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EXTRACTION PROCESS FOR SEPARATING A HYDROCARBON FROM A MIXTURE THEREOF EMPLOYING PYRIDINE OXIDE OR ALKYL PYRIDINE OXIDE

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This invention relates to a process for the partial or complete resolution of hydrocarbon mixtures into their components by selective extraction thereof with a solvent selected from the class consisting of pyridine oxide and alkylpyridine oxides or mixtures thereof. In one particular aspect, this invention relates to the selective extraction of aromatic hydrocarbons from mixtures of aromatic and aliphatic hydrocarbons which are commercially produced as processed or unprocessed petroleum oils or mineral oils, oil fractions containing neutral organic oxygen compounds (derived from the Fischer-Tropsch and similar syntheses), coal tar oils, shale oils and the like. Various aromatic hydrocarbons are of value as solvents and for the preparation of resins, plasticizers and various other chemical derivatives; in addition, their removal from various hydrocarbon stocks containing the same may be desired in order to prepare partially dearomatized hydrocarbon stocks for thermal or catalytic cracking, for hydrogenation operations, for use as heater oils and for other purposes.

With the commercial development of new processes for producing aromatic hydrocarbons boiling within the gasoline boiling range by cyclization-dehydrogenation of paraffinic hydrocarbons and by the dehydrogenation of cycloalkanes there has come an increased demand for processes to separate and concentrate the aromatic hydrocarbons thus produced. Thus, with the commercial development of such processes as hydroforming, platinum catalyst reforming of naphthas, and the like, a tremendous potential has been created for the production of nitration-grade aromatics such as benzene, toluene and xylenes for use by both the petroleum and chemical industries.

It is an object of my invention to provide a process for the selective extraction of hydrocarbon mixtures with specified novel solvents. Another object of my invention is to provide the art of selective extraction of hydrocarbon mixtures with novel solvents, viz. pyridine oxide and alkylpyridine oxides. A further object of my invention is to provide for the employment of new solvents in a process for the selective extraction of aromatic hydrocarbons from homogeneous liquid mixtures thereof with aliphatic hydrocarbons, particularly saturated hydrocarbons. A further object is to provide processes for the concentration and purification of aromatic hydrocarbons, particularly those containing not more than about 10 carbon atoms per molecule. An additional object is to provide a process for the selective extraction of aromatic hydrocarbons from mixtures thereof with olefinic hydrocarbons. Yet another object is to provide a process for the selective extraction of olefinic hydrocarbons from saturated hydrocarbons. Other objects are to provide processes for the selective extraction of isoparaffinic and cycloparaffinic hydrocarbons from the normal paraffins. One more object is to provide a process for the selective extraction of cyclic olefins from acyclic olefins, for example, the selective extraction of cyclohexene from mixtures thereof with n-hexene. A further

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object of this invention is to provide a process for the separation of close-boiling or azeotropic mixtures of aromatic hydrocarbons with saturated hydrocarbons by extraction or extractive distillation with pyridine oxide or alkylpyridine oxides. Another object is to provide a process for refining hydrocarbon oils by extraction with novel solvents. These and other objects of my invention will become apparent from the ensuing description thereof.

Pyridine oxide has the structural formula



and alkylpyridine oxides contain nuclear C-alkyl groups, e. g. as in the N-oxides, derived from the picolines, lutidines, collidines, methylethylpyridines (especially 2-methyl-5-ethylpyridine), propylpyridines, butylpyridines and other homologs of pyridine.

Pyridine oxide and alkylpyridine oxides supercool readily and can be obtained and employed in selective extraction as liquid materials at temperatures well below the melting points of the pure compounds, due to supercooling, the presence of extracted hydrocarbons in the solvents and, if desired, by the addition of auxiliary solvents which can be employed to lower the melting point of the pure solvents substantially. The oil to be extracted can be mixed with solid pyridine oxide, which selectively absorbs the most polar constituents of the feed and liquefies in the process to produce a distinct extract phase.

Under otherwise constant operating conditions (temperature, ratio of solvent to feed, extraction temperature, molecular weight of the feed stock, etc.) the solvent power of my novel solvents increases through the series: normal paraffins, isoparaffins, cycloparaffins, acyclic olefins, non-conjugated diolefins, cyclic olefins, conjugated diolefins, aromatics and aromatics containing unsaturated substituents. In general, hydrocarbons of mixed type, for example, alkyl aromatics, are absorbed in the solvents of this invention to a degree intermediate to the degree of solution of the pure structure components (unsubstituted aromatics and paraffins).

