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2,053,485

PROCESS FOR REFINING MINERAL OIL

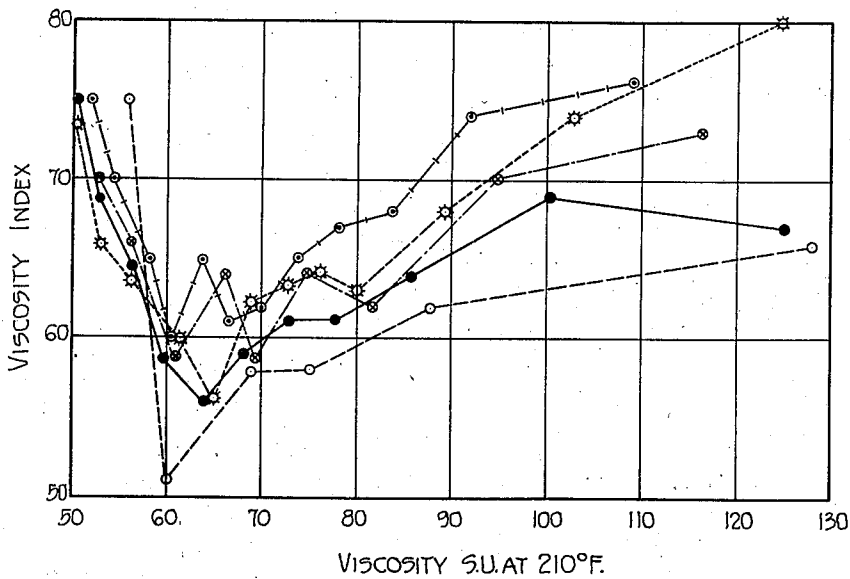
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SYMBOL	AUXILIARY SOLVENT
○—	Benzol
⊗—	Concentrated Bicyclic Extract
●—	α Methyl Naphthalene
⊕—	Benzol + Naphthalene (⊕)
⊗—	Benzol + Diphenyl + Naphthalene (⊗)

LEGEND:

(⊕) Containing 71% Benzol

(⊗) Containing 31% Benzol & 42% Diphenyl



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By their Attorney

[Signature]

UNITED STATES PATENT OFFICE

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PROCESS FOR REFINING MINERAL OIL

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20 Claims. (Cl. 196—13)

Our invention relates to a process for separating normally liquid hydrocarbon mixtures by extraction with selective solvents. More particularly, the invention relates to the improving of the extraction methods by the use of polycyclic aromatic hydrocarbons as an auxiliary solvent in connection with a selective solvent.

It is known that suitable selective solvents can be used to extract various types of hydrocarbon mixtures, such as crude petroleum oils, lubricating, transformer and spindle oils, heavy or light naphthas, etc., either natural or synthetic. The extraction process of our invention has as its main object an efficient separation of hydrocarbon mixtures into so called aromatic and non-aromatic groups of components. It consists, briefly, in bringing the hydrocarbon mixture into contact with a selective solvent in the presence of an effective quantity of polycyclic aromatic hydrocarbons, thereby causing two layers to form. The raffinate layer contains mainly the non-aromatic constituents of the mixture and/or certain impurities which may be present in mineral oils. Each of the layers may then be treated to separate its hydrocarbon portion from the solvents.

The use of benzol or toluol or similar monocyclic aromatic hydrocarbons as an auxiliary solvent or solvent diluent in extracting hydrocarbon mixtures is known, the advantage of such extraction processes being an improved efficiency of separation of the components of the mixture under suitable temperature conditions.

The present invention is based on the discovery that polycyclic hydrocarbons containing aromatic rings, and particularly bicyclic aromatic hydrocarbons are even more effective than monocyclic hydrocarbons when used as a solvent diluent in extracting hydrocarbon mixtures. As used in the present specification and claims, the terms "polycyclic hydrocarbons" and "polycyclic aromatic hydrocarbons" are used to designate compounds having an aromatic, i. e., a six membered ring, in addition to at least one other ring, which may or may not be an aromatic ring. Among such diluents may be mentioned, for example, among the bicyclic compounds: naphthalene, and its homologues, such as mono- or poly-alkyl naphthalenes, as α -methyl naphthalene, other mono- or poly-methyl naphthalenes, mono- or poly-ethyl naphthalenes, diphenyl, its homologues, such as ditolyl, mono- or poly-alkyl diphenyl or methyl- or poly-methyl, ethyl- or poly-ethyl diphenyls, diphenyl alkanes, such as diphenyl methane, diphenyl ethane, stilbene, tolane, etc., all partially hydrogenated or not; among the tricyclic compounds: anthracene and its homologues, as alkyl- or poly-alkyl anthracene, as methyl- or poly-methyl anthracene, ethyl- or poly-ethyl anthracene, phenanthrene and its homologues, such as

