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SEPARATION OF HYDROCARBONS

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This invention relates to the preparation of pure hydrocarbons from petroleum fractions or, more particularly, from narrow boiling fractions of petroleum. More specifically it relates to a method of treatment of a complex hydrocarbon mixture to cause the separation of relatively unsaturated or olefinic hydrocarbons or of aromatic hydrocarbons from relatively saturated or paraffinic hydrocarbons or from naphthenic hydrocarbons.

An object of the present invention is to provide a means of separating individual hydrocarbons from mixtures of hydrocarbons having boiling points so close as to prevent separation by means of ordinary distillation processes. The method is less complex and involves fewer steps than chemical methods of separation and yields a purer product than that produced by processes involving extraction with selective solvents.

Another object of the invention is to separate one or more hydrocarbons or classes of hydrocarbons, such as paraffins, olefins, diolefins and aromatics, which hydrocarbons have approximately the same boiling temperature, from a petroleum fraction containing two or more different classes of hydrocarbons, said petroleum fraction being normally gaseous or normally liquid and preferably having a narrow boiling range.

A particular object of the invention is to separate relatively olefinic hydrocarbons from relatively non-olefinic hydrocarbons having approximately the same boiling point range and particularly to separate the diolefins from monoolefins and paraffins in the case of relatively narrow boiling fractions containing these hydrocarbons, said fractions being those such as may be obtained by the fractional distillation of the products of petroleum cracking or dehydrogenation processes.

It is also an object of my invention to separate aromatic hydrocarbons from non-aromatic hydrocarbons having approximately the same boiling points or boiling point range.

The difficulty in separating hydrocarbons having similar boiling points is well recognized and many methods have been suggested which include, in addition to chemical methods which are usually costly and uneconomical, the use of highly efficient fractional distillation processes, solvent extraction processes and combinations of solvent extraction processes and distillation processes which in some instances may be described as vapor phase solvent extraction processes. These processes are rather inefficient and uneconomical. On the other hand, processes involving the distillation of the hydrocarbon fraction in the presence of compounds which form minimum boiling azeotropes with certain of the hydrocarbons in the mixture have resulted in the separation of relatively pure hydrocarbons with high yields. The present invention relates to an improvement in an azeotropic distillation process.

According to my invention the separation of a specific hydrocarbon or hydrocarbon fraction from a mixture of hydrocarbons having substantially the same boiling range is accomplished by azeotropic distillation using as an azeotrope former an organic nitrite having the general formula R—O—N=O in which R is an alkyl radical. The addition of the azeotrope former, i. e., the organic nitrite, to the petroleum fraction has the effect of forming an azeotrope with certain of the hydrocarbons or hydrocarbon components, the azeotrope having a lower boiling point or range than its hydrocarbon component or than the hydrocarbons which do not form azeotropes under the conditions of the distillation. Fractional distillation of the petroleum fraction containing the azetrope former results in the distillation of certain components or classes of components contained in the hydrocarbon fraction together with the azeotrope former at a temperature lower than the boiling point of the distilled hydrocarbons. Such mixtures of distilled hydrocarbons and azeotrope former are referred to as minimum boiling azeotropes. The other component or classes of components which do not form azeotropes with the azeotrope former remain as a distillation residue.

Thus where it is desired to separate relatively olefinic hydrocarbons, which for the purposes of this description will include diolefins, from relatively non-olefinic hydrocarbons which likewise will include monoolefins and paraffins, the narrow boiling range complex hydrocarbon mixture to which is added as appropriate amount of an azeotrope former is fractionally distilled. The relatively non-olefinic component forms azeotropes with the organic nitrite and may be distilled leaving as a residue or bottoms the relatively olefinic component which generally does not form an azeotrope with the organic nitrite. More specifically in separating, for example, diolefins from monoolefins and paraffins an appropriate amount of a suitable organic nitrite is added to the complex hydrocarbon mixture and upon fractional distillation the azeotropes formed between the organic nitrite and paraffins and the monoolefins vaporize at temperatures below the boiling point of the diolefins and are obtained as distillate and the diolefinic hydrocarbon material may be obtained as a residue relatively free of paraffinic and monoolefinic impurities.

In practicing my invention it may be desirable in some cases to effect the separation and isolation of three or more components originally present in a petroleum fraction. Thus in the case of the fraction referred to above containing paraffins, monoolefins and diolefins the separation of

the three components may be accomplished by adding an azeotrope former and carefully fractionating and segregating the distillate. The paraffin component forms the lowest boiling azeotrope and will, therefore, be the first to distill. The monoolefin component which also forms an azeotrope, then distills and leaves the diolefin component as a residue. This latter component may then be distilled if desired and thus separated by fractional distillation from any remaining azeotrope former.

