

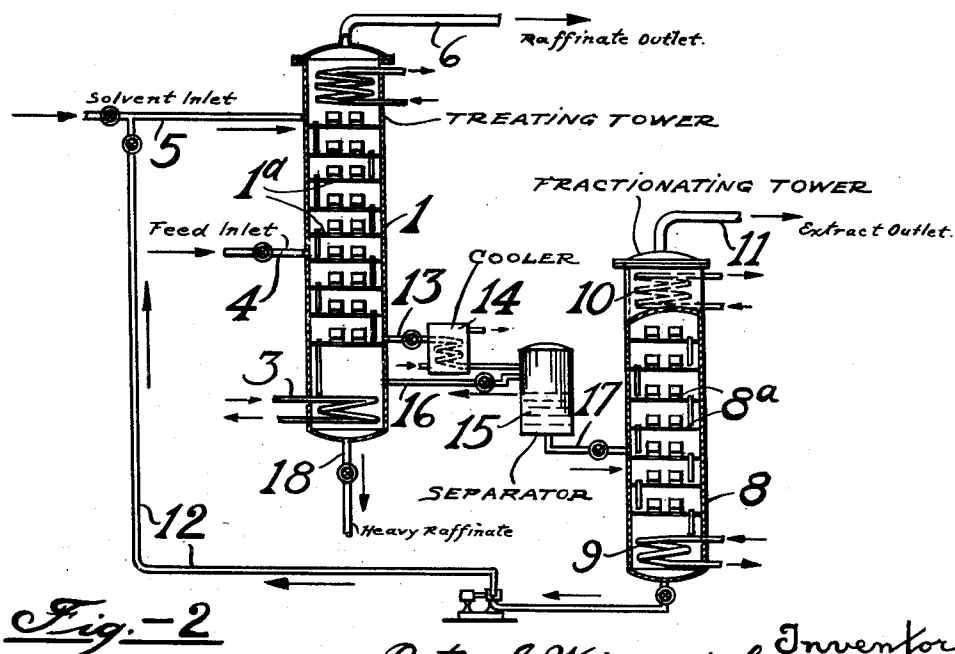
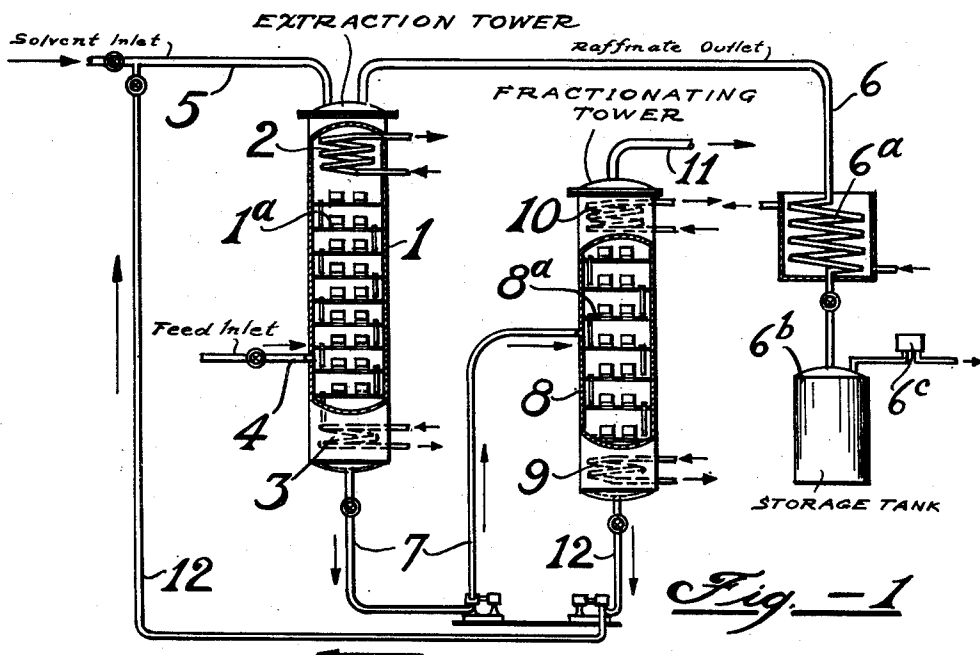
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PROCESS OF PRODUCING A GASOLINE FRACTION OF HIGH ANTIKNOCK GRADE