alkyl- or poly-alkyl phenanthrene, as retene, mono- or poly-methyl phenanthrene, triphenyl methane, triphenyl benzene; among other polycyclic compounds: indene, mono- or poly-alkyl indene, polyphenyl alkanes, dianthracene, etc., all partially hydrogenated or not; or mixtures of any of the above polycyclic compounds, or their solutions in aliphatic hydrocarbons, as light naphthas, and preferably in cyclic hydrocarbons, such as benzol or toluol. For example, such solutions may be used as: benzol and naphthalene; benzol and diphenyl; benzol, diphenyl and naphthalene; an aromatic portion of a mineral oil distillate containing considerable quantities of poly- or bicyclic aromatic hydrocarbons, such as an extract wherein bicyclic aromatic hydrocarbons have been concentrated beyond a certain critical concentration by intensive solvent extraction, etc. It should be noted, however, that while some of such solutions, like ordinary Edeleanu kerosene extracts, for example, may contain a certain quantity of bicyclic aromatics, this quantity is generally too small to be effective in causing an improvement in the efficiency of the solvent extraction, when the extract is substituted, for benzol as an auxiliary solvent.

Moreover, the effectiveness of such extracts, when they are used as solvent diluents, is usually greatly impeded by relatively high contents of aliphatic and naphthenic components. However, extracts can be subjected to further refining treatments, such as intensive solvent extraction, whereby their non-aromatic components are substantially removed and the concentration of the total and bicyclic aromatic hydrocarbons is made sufficiently high to make such treated extracts even more effective as solvent diluents than pure benzol, the latter being one of the most effective diluents among monocyclic aromatics. From experience it has been found that in order to be so effective such concentrated bicyclic extracts must contain at least 90% total aromatic components (preferably over 95%), of which at least an appreciable portion should be bicyclic aromatic hydrocarbons.

Since naphthalene, diphenyl, other polycyclic hydrocarbons, and many of their alkyl substituted derivatives boil within the range of 180°-300° C., it was often found particularly advantageous from the practical viewpoint to obtain the desired concentrated extracts from that portion of the hydrocarbon oil, which is usually known as kerosene distillate, and which boils substantially within the range of about 180° C.-300° C. It should be understood, however, that any mixed base or naphthenic base crude or cracked distillate or residue containing a substantial fraction boiling between about 180° C.-300° C. can be used as a source of the desirable concentrated bicyclic extract. Since the specific gravity of bicyclic aro-

matic hydrocarbons is substantially higher than the specific gravity of the monocyclic or aliphatic hydrocarbons boiling at the same temperatures, such concentrated bicyclic extracts would, due to their high total aromatic content, possess considerably higher specific gravity than pure benzol or ordinary "naphthenic" extracts obtained by customary methods of extraction. In general, it was found that the following properties usually must be present if a concentrated bicyclic extract derived from a hydrocarbon oil is to be equally or more effective than benzol when used as a solvent diluent:

Boiling range °C.....	180 -300
Gravity °A. P. I.....	8.0- 25.0
Total aromatics, by vol.....	90 -100%

As stated hereinbefore, the bicyclic aromatic diluents boiling above 300° C., may also be used, the above range stating only the preferred type of the diluent. The bicyclic aromatics may also be dissolved in non-aromatic hydrocarbons or other solvents to produce the auxiliary solvent of our invention. In this case the gravity and other characteristics will not necessarily fall within the limits recited, but will depend on the nature of the non-aromatic hydrocarbon used.