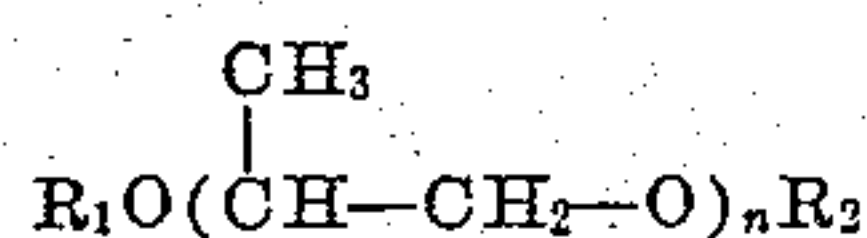
In general, extraction operations can be conducted at temperatures between about 0° C. and about 150° C., more or less, depending upon the particular charging stock, the particular solvent or solvents, the solvent:feed ratio, the number of extraction stages, the degree of extraction which is sought, the proportions of auxiliary solvents (if any), etc., as will be apparent to one skilled in the art. Usually liquid-liquid extraction is effected at temperatures between about 30° C. and about 150° C. and in the extraction of naphtha boiling range stocks, I prefer to employ temperatures between about 40° C. and about 80° C. Generally, the selection of a suitable extraction temperature is not critical.

The ratio of solvent to hydrocarbon feed stock, in liquid extractions, must be sufficient to exceed its solubility under the extraction conditions in said feed stock in order to form two distinct liquid phases, viz. a raffinate phase containing little or no solvent and an immiscible extract phase comprising the amine oxide and extracted hydrocarbons. Generally, I may employ between about 0.5 and about 50 volumes of solvent per volume of hydrocarbon charging stock. Ordinarily, I prefer to employ between about 1 and about 20 volumes of solvent per volume of feed stock, especially in the treatment of naphtha boiling range stocks (about 400° F. end-point). Sufficient pressure is maintained within the extraction zone to prevent substantial volatilization of the hydrocarbon charging stock or solvent under the liquid-liquid extrac-

tion conditions. It is obvious that pressure and temperature are related variables in the extraction process. Usually pressures within the range of about 0 to about 100 p. s. i. are sufficient, it being appreciated that the particular pressure which is required in a given case can be determined readily by experiment.

Any means of separating extracted materials from the extract phase and of recovering solvent therefrom may be employed. Thus under certain conditions, it may be desirable to distill extracted materials from a relatively involatile solvent or to wash them out of the extract layer with a paraffin hydrocarbon having a different boiling point. Also, the amine oxide solvents may in some instances be recovered from the extract layer by crystallization or washing with a solvent which is highly selective therefor, such as cold water, acetone, ethers, etc. The amine oxide solvents hydrate readily, but they can easily be dehydrated, e. g. by azeotropic distillation with benzene, and returned for use in the extraction process.

It may be desirable to employ diluents or auxiliary solvents in specific cases in order to modify solvent selectivity, to lower solvent melting point (thereby permitting extraction to be effected at relatively low temperatures, e. g., well below the melting point of the solvent) or for other reasons. The amount of auxiliary solvent can be selected with reference to specific cases; ordinarily, between about 1 and about 20 weight percent or even more, based on the principal solvent, may be employed. The auxiliary solvent should be miscible to the desired extent with the principal solvent, and should preferably be a neutral compound. As examples of auxiliary solvents which may be employed, one may mention the sulfolanes, for example, 2,4-dimethylsulfolane, 2,3-dimethylsulfolane and the like; various nitriles such as acetonitrile, bis-2-cyanoethyl ether and the like; various ethers such as diethyl ether, methyl-tert-butyl ether; glycols or their ethers having the structure $R_1O(CH_2CH_2O)_nR_2$ and