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PROCESS OF PRODUCING A GASOLINE
FRACTION OF HIGH ANTIKNOCK
GRADE

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9 Claims. (Cl. 196—13)

This invention relates to the selective extraction of petroleum distillates in the vapor phase with a high boiling stable solvent which is liquid at the extraction temperature. The invention will be fully understood from the following description. When read in conjunction with the drawing

Figure 1 is a diagrammatic side elevation, partly in section of the apparatus adapted for carrying out the invention, and

Figure 2 is a similar side elevation of a modified form of the apparatus.

Numerous extraction processes are known wherein various solvents such as phenol, sulfur dioxide, nitrobenzene, furfural and the like are employed for selectively separating the various types of components which are present in petroleum oils. Such processes are carried out in the liquid phase, that is both the petroleum oil and the solvent are liquid at the treating temperatures. The treating temperatures are usually low in order to maintain a liquid phase system. Furthermore, the selective solvents are of a relatively low boiling point, since their recovery mainly depends upon their removal from the raffinate and extraction by means of distillation.

The process described hereinafter involves the separation of various types of hydrocarbons to be found in a petroleum distillate by counter-current extraction of the vapors of the distillate with a heat-stable, high boiling, liquid selective solvent.

The stocks which may be treated in this manner are gasolines, naphthas, kerosenes, fuel or burning oils, heating or refined oils, solvent extracts, gas oils, and even white oils, treated or hydrogenated oils and lubricating oils. For instance, ordinary solvent naphthas, such as those boiling between 160 to 255° F. and having a Kauri Butanol value of about 33 may be so treated to yield naphthas having Kauri Butanol values in the neighborhood of 40 and above. Hydrogenated or hydrofined petroleum solvents may also produce solvent naphthas having Kauri Butanol values of over 70 or even higher when treated according to the present invention. In the case of gasolines, the process may be advantageously employed for improving octane number. The gasoline stocks used may boil from about 90° to about 420° F. or higher, although it is preferable to extract those boiling above 185° F. Straight run, vapor phase or liquid phase cracked gasolines may be so treated. The solvent may extract either the hydrocarbons of

low octane number or those of high octane number, depending upon the type of solvent used. Straight hydrocarbons are known to be of low octane number and branched chain and cyclic hydrocarbons are of high octane number.

Since the lower boiling hydrocarbons are generally of fairly high octane number, I find it often desirable to subject the heavier ends to extraction. The high octane number hydrocarbons so separated may then be mixed with the light hydrocarbons giving a superior gasoline, often having octane numbers of above 70 by the C. F. R. method. Extracts, obtained by extracting gasoline with cyclic types of solvents, obtained according to this invention will also in many cases have octane numbers above 70.

In the case of refined oils, the process of the present invention may be advantageously employed for improving ring number and aniline point, as well as the gravity, refractive index, and the like. Straight chain hydrocarbons of paraffin type are very desirable in refined oils while others are less desirable. Refined oil distillates boiling between 350° and 530° F. are very suitable for treatment. Other material such as solvent naphtha, fuel oil, diesel fuel, burning oils, furnace oils, gas oils, light lubricating oils, etc. may be treated according to the present invention. In the preparation of diesel fuel, for instance, it is desirable to employ a stock which is highly paraffinic or detonating in nature so as to insure substantially complete combustion of the fuel. Likewise, in burning oils or kerosenes, it is preferable to use stocks of high paraffinicity in order to obtain a non-smoking flame. By means of this invention, it is possible to separate the desirable from the undesirable hydrocarbons, thereby obtaining a superior product.

With higher boiling lubricating oils the process becomes more difficult to operate since it is harder to find a stable and sufficiently high boiling solvent for efficiently extracting the hydrocarbons according to the invention.