Where the term "concentrated bicyclic extract" is used in this specification, it is to be understood to include aromatic portions of mineral oil fractions containing effective concentrations of bicyclic aromatic hydrocarbons as discussed above and particularly the bicyclic concentrates possessing above mentioned physical and chemical properties.

Among the selective solvents which may be used singly or mixed as extracting agents in the refining of mineral oils or other hydrocarbon mixtures are sulfur dioxide, furfural, $\beta\beta'$ -dichloro-ethyl ether, acetone, nitromethane, nitrobenzene, propionitrile, dimethyl sulphate, dimethyl sulphite, methyl formate, phenols, aromatic or aliphatic amines, pyridine, isoquinoline, quinoline, quinaldine, picolines, lutidines, and other substantially pure or industrial solvents, such as petroleum nitrogen bases, various alcohols, esters, etc. These specific solvents represent, however, only typical examples of a large number of known selective solvents capable of separating mineral oils or hydrocarbon mixtures into aromatic and non-aromatic components (sometimes referred to as naphthenic and paraffinic or as non-paraffinic and paraffinic), which solvents are intended to be within the scope of this invention. These main solvents used for extracting hydrocarbon mixtures have the common characteristic that, at the extraction temperatures, they are only partly miscible with the mixture being extracted and act as preferential solvents for both non-paraffinic hydrocarbons and polar organic compounds containing sulfur, nitrogen, oxygen, etc. With the paraffinic hydrocarbons they are miscible only to a lesser extent.

Likewise, the auxiliary solvents, whose presence in the extraction mixtures improves the efficiency of extraction, are merely represented by the specific polycyclic hydrocarbons, or the various mixtures or solutions recited, and may be selected from a number of other polycyclic hydrocarbons containing one six membered ring and at least one additional ring which may or may not be six membered, which produce the desired effect, and which can be separated relatively easily from the material being treated, for example, by dis-

tillation, and have no detrimental effect on the refined products.

It will be understood, therefore, that the present invention is to include within its scope the extraction processes for extracting mineral oils or other hydrocarbon mixtures employing a selective solvent in the presence of an auxiliary solvent having a high content of polycyclic aromatic hydrocarbons.

Generally speaking, the efficiency of extraction is determined by the solvent power and the selectivity of the solvent (or solvent mixture) with regard to the components of the mixture being extracted. This efficiency may be expressed in terms of the quantity or quality of the raffinate.

Thus, if the masses or volumes of the relative yield and of the main or selective solvent are kept constant, the quality of the raffinate may be taken as a measure of the efficiency of the extraction.

Alternatively, it may be desired to produce the maximum quantity of the raffinate of a specified purity, while keeping the mass or volume of the main or selective solvent constant. Under these conditions the quantity of the raffinate may be taken as a measure of the efficiency.

The efficiency of the various extractions may also be measured by comparing the extent to which the solvent is conserved when the same raffinate is made with or without the use of the auxiliary solvent described in this specification.

By conducting the extraction in accordance with the present invention, i. e., by using a main selective solvent in the presence of polycyclic aromatic hydrocarbons, it becomes possible to improve the quality and/or quantity of the mineral oil raffinate, and/or to conserve the main solvent.

The method of this invention also makes it possible to improve mineral oils having relatively low contents of naphthenic or aromatic components, which contents it is difficult or impossible to reduce by extraction with the main solvent alone or in the presence of a monocyclic aromatic diluent only, like benzol.

The increased extraction efficiency of the mixed solvent process employing polycyclic aromatics in the auxiliary solvents, as compared with the efficiency of the corresponding single solvent process or with the mixed solvent process employing only benzene or compositions other than those of the present invention for the auxiliary solvent, is apparently due to the favorable effect of the mixed solvent of this invention on the distribution ratios of the nonparaffinic and paraffinic components of the oil being treated in the extract and raffinate phases. In other words, the relative content of the preferentially soluble components in the selective solvent is increased in the presence of the auxiliary polycyclic aromatics, so that when such a mixed solvent is used it becomes possible, under suitable temperature conditions, to produce a greater quantity of raffinate from a given quantity of oil, and this raffinate often will be richer in paraffinic components than it would have been possible to obtain if the extraction were conducted in the absence of these polycyclic aromatics.