wherein R_1 and R_2 are hydrogen or alkyl groups and n is an integer having a value between 1 and 3, inclusive, tetrahydrofuran and the like; halogenated hydrocarbon solvents such as chloroform, carbon tetrachloride, ethylene dichloride, ethylene dibromide, trichloroethane, tetrachloroethane and the like; esters of carbonic acid, monocarboxylic acids, and dicarboxylic acids, for instance, diethyl carbonate, bis-2-hydroxyethyl carbonate, bis-2-chloroethyl carbonate, bis-2-methoxyethyl carbonate, ethylene carbonate, n-butyl formate, methyl furoate, dimethyl oxalate, diethyl succinate, dimethyl phthalate, dimethylisophthalate, and the like; neutral organic nitrogen compounds such as N,N-dialkyl formamides (particularly dimethyl formamide), dimethyl hydantoin and the like, nitro aromatics such as nitrobenzene and the like; ketones, for example, acetone, methyl ethyl ketone, methyl isobutyl ketone and the like; aldehydes, for example, furfural, crotonaldehyde and the like; butyrolactone, butyrolactam, etc.

Anti-solvents or diluents may also be employed in the practice of the present invention. Thus, diluents such as saturated hydrocarbons, perfluorocarbons, perfluoroamines, perfluoroethers, etc. may be added to the feed stock to be dearomatized or introduced directly into the extraction zone.

In the process of the present invention the selective solvent is employed as a liquid, melt or solution and the feed stock may be charged to the process as a liquid or solution, or, in some instances, as vapors (extractive distillation). In extractive distillation, the temperature should be between the dew point of the hydrocarbon mixture and about 240° C. and contacting of the liquid solvent and feed vapors is usually countercurrent.

Numerous hydrocarbon oil fractions derived from pe-

troleum, coal, shale, etc., are known to contain aromatic hydrocarbons and organic sulfur compounds whose removal is sought in order to produce refined hydrocarbon oils. Such oils may boil within the boiling range of (and the oils may be generally characterized as) gasoline or naphtha, cracked naphthas, coke still naphthas, kerosene, virgin gas oil, cracked gas oil, hydroformer bottoms, heater oil, furnace oil, diesel fuel, transformer oil, crude oil, reduced crude oil, vis-broken crude oil, lubricating oil distillates, etc.

The present process may also be applied to the refining of various coal tar fractions and coal tar distillates, or of neutralized Fischer-Tropsch process fractions. In the refining of oil fractions the present refining agents serve not only to effect selective extraction of aromatic hydrocarbons (and olefins, to some extent) but also to remove sulfur compounds, oxygen compounds and nitrogen compounds. It should be understood that the above specific examples of charging stocks which may be refined in accordance with the present invention are illustrative only and are not intended to delimit the field of applicability of the process of the present invention.

Other applications of the extraction process of my invention are in the selective extraction of normally gaseous olefins or diolefins from their mixture with normally gaseous paraffins, for example the selective extraction of ethylene from gaseous hydrocarbon streams containing ethane and methane, hydrogen, etc., the selective extraction of propylene from propylene-containing gas streams and the like. My invention is likewise applicable to the selective extraction of acetylene from gas mixtures containing the same and methane, hydrogen, ethane, ethylene, etc. By the employment of the extraction or absorption process of the present invention, it is possible to produce normally gaseous unsaturated hydrocarbons of high concentration or purity, which is deemed to be extremely desirable in the further treatment or chemical conversion of said hydrocarbons.

The present invention can be carried out in batch, continuous or semi-continuous operating cycles, and in one or more actual or theoretical stages, employing contacting and separation equipment such as has heretofore been employed in the selective solvent refining of petroleum stocks. Various types of liquid-liquid extraction operations and suitable extraction equipment are described, for example, in "Chemical Engineers' Handbook" (McGraw-Hill Publishing Co., Inc., N. Y., 1950), pp 716 ff. and 747 ff. It should be understood that the specific equipment employed forms no part of the present invention and that any equipment adaptable for the purposes of contacting the solvent with the hydrocarbon charging stock and thereafter separating an extract phase from the refined charging stock can be employed for the purposes of the invention.

Pyridine oxide exhibits enormous selectivity for the selective extraction of gasoline boiling range aromatic hydrocarbons from associated aliphatic hydrocarbons; coupled with this high selectivity is a surprisingly high total solvent capacity. Both of these characteristics render this solvent extremely attractive for large scale usage. Coupled with the above-mentioned desirable solvent characteristics are the further desirable characteristics that pyridine oxide forms a low viscosity liquid which can be contacted thoroughly with the hydrocarbon and forms a sharp interface during liquid-liquid extractions.