Separation of the three aforementioned hydrocarbon components may be accomplished more effectively by adding thereto just sufficient azeotrope former to form an azeotrope with the paraffin component and the mixture distilled until all of the paraffins have been vaporized and removed from the mixture of monoolefins and diolefins remaining as a residue. By this means it is possible to make a relatively sharp separation because of the greater spread existing between the boiling range of the paraffin azeotrope and that of the monoolefin component than between the boiling range of the paraffin azeotrope and the monoolefin azeotrope. After removal of the paraffin component an additional quantity of azeotrope former is added which is just sufficient to form an azeotrope with the monoolefin component. Further distillation results in the separation of the monoolefin as an azeotropic distillate and leaving the diolefin as a distillation bottoms or residue.

Thus by controlling the temperature and amount of azeotrope former, the azeotropic distillation may be controlled to distill overhead either the paraffins alone or a mixture of paraffins and monoolefins, leaving the diolefins as a distillation residue.

While the inventilon is adapted to the separation of hydrocarbon fractions into hydrocarbon components having characteristics different from each other, I have found that this process is particularly adaptable to the separation of butadiene in a relatively pure form from cracked or dehydrogenated petroleum fractions. The separation and recovery of butadiene from the products of cracking of petroleum fractions or from dehydrogenated petroleum fractions is particularly difficult. By straight distillation of certain cracked petroleum products it is possible to obtain a fraction containing 50 to 60% by volume of butadiene and correspondingly 50 to 40% by volume of predominately C_4 hydrocarbons consisting primarily of the paraffinic and monoolefinic types. However, due to the rather close boiling points of these compounds, i. e., from a −12° C. for isobutane to a +3.7° C. for cis butene-2, it is not commercially feasible to make a complete separation of these hydrocarbons by straight distillation processes. It is particularly difficult to separate butadiene from this mixture of hydrocarbons by fractional distillation because its boiling point, which is a −4.7° C., falls approximately in the middle of the boiling point range of the C_4 hydrocarbon fraction. Moreover, butadiene forms a minimum boiling point azeotrope with normal butane thus effectively preventing its separation by ordinary distillation methods.

In carrying out my invention I have found that the alkyl nitrites are excellent azeotrope formers and those nitrites boiling between about −16° C. and 175° C. and including the normal and the various isomeric alkyl nitrites from methyl to octyl nitrite are particularly useful. The particular organic nitrite to be used for the treatment of a given hydrocarbon fraction is selected on the basis of its boiling point. Thus the azeotrope former will desirably have a boiling point at or relatively near the average boiling point of the hydrocarbon fraction to be treated. For example, the organic nitrite will desirably have a boiling point within 25° C. above to 50° C. below the average boiling point of the hydrocarbon fraction and preferably it will have a boiling point within 10° C. above to 30° C. below the average boiling point of the hydrocarbon stock.

When separating the hydrocarbon components of a C_4 fraction of cracked petroleum having an average boiling point of about a −4° C. and which may be described as a butadiene fraction I may use either the methyl nitrite (boiling point about −16° C.) or the ethyl nitrite (boiling point 17° C.) although the use of the methyl nitrite is preferable. Similarly in treating a C_5 fraction of cracked petroleum having an average boiling point of approximately 65° C. any of the propyl or butyl nitrites or mixtures of these nitrites might be used as the azeotrope formers although I prefer to employ one of the propyl nitrites. The boiling point of normal propyl nitrite is 57° C. or 8° C. below the average boiling point of the above mentioned C_5 fraction.

As indicated above, the proportion of azeotrope former to be used may be varied over wide limits and will depend upon the composition of the hydrocarbon fraction, the efficiency of the operation, the desired purity of the product, and the technique to be used in the distillation. For example, in separating paraffins from monoolefins, both of which form azeotropes with added azeotrope forming agent, it is desirable to add a quantity of the azeotrope former which will distill completely with the paraffins and which will cause the complete removal of the paraffins. The addition of a quantity less than this specified amount will leave some of the paraffins in the olefinic distillation residue. The addition of more than the specified amount will form an azeotrope with the olefins thus bringing the distillation temperature of the olefins nearer to that of the paraffin azeotrope and making the separation of these two components more difficult.

In separating the relatively olefinic hydrocarbons from the relatively non-olefinic hydrocarbons, such as for example in separating butadiene from the butenes and the butanes present in a closely fractionated C_4 fraction of cracked petroleum, the amount of azeotrope former to be used is not as critical as in the above-described example. In this instance the butadiene does not form an azeotrope with for example methyl nitrite so that although it is desirable to use sufficient azeotrope former to distill all of the relatively non-olefinic components an excess of the azeotrope former may be employed. When using methyl nitrite as the azeotrope former any excess methyl nitrite remaining after the complete removal of the paraffinic and monoolefinic components may be distilled leaving the butadiene as a residue.