Since the addition of these auxiliary solvents will often produce a solvent mixture possessing a greater solvent power for oils (paraffinic as well as non-paraffinic) than the main solvent, the relative selectivity of the solvent mixture and the yield of the raffinate may, under certain circum-

stances, be impaired, but a raffinate of greater purity will be produced. Also, by suitable lowering of the temperature of extraction the impaired selectivity will be restored, thereby increasing the yield of the raffinate and further increasing the efficiency. In general, the extraction temperature is so selected as to create optimum conditions from the viewpoints of economy of operation, yield, purity of product, conservation of solvents, etc.

The manipulative details of practicing the invention may vary widely to suit local conditions and specific properties of the substances used in each case. For example, in a so-called batch extraction system the auxiliary solvent may be mixed with the hydrocarbon mixture undergoing treatment either before or at the time the hydrocarbon mixture is contacted with the main solvent; or the whole or a part of the auxiliary solvent may be mixed with the main solvent prior to contacting it with the hydrocarbon mixture. However, in its preferred form, the process is carried out by conducting the mixed solvent, i. e. a selective solvent containing polycyclic aromatics, countercurrently to and in contact with the hydrocarbon mixture being treated.

It has heretofore been proposed to dilute certain lubricating oils with low boiling hydrocarbons and/or low boiling hydrocarbon raffinates or extractives prior to treatment with sulfur dioxide for the purpose of reducing the viscosity of the oil and of obtaining a more facile separation of the extract and raffinate layers. The dilution of the phases was the only effect previously expected from the use of light diluents. For that reason the diluents selected for this purpose were either entirely free of bicyclic aromatic hydrocarbons, such as low boiling distillates of gasoline type, or contained only ineffective amounts of bicyclic aromatic hydrocarbons, like unextracted kerosene distillates or ordinary Edeleanu kerosene extracts or raffinates.

It was recognized that, when such diluents are used for reducing the viscosity of an extraction mixture, particularly in so called batch processes, it is immaterial whether the diluent is added either to the oil or the solvent, or to the mixture of the two.

However, in the present method of extraction, where the solvent diluent is used to cause a more advantageous separation of paraffinic and non-paraffinic oil components in the raffinate and extract phases, it is preferable to employ countercurrent method of extraction, in which case introducing a diluent of this invention into an extraction zone together with the solvent, or, in general, near the point where the raffinate phase is withdrawn from the extraction zone, becomes essential.

In practicing this invention, the main solvent usually together with the auxiliary solvent, or diluent, is caused to pass countercurrently to and in contact with the hydrocarbon mixture being extracted through a mixing-settling or extraction zone, which may consist of a contact column or a series of alternate mixing and phase-separating devices. The resulting extract and raffinate phases are separated, usually by gravity, or centrifuging, and withdrawn at the opposite ends of the zone; the main and auxiliary solvents are then removed from each of the phases, either together or in separate stages, by any suitable means, as by distillation, absorption, etc. The recovered solvents may be reused repeatedly. The auxiliary solvent or a portion thereof may be left

in the raffinate or in the extract, if it improves the quality of the product e. g., if it enhances its anti-knock property, as in the case of extracting gasoline.

Sometimes it may be advantageous to withdraw at least a portion of the extract phase at an intermediate point of the extraction zone (e. g., between two adjacent phase-separating and mixing devices), remove at least a portion of the auxiliary solvent from the withdrawn phase and return the residual portion of the withdrawn phase to the extraction zone near the point where the said phase was withdrawn. By repeating this operation at successive points of the extraction zone, the effect of having a progressively decreasing concentration of the auxiliary solvent in the direction of flow of the extract phase can be obtained, which often may further improve the extraction efficiency of our process.

While it is practical and may be desirable in some cases to carry out the extraction of mineral oils by means of the main and auxiliary solvents at such temperatures, at which the auxiliary solvent is only partially soluble in either the main solvent or the oil being extracted, or in both, it should be noted that the extraction process of this invention is usually operated at the temperatures at which the auxiliary solvent becomes miscible in all proportions with either the main (selective) solvent, or the oil, or both.