The process may be carried out under atmospheric pressure, higher than atmospheric pressure, or under vacuum. The higher boiling the distillate to be treated the lower should be the pressure in order to avoid too high treating temperatures, which may result in thermal decomposition. It is not limited to narrow fractions, since wide cuts as for example those boiling between 185° F. and 600° F. or even wider ranges may be utilized. Crudes of various types may be so treated. Treating temperatures of between

185° F. to 600° F. and higher may be used, although the preferred temperature is that just above the boiling point of the total distillate.

The various types of components of the distillate are extracted with different types of solvent. The most important types of solvents and types of hydrocarbons removed thereby are the following: Branched types of hydrocarbons such as tertiary pentane, iso-octane, etc. are removed by the use of solvents of the metallic or metalloid halide type. We may mention as examples, SbCl₃, SbCl₅, SbF₃, AsF₃, BCl₃, BF₃, aluminum or bismuth halides, etc. These halides may be used either alone or preferably dissolved in solvent such as chlorinated naphthalene, chlorinated diphenyl, trichlorotoluene, tricresyl phosphate, etc., and the hydrocarbons may be recovered therefrom by distillation, dilution with water, extraction etc.

Cyclic types such as naphthene or aromatic hydrocarbons and similar compounds may be extracted from a petroleum distillate by means of heat-stable organic compounds preferably of the cyclic or aromatic type boiling above 450° F. or preferably above 500° F. at atmospheric pressure. The following examples are given as high boiling solvents having a preferential solvent action for cyclic type of hydrocarbons. Cresylic acids, alkylated aromatic hydrocarbons such as propylated phenanthrene, high boiling highly cyclic fractions of petroleum oils, dibenzyl phthalate, butyl benzyl phthalate, ethyl benzyl malonate, methyl glycol phthalate, n-amyl phthalate, mixed esters of phthalic and glycollic acids, alkylated phenols, aromatic ethers such as dibenzyl ether, diphenyl oxide, or hexyl phenyl ether, halogenated aromatics such as toluene trichloride, chlorinated naphthalene, chlorinated diphenyl, other aromatic esters, such as n-butyl phthalate, benzyl butyrate, benzyl benzoate, voltolized aromatic organic compounds, ethyl salicylate, creosote carbonate, cresyllaurate, naphthoyl benzoic benzoyl or cyclohexyl esters, triphenyl phosphate, tricresyl phosphate, and the like. The preferred solvents are the esters and/or ethers containing a cyclic group. Of especial value for this purpose are tricresyl phosphate and/or triphenyl phosphates.

The straight chain type of compounds are extracted by solvents boiling above 450° F. and preferably above 500° F. of the type of fatty compounds, such as vegetable oils, glycerides, either as such, or thickened by heat or oxidation or voltolization, fatty alcohols, esters of fatty acids having 5 or more carbon atoms, esters of fatty alcohols, and mineral natural and synthetic waxes. As examples may be mentioned castor oil, glyceryl oleate, glycol stearate, menhaden oil, palm oil, cottonseed oil, high boiling Pennsylvania oils, paraffin wax, voltolized paraffin, carnauba wax, montan wax, synthetic waxes, glyceryl borate, montanol, alkyl stearates, alkyl oleates, triethyl citrate, and the like.

In the extraction of the various types of compounds it is essential that the solvents employed have boiling points substantially higher than the stock treated. For this reason solvents boiling above 450° F. and preferably above 500° F. are used. It is essential that the solvents used be stable at the temperatures employed. In the case of refined oils, kerosenes, and the like, it is preferable to employ solvents boiling above 550° F. and preferably above 600° F., while in the extraction of lubricating oils, solvents having boiling points higher than 700° F. or 800° F. are

desirable. The solvents may be used alone or in admixture with each other.