The following table shows the results of the extraction of a 50 volume percent n-heptane-50 volume percent toluene feed with pyridine oxide and 2-picoline oxide, respectively. The table also affords a comparison of the efficiency of these solvents with diethylene glycol, which enjoys large commercial usage for the selective extraction of aromatics from naphtha fractions produced by catalytic reforming operations. Single-stage extractions were effected with amine oxide solvent:hydrocarbon feed ratio of one at 30° C. Diethylene glycol was employed in the

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same ratio to feed at 40° C. The β values were calculated from the following equation:

$$\beta = \frac{\text{molar ratio of toluene/n-heptane in extract phase}}{\text{molar ratio of toluene/n-heptane in raffinate phase}}$$

The symbol β is the so-called "selectivity factor," corresponding to the well known relative volatility or alpha factor in distillation processes.

Solvent	Extract, volume percent of feed	Volume percent toluene in extract	Volume percent toluene extracted	β
Pyridine oxide.....	18	94	30	17
2-Picoline oxide.....	44.5	81	63	8.3
Diethylene glycol.....	10.6	90	19.1	10.8

The foregoing examples have illustrated specific aspects of my invention, which is not limited thereto. The extraction process of the present invention is readily applicable to the separation of hydrocarbon mixtures and hydrocarbon types not specifically illustrated in the foregoing examples, e. g., the selective separation of olefins from aromatics, naphthenes from paraffins, naphthenes from aromatics, olefins from saturated hydrocarbons, naphthenes from paraffins, cyclo-olefins from acyclic olefins, mono-olefins from conjugated diolefins, of conjugated diolefins from non-conjugated diolefins, of diolefins from aromatics, etc.

Having thus described my process, what I claim is:

1. A process for the selective extraction of an aromatic hydrocarbon from a liquid hydrocarbon mixture containing the same and an aliphatic hydrocarbon, which process comprises contacting said hydrocarbon mixture with a solvent selected from the group consisting of pyridine oxide and mono- and poly-alkylpyridine oxides in which the alkyl groups are lower alkyl up to and including butyl in an amount sufficient at least to form a distinct liquid phase, and separating an extract phase comprising said solvent and said aromatic hydrocarbon.

2. A process for the selective extraction of an aromatic hydrocarbon from a liquid hydrocarbon mixture containing the same and an aliphatic hydrocarbon, which process comprises contacting each volume of said hydrocarbon mixture in the liquid condition with between about 0.5

and about 50 volumes of a solvent selected from the group consisting of pyridine oxide and mono- and poly-alkylpyridine oxides in which the alkyl groups are lower alkyl up to and including butyl at a temperature between about 0° C. and about 150° C., and separating a raffinate phase from an extract phase comprising said solvent and said aromatic hydrocarbon.

3. The process of claim 2 wherein said hydrocarbon mixture boils within the gasoline boiling range.

4. The process of claim 2 wherein said hydrocarbon mixture comprises essentially monocyclic aromatic hydrocarbons containing not more than 10 carbon atoms per molecule and saturated hydrocarbons.

5. A process for the selective extraction of an aromatic hydrocarbon from a naphtha fraction containing the same, which process comprises contacting said naphtha in the liquid condition with a solvent selected from the group consisting of pyridine oxide and mono- and poly-alkylpyridine oxides in which the alkyl groups are lower alkyl up to and including butyl in an amount sufficient at least to form a distinct liquid phase, separating a raffinate phase from an extract phase comprising said solvent and said aromatic hydrocarbon, and distilling said aromatic hydrocarbon from said extract phase.

6. The process of claim 5 wherein the extraction is conducted at temperatures between about 0° C. and about 150° C.

7. The process of claim 5 wherein said solvent is a picoline oxide.

8. A process for the selective extraction of an aromatic hydrocarbon from a naphtha fraction containing the same, which process comprises contacting said naphtha in the liquid condition with pyridine oxide in an amount sufficient at least to form a distinct liquid phase, and separating a raffinate phase from an extract phase comprising said pyridine oxide and said aromatic hydrocarbon.

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