The process of this invention is effective not only with oils which may be viscous at extraction temperatures, but also with hydrocarbon mixtures which are easy flowing or non-viscous at such temperatures, e. g. gasolines. In many cases, the oils which may be regarded as being viscous at ordinary temperatures (say, over 80 seconds at 100° F. Saybolt Universal) would become easy flowing at the slightly elevated temperatures of extraction with furfural, for example, or phenol, or some other selective solvent, so that their dilution for the purpose of reducing their viscosity would be unnecessary. The use of auxiliary solvent, or diluents, in these cases would serve only the purpose of improving the extraction efficiency through the effect of such diluents on the distribution of the components being extracted between the extract and raffinate phases, no dilution being necessary. Bicyclic aromatic diluents, preferably such as those boiling between about 180° C.-300° C., may be used with advantage in extracting oils which are not viscous at the extraction temperature, such as gasolines, or light naphthas boiling at temperatures below those of said diluents.

In order to make the details and nature of the invention more fully understood, the following examples and description of the auxiliary solvents suitable for our new process are set forth.

Example I

A Coalinga bulk distillate was extracted with 200% SO₂ and a primary raffinate obtained, having a gravity of 23° A. P. I., and a viscosity of 457 seconds S. U. at 100° F. Three samples of this primary Edeleanu raffinate were refined separately with liquid SO₂, using as the auxiliary solvent: benzol for the first sample, a concentrated bicyclic extract of the following characteristics: gravity 18.1° A. P. I., boiling range 198-275° C., and containing 47% by wt. bicyclic aromatics, for the second sample, and a mixture of 31% benzol, 42% diphenyl and 27% naphthalene for the third sample. The refining treatment consisted of: (1) Two extractions with

200% of a mixture of 75 parts of SO₂ and 25 parts of the auxiliary solvent: (2) one extraction with 100% of mixture of 65 parts of SO₂ and 35 parts of the auxiliary solvent; the percentages express quantities of mixed solvents based on the primary Edeleanu raffinate. The treating temperature was between 45° and 50° F. These finished raffinates obtained in each treatment were then fractionated, and the viscosity index for each cut determined. From these cuts an oil was blended to meet S. A. E. 40 viscosity specifications. The viscosity indices of S. A. E. 40 motor oil blends are given in the table:

Auxiliary solvent	Bicyclics in auxiliary solvent	V. I. of S. A. E. 40 motor oil from raffinate	Yield of S. A. E. 40 motor oil on Coalinga distillate
	Percent		
Benzol	0	62	23.9
Concentrated bicyclic extract	47	64	23.8
Benzol+naphthalene+diphenyl	69	67	24.0

These results indicate that the substitution of concentrated bicyclic extract for benzol produces a material increase in the yield when the quality is unaltered. If the extraction with concentrated kerosene extract as a diluent were carried out under conditions to produce a lower yield, the quality of the product would be materially increased.

When using the benzol-naphthalene-diphenyl mixture as a diluent, such an improvement in the quality was achieved.

Example II

A Coalinga bulk distillate was treated twice with 200% SO₂. Five samples of the resulting primary raffinate were separately treated, each being successively subjected to the same steps, but using different auxiliary solvents in each instance, these solvents being, respectively, (a) benzene; (b) concentrated extract used in Example I; (c) α methyl naphthalene; (d) a mixture containing 71% benzol and 29% naphthalene; (e) a mixture containing 31% benzol, 42% diphenyl, and 27% naphthalene. The treatment steps were (1) two extractions were 200% of a mixture of 75 parts of SO₂ and 25 parts of auxiliary solvent; (2) one extraction with 100% of a mixture of 67 parts of SO₂ and 33 parts of the auxiliary solvent.

The resulting raffinate obtained in each treatment was fractionated, and the viscosity index for each cut determined. The viscosity indices were plotted, and are shown in the drawing. The comparable yields of S. A. E. 40 blends based on distillate for each of the auxiliary solvents were as follows:

	Yield, vol.	V. I. of S. A. E. 40 blend
	Percent	
(a) Benzol	23.9	62
(b) Concentrated bicyclic	23.8	64
(c) α Methyl naphthalene	24.1	63
(d) Benzol and naphthalene	18.1	67
(e) Benzol, diphenyl and naphthalene	24.0	66

These data demonstrate that the degree of refinement and/or the yield are substantially improved by the use of the auxiliary solvents which contain bicyclic aromatics. In every case the viscosity indices of the valuable cuts above 60

seconds, S. U. at 210° F. have been improved by the substitution of the diluents containing polycyclic aromatics for benzol, and the yields were improved in every case, except when the benzol-naphthalene mixture was used, which, however, resulted in an unusually high V. I. product.