The solvents which I employ may be volatile at the working temperature, although it has been found preferable to employ substantially non-volatile solvents, i. e. it is desirable to prevent substantial amounts of the solvent from distilling overhead. However, it is possible to introduce another solvent, such as phenyl, nitrobenzene, aniline, furfural, etc. The solvents employed which are volatile vary in structure according to the type of extraction desired. For instance, if the separation of branched chain compounds is desired from the relatively straight chain hydrocarbons, a solvent for the former may be employed and will extract from the vapors branched hydrocarbons allowing the straight chain type of compounds to go overhead. The solvents employed in this invention may be either liquids or solids at room temperature, although it is desirable to employ those which will be in the liquid phase at the working temperature. However, slurries of solids in liquids are not excluded. The solids may also react with the hydrocarbons extracted, but the hydrocarbons must be easily recoverable therefrom by distillation, dilution with water, extraction or precipitation with other solvents, separation by cooling until two phases appear, and the like.

In carrying out the extraction the petroleum distillate is vaporized and passed into intimate contact with the liquid solvent countercurrently. Contacting means such as Raschig rings, bellcap plates, etc. may be employed to effect an intimate contact of the vapors with the liquid and to allow a thorough extraction of the distillate vapors. The unabsorbed distillate vapors which will be called raffinate pass overhead and are condensed while the liquid solvent containing the extract passes through the lower section of the treating tower. The solvent may be freed from the extract by various methods such as, for example, by distillation or by cooling followed by a mechanical separation of the layers formed during the cooling.

Referring now to Figure 1 of the drawing, numeral 1 designates the extraction tower which is provided in this case with bellcap plates, a cooling coil 2, and a heating coil 3, are provided at the top and bottom, respectively, of the tower. The feed line 4 serves for the introduction of the petroleum distillate, and 5 for the introduction of the high boiling liquid solvent from respective tanks (not shown). The raffinate is removed through an overhead vapor line 6 and cooler 6a into the storage tank 6b. Means for maintaining vacuum such as vacuum pumps 6c may be provided. The solvent containing the extract is removed through the bottom line 7, into the fractionating tower 8, which again is provided with bellcap plates, heating coil 9, and cooling coil 10. The extract which is separated here from the solvent is removed through vapor line 11 and condensed, while the solvent is brought back through line 12, into the solvent line 5. A cooler may be provided in line 12 if so desired.

In Figure 2 the numerals 1 to 6 and 8 to 12 designate parts having identical functions with similar parts in Figure 1. Instead of the line 7 of Figure 1, there is provided here a line 13 with a cooler 14, which may not be required if two layers are already present discharging into a separator 15. In the separator a certain amount of heavier raffinate separates out and is returned to the

treating tower 1 through line 16. The solvent and the extract are passed through line 17 to the fractionating tower 8 while a heavy raffinate is removed in liquid form from the bottom of tower 1 through line 18.

The following examples will illustrate my invention.

Example 1

During the distillation of a petroleum naphtha boiling between 190 to 285° F. in a bubble cap column, a liquid solvent composed of 50% tricresyl phosphate and 50% triphenyl phosphate, in an amount equivalent to 2-6 times the volume of the overhead distillate of the fractionating column, is allowed to run from the top of the column in order to scrub countercurrently the hydrocarbon vapors going up the column. The hydrocarbon feed is run into the center of the column. The solvent mixture described above possesses a selective solvent action for the cyclic type of hydrocarbons, extracting them from the vapors, taking them down the column. This extract is drawn off the bottom of the tower, run into a separate fractionating column or flash tower, at the top of which is taken overhead the improved extracted naphtha, while the solvent mixture is drawn off the bottom ready for re-use in the extraction step. The naphtha so prepared from the extract has an improved solvency as determined by the Kauri Butanol value when compared with the original feed stock.

