. From the raffinate of the second extraction step a third extraction may be made to separate an extract comprising naphthenes and a final raffinate comprising aromatic hydrocarbons. The perfluorocarbons may be employed to effect the separation of acyclic and cyclic hydrocarbons by adjusting the solvent to oil ratio according to the character of the stock. In this case the solvent is employed in sufficient amount to extract the isoparaffins, normal paraffins and olefins leaving naphthenes and aromatics as the raffinate.

The perfluorocarbons may also be employed to separate hydrocarbon mixtures of less diverse composition than petroleum distillates. Hydrocarbon mixtures consisting essentially of only two hydrocarbon types may be separated. For example, the reaction product of a paraffin isomerization reaction may be extracted with a perfluorocarbon to remove the branched-chain isomers as an extract leaving relatively straight-chain hydrocarbons in the raffinate which may be recycled to the isomerization step.

The following examples illustrate the employment of the perfluorocarbons to separate hydrocarbon mixtures in the manner above described.

EXAMPLE 1.

A mixture of 53.7 volume per cent normal heptane and 46.3 volume per cent benzene was extracted with perfluoromethyl cyclohexane. An upper raffinate phase comprising hydrocarbons and a lower extract phase comprising perfluoromethyl cyclohexane and hydrocarbons were separated. The composition of the hydrocarbons contained in both phases was determined by analysis. The extraction coefficient, beta, was calculated according to the formula:

$$\text{Beta} = \frac{\text{Heptane in Extract} + \text{Benzene in Extract}}{\text{Heptane in Raffinate} + \text{Benzene in Raffinate}}$$

The amounts of benzene and heptane in the extract and raffinate were expressed in volume per cent on a perfluorocarbon-free basis. The value of the extraction coefficient was found to be 2.5.

EXAMPLE 2

A mixture of 21.7 volume per cent heptane and 78.3 volume per cent benzene was extracted with perfluoro-methyl cyclohexane. Phase separation, analysis, and calculation of the extraction coefficient were made as in Example 1. The extraction coefficient was found to be 2.3.

The examples illustrate the selectivity of the perfluorocarbons for the paraffinic component of a paraffin-aromatic mixture. This selectivity is opposite to that shown by such solvents as sulfur dioxide and furfural which selectively dissolve the aromatics from such mixtures.

The high liquid densities, 1.5–2.0 g./cc. of the perfluorocarbons facilitate phase separation in all of the liquid-liquid extractions above described.

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It has been found that hydrocarbons boiling above the boiling range of kerosene, that is, above about 550° F., may not readily be separated by extraction with perfluorocarbons due to the low solubilities of such hydrocarbons in perfluorocarbon solvents. Accordingly, it is preferred to treat petroleum distillates boiling in the boiling range of gasoline and kerosene with perfluorocarbon solvents to effect their separation according to the invention.

It is also preferred to employ perfluorocarbon solvents containing at least three and not more than twelve carbon atoms. Lighter perfluorocarbons have very low boiling points and require considerable pressures to maintain the desired liquid phase conditions in the extraction process. Perfluorocarbons containing more than twelve carbon atoms have reduced solubilities for the hydrocarbons so that the solvent-hydrocarbon ratio required in making separations becomes very high.

It may be seen from the examples that the extraction coefficients are not large, accordingly several stages of extraction may be needed and may be provided where a high degree of separation of the components of a hydrocarbon mixture is desired.

I claim:

1. The method of separating a petroleum distillate boiling in the boiling range of gasoline and kerosene and containing paraffinic, olefinic, naphthenic and aromatic hydrocarbons which comprises first extracting the distillate with a perfluorocarbon containing 3 to 12 carbon atoms to separate an extract comprising paraffins and olefins, and extracting the raffinate of the first extraction with a perfluorocarbon containing 3 to 12 carbon atoms to separate an extract comprising naphthenic hydrocarbons.

2. A method of separating components of a mixture of normally liquid cyclic and acyclic hydrocarbons boiling below 550° F. in which the cyclic hydrocarbons predominate which comprises contacting said mixture in the liquid phase with a perfluorocarbon containing 3-12 carbon atoms under conditions forming a two-phase system and selectively separating a solvent extract containing predominantly acyclic hydrocarbons.

3. A method of separating components of pe-

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roleum fractions boiling in the range of gasoline and kerosene which comprises contacting said fractions in the liquid phase with a perfluorocarbon containing 3-12 carbon atoms to produce a separation into two phases and selectively separating the perfluorocarbon extract phase containing predominantly acyclic hydrocarbons.

4. A method of separating components of a mixture of normally liquid aromatic and non-aromatic hydrocarbons boiling below 550° F. in which the aromatic hydrocarbons predominate which comprises contacting said mixture in the liquid phase with a perfluorocarbon containing 3-12 carbon atoms to produce a separation into two phases and selectively separating a perfluorocarbon extract phase containing predominantly non-aromatic hydrocarbons.

5. A method of separating components of a normally liquid hydrocarbon mixture boiling below 550° F. containing a minor proportion of paraffinic hydrocarbons which comprises contacting said mixture in the liquid phase with a perfluorocarbon containing 3-12 carbon atoms to produce a separation into two phases and selectively separating a perfluorocarbon extract phase containing a major proportion of paraffinic hydrocarbons.

6. A method of separating components of a mixture of normally liquid hydrocarbons boiling below 550° F. containing a minor proportion of branched chain paraffinic hydrocarbons which comprises contacting said mixture in the liquid phase with a perfluorocarbon containing 3-12 carbon atoms to separate a solvent extract containing a major proportion of branched chain paraffins.

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