The general method of refining mineral oils as illustrated by the above examples was found very useful in many cases. In general, it consists of subjecting an oil to extraction with a selective solvent to remove the most soluble oil components, and then refining the resulting raffinate, or the raffinate phase (oil plus solvent), by extracting it with the same or different solvents in the presence of a polycyclic aromatic diluent, as described.

While we have illustrated our invention by using certain specific auxiliary solvents, our invention is not limited thereto. Any hydrocarbon mixture, a substantial portion of which consists of polycyclic aromatic hydrocarbons, can be used as auxiliary solvent.

The amounts of the auxiliary solvent necessary to improve the extraction efficiency will vary with the nature of the oil being extracted, the main solvent used, etc., and no general figure can be stated, although it was found from experience that the ratio of the selective solvent to the diluent usually should be between one and four. By the term "effective quantity", as used in the claims, we mean such a quantity of polycyclic aromatic hydrocarbons as will substantially improve the extraction characteristics for the particular conditions encountered, it being understood that this quantity may be determined readily by one skilled in the art. More specifically, when such polycyclics are used alone or in mixtures with diluents other than and less effective than benzol this term may designate such concentrations of polycyclics in the extraction mixtures which improve the efficiency of extraction beyond that attainable with benzol.

We claim as our invention:

1. In an extraction process for separating liquid hydrocarbon mixtures into their component groups, the steps of extracting the mixture with a selective solvent in the presence of an effective quantity of a polycyclic aromatic hydrocarbon diluent to produce two liquid phases, and subsequently separating said liquid phases.

2. The process of claim 1, wherein the polycyclic aromatic hydrocarbons are selected from the group: naphthalene, alkyl naphthalenes, diphenyl, alkyl diphenyls, diphenyl alkanes, anthracene, alkyl anthracenes, phenanthrene, alkyl phenanthrene, triphenyl benzene, triphenyl alkanes, indene, alkyl indenenes, and partially hydrogenated homologues of said compounds.

3. In an extraction process for separating liquid hydrocarbon mixtures into their component groups, the steps of extracting the mixture with a selective solvent in the presence of an effective quantity of a bicyclic aromatic hydrocarbon diluent to produce two liquid phases, and subsequently separating said liquid phases.

4. The process of claim 3, wherein the diluent is a mixture selected from the group consisting of a mixture of benzol, diphenyl and naphthalene, a mixture of benzol and naphthalene, a mixture of benzol and α methyl naphthalene.

5. In an extraction process for separating liquid hydrocarbon mixtures into their component groups, the steps of extracting the mixture with a selective solvent in the presence of an aro-

matic hydrocarbon diluent having a gravity between 8.0° A. P. I. and 24.0° A. P. I. and boiling between about 180° C. and 300° C. to produce two liquid phases, and subsequently separating said liquid phases.

6. A process for extracting a liquid hydrocarbon mixture containing aromatic constituents comprising flowing said mixture countercurrently to and in contact with a stream of a selective solvent containing an effective quantity of polycyclic aromatic hydrocarbons to produce two liquid phases, and subsequently separating said liquid phases.

7. A process for refining petroleum lubricating oil comprising extracting the oil with a solvent selected from the group: liquid sulfur dioxide, dichlorethylether, acetone, nitromethane, nitrobenzene, propionitrile, dimethyl sulphate, dimethyl sulphite, methyl formate, phenols, aromatic and aliphatic amines, nitriles and thionitriles, pyridine, quinolines, picolines, lutidines, and petroleum nitrogen bases, in the presence of an aromatic diluent containing an effective quantity of polycyclic aromatic hydrocarbons to produce two liquid phases, and subsequently separating said liquid phases.

8. A process for refining petroleum lubricating oil comprising extracting the oil at least once with a selective solvent to produce a raffinate containing smaller amounts of aromatics, and then further reducing the aromatic content of said raffinate by extracting said raffinate with a selective solvent plus an aromatic diluent containing an effective quantity of polycyclic aromatic hydrocarbons to produce two liquid phases, and subsequently separating said liquid phases.