Example 2

A gasoline having an approximate boiling range of 40-460° F. is fractionated in a bubble cap column (Fig. 2). Tricresyl phosphate is run countercurrent to the vapors in an amount equivalent to 1 to 10 volumes of the feed stock entering near the top of the column. This allows the phosphate solvent to extract mainly the heavier fractions of the gasoline, removing therefrom, by selective solvent action, the hydrocarbons having the higher octane number, and carrying them down the column. This extract is then drawn off near the bottom of the tower, as for example at one of the bottom plates through the cooler 14 and separator 15. Heavy raffinate is removed through line 18. The improved heavy gasoline is stripped from the solvent by distillation or otherwise. This improved gasoline may then be used as such, or blended with the distillate from the extraction tower 1 to give a fuel having superior anti-knock properties. The advantage in employing such a blend is based on the fact that, ordinarily, the light ends of gasoline have such a good octane number that for ordinary automotive use, no antiknock improvement is necessary. The heavier ends, however, have a lower octane number, and by extraction of these hydrocarbons, an improved hydrocarbon product is obtained which may then be blended with the light fractions in order to produce a fuel of superior antiknock properties.

My process may be carried out separately, or in conjunction with refinery operations, as for example, during distillation, rectification, dephlegmation, and the like. The solvents may be used alone, or in admixture with each other. Water and/or materials capable of forming azeotropic mixtures with the overhead hydrocarbons may also be added either with the feed, or with the solvent.

Sulfur compounds, nitrogen compounds, and the like, may be removed from the hydrocarbon mixture by this means, the solvent used being a

high boiling sulfur or nitrogen compound or other similar selective compound.

The present invention is not to be limited by the examples given for illustration but only by the following claims in which it is my intention to claim all novelty inherent in the invention.

What I claim is:

1. The process of producing a gasoline of high knock rating which comprises subjecting a gasoline to distillation, removing the light ends, subjecting the heavy ends while in the vapor state to the action of a solvent selected from the group consisting of esters and ethers containing an aromatic nucleus having an affinity for cyclic compounds and a boiling point above that of the heavy ends, separating the extract from the raffinate, and separating the solvent from the extract.

2. The process according to claim 1, in which the gasoline employed as starting material has a boiling range from about 90° to 420° F. and the light ends initially removed boil up to 185° F.

3. The process according to claim 1, in which the solvent employed is a heat stable liquid cyclic compound boiling above 450° F.

4. The process according to claim 1, in which the solvent employed is an ester of phosphoric acid containing an aromatic nucleus.

5. The process of increasing the concentration of cyclic hydrocarbons in a gasoline, which comprises distilling the gasoline in the presence of an organic compound of cyclic structure selected from the group consisting of esters and ethers containing an aromatic nucleus having a boiling point higher than the paraffinic constituents of the gasoline whereby a distillation residue, having an increased concentration of cyclic hydrocarbons, is obtained.

6. The process of producing a gasoline fraction of high anti-knock grade which comprises vaporizing the gasoline, introducing the vapors into an enlarged zone, passing the said vapors countercurrent to and in fractionating relationship to an ester containing an aromatic nucleus, having a boiling range above the boiling range of said gasoline and having a selective absorptive power for cyclic hydrocarbons, removing said ester with the absorbed constituents of the gasoline from the bottom of said zone and separating from said ester, by distillation, the gasoline fraction of improved knock rating.

7. Process according to claim 6 in which the liquid with its absorbed constituent from the first zone is introduced into a second zone, the gasoline of improved knock-rating is taken off from the top of said second zone, the absorptive liquid is removed from the bottom of said zone and recycled to the top of said first zone.

8. Process according to claim 5 in which the solvent is an ester of phosphoric acid containing an aromatic nucleus.

9. The process for improving the octane number of gasoline which comprises vaporizing the gasoline, introducing said vapors into an enlarged zone, passing said vapors in said zone countercurrent to an ester containing an aromatic nucleus having selective solvent power for cyclic hydrocarbons and having a boiling point above the boiling range of the gasoline, removing said solvent with the extracted constituents of the gasoline from the bottom of said zone, and separating the extracted constituents from the solvent by distillation.

4

CERTIFICATE OF CORRECTION.

Patent No. 2,123,642.

July 12, 1938.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, line 26, for "extraction" read --extract--; page 2, second column, line 9, for "phenyl" read --phenol--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 16th day of June, A. D. 1942.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.