9. A process for refining hydrocarbon mixtures comprising extracting said mixture with a selective solvent in the presence of an aromatic diluent containing an effective quantity of polycyclic aromatic hydrocarbons, said diluent being present in such amounts that the ratio of the main solvent to the diluent is between one and four to produce two liquid phases, and subsequently separating said liquid phases.

10. The process according to claim 9 in which the aromatic diluent is the aromatic portion of a mineral oil distillate having a gravity between 8.0° A. P. I. and 24.0° A. P. I. and boiling between about 180° C. and 300° C.

11. The process according to claim 9 in which the polycyclic hydrocarbons are selected from the groups naphthalene, alkyl naphthalenes, diphenyl, alkyl diphenyls, diphenyl alkanes, anthracene, alkyl anthracene, phenanthrene, alkyl phenanthrene, triphenyl benzene, triphenyl alkanes, indene and alkyl indenenes, and partially hydrogenated homologues of said compounds.

12. A process for refining a hydrocarbon mixture containing aromatic constituents comprising extracting said mixture at least once with a selective solvent to produce a primary liquid raffinate containing smaller amounts of aromatics than the original mixture, and treating said primary raffinate at least once with a selective solvent containing an aromatic diluent containing an effective quantity of polycyclic aromatics, the ratio of the selective solvent to the aromatic diluent being between one and four, to produce a secondary raffinate having a lower aromatic content than said first raffinate.

13. The process according to claim 12, in which the aromatic diluent is the aromatic portion of a mineral oil distillate having a gravity between

8.0° A. P. I. and 24.0° A. P. I. and boiling between about 180° C. and 300° C.

14. In an extraction process for treating hydrocarbon mixtures the steps of counterflowing under extracting conditions a stream of the hydrocarbon mixture and concurrent streams of a selective solvent and a diluent containing an effective quantity of polycyclic aromatic hydrocarbons, thereby producing liquid extract and raffinate phases, and separating said two phases.

15. In an extraction process for treating hydrocarbon mixtures the steps of introducing at one point of an extraction zone the said mixture, introducing at another point of the zone a selective solvent containing an effective quantity of polycyclic aromatic hydrocarbon, counterflowing the mixture and the solvent through the zone while in contact with each other, thereby producing liquid extract and raffinate phases, and separating said two phases.

16. In a process of extracting hydrocarbon mixtures by forming two liquid phases by means of a selective solvent and benzol the steps of carrying out said extracting process in the presence of an effective amount of polycyclic aromatic hydrocarbon.

17. In a process of extracting hydrocarbon mixtures by forming two liquid phases by means of a selective solvent diluted with benzol the steps of carrying out said extracting process in the presence of an effective amount of polycyclic aromatic hydrocarbon.

18. In an extraction process for treating hydrocarbon mixtures, the steps of introducing at one point of an extraction zone the said mixture, introducing at another point of the zone a selective solvent containing benzol and an effective amount of polycyclic aromatic hydrocarbon, counterflowing the mixture and the solvent through the zone while in contact with each other, thereby producing liquid extract and raffinate phases, and separating said two phases.

19. In an extraction process for treating hydrocarbon mixtures, which comprises the steps of introducing at a first point of an extraction zone the said mixture, introducing at a second point of the zone a selective solvent, counterflowing the mixture and the solvent through the zone in contact with each other, thereby producing liquid extract and raffinate phases, withdrawing the raffinate phase at a point near said second point and withdrawing the extract phase at a third point of the zone, the improvement which consists of introducing near said second point of the zone a diluent containing an effective quantity of polycyclic aromatic hydrocarbons.

20. In an extraction process for treating hydrocarbon mixtures, the steps of counterflowing in an extraction zone a stream of the hydrocarbon mixture and a stream of a selective solvent and a diluent containing an effective quantity of polycyclic aromatic hydrocarbons thereby producing an extract and a raffinate phase withdrawing a portion of the extract phase at least at one intermediate point of the extraction zone, removing a portion of the diluent from the withdrawn extract phase, and returning the residual portion of the extract phase to the extraction zone at a point near the point at which said phase was withdrawn, and separating the extract and raffinate phases.

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