The pressures employed in carrying out the azeotropic distillation using an organic nitrite as the azeotrope former may vary from substantially zero, i. e., from 1 to 2 mm. of mercury pressure, to pressures of 300 pounds per square inch absolute or even higher, although I prefer to operate between about 15 mm. of mercury pressure and about 100 pounds per square inch and in some instances, particularly when treating the lower molecular weight hydrocarbon fractions, the pre-

ferred pressure range will be in the order of from normal atmospheric pressure to 200 pounds per square inch absolute. The pressure employed will depend upon the particular hydrocarbon fraction being treated and upon the particular organic nitrite being used as the azeotrope former as well as upon the separation desired and upon various economic considerations. It is known that the composition as well as the boiling point or range of azeotropes comprising hydrocarbons and organic nitrites will vary with changes in pressure. In general the higher the pressure the higher will be the ratio of hydrocarbon to organic nitrite in a given azeotrope although the relative effects of pressure upon the boiling points of various hydrocarbon components are not constant and it may be advantageous in some instances to employ the higher pressures in order to obtain a greater spread between the boiling points of the azeotropes of the various hydrocarbon components. In distilling unsaturated and particularly relatively olefinic petroleum fractions it is preferable that distillation temperatures be employed which are not high enough to cause polymerization of the more olefinic hydrocarbons. Since distillation temperature is a function of pressure and increases with an increase in pressure it is apparent that there is a maximum allowable pressure for the treatment of a given hydrocarbon fraction and this maximum pressure will depend upon the relative ease with which polymerization occurs in the hydrocarbon fraction. In general, however, economic considerations make it preferable to operate at or relatively near atmospheric pressure or in the lower pressure ranges hereinbefore indicated.

The azeotrope, produced as an overhead in an azeotropic distillation is separated into its components, i. e., azeotrope former and hydrocarbon, by adding a third component which is soluble in the azeotrope former or which dissolves the azeotrope former and which causes phase separation or stratification of the azeotrope. The quantity of the said third component, which will be hereinafter referred to as solvent, to be used will be that amount required to effect a substantially complete separation of the hydrocarbon component as one phase and the azeotrope former and the solvent as a second phase. The phases are separated by decantation and the hydrocarbon phase may be contacted and/or extracted one or more times with fresh portions of the said solvent to remove completely any azeotrope former which may remain in the said hydrocarbon fraction. The phase comprising the azeotrope former and solvent is separated by fractional distillation and the pure azeotrope former may be returned to the azeotrope distillation step for reuse.

Substances which may be used as solvents to effect the desired phase separation of an azeotrope comprising hydrocarbon material and organic nitrite include water, the lower molecular weight aliphatic alcohols and glycols, and glycerol. Of the alcohols I prefer to use methanol, ethanol, the propanols, and the butanols, and of the glycols, ethylene glycol and propylene glycol, although I may in certain instances use higher molecular weight alcohols and glycols. While I may use any or all these substances I prefer to use water alone or mixtures of water with one or more of the said alcohols, glycols or glycerol. The particular ratio of water to alcohol or glycol, or glycerol to be used will depend upon the specific azeotrope being treated, i. e., upon the hydrocarbon or hydrocarbon component as well as upon the nitrite, and it will also depend upon the process to be employed in recovering the azeotrope former.

The separation of the azeotrope may be considered to be a solvent extraction process in which the azeotrope former is selectively extracted from the hydrocarbon component by means of a solvent, the solvent being relatively immiscible with the hydrocarbon component and relatively miscible with the organic nitrite. The solvent extraction process may be carried out as a batch operation, as hereinbefore described, or it may be effected by any or all of the general methods well known to those skilled in the art, such as for example, it may be carried out in a continuous countercurrent extractor in which the azeotrope enters an extraction column at a point near its base and flows countercurrent to the solvent which enters the column at a point near the top. In its downward flow the solvent contacts the rising azeotrope and/or partially extracted azeotrope and selectively dissolves the azeotrope former. The pure hydrocarbon component is produced at the top of the column and the solvent containing azeotrope former but free from hydrocarbon is drawn from the bottom of the column.

Separation of the mixture of solvent and azeotrope former is then accomplished by fractional distillation and the method of carrying out this separation will depend upon the particular nitrite employed and upon the particular solvent used for its recovery. A mixture of solvent and azeotrope former, obtained by extraction of an azeotrope produced in the separation of a C_4 fraction of cracked petroleum, might consist of methyl nitrite, methanol and water, a mixture of the latter two compounds having been used as the solvent for treating the azeotrope. In this instance the methyl nitrite could be separated in a pure form from the alcohol-water solvent by a simple topping distillation, the methyl nitrite being obtained as a distillate at about −16° C. leaving as a residue the mixture of alcohol and water. In the distillation of a mixture of isopropanol, water and normal hexyl nitrite obtained by the extraction of an azeotrope produced in the separation of a petroleum fraction having an average boiling point of about 140° C. the alcohol and water distill first leaving the hexyl nitrite as a residue. The nitrite may be withdrawn from the still without further treatment or the distillation may be continued and the nitrite recovered as a distillation fraction.

The foregoing azeotropic distillation process is also applicable to the separation of aromatic hydrocarbons from non-aromatic hydrocarbons, such as paraffins, naphthenes or olefins or mixtures thereof. Thus a petroleum fraction containing aromatics whose boiling range includes that of the aromatic compound to be isolated, for instance 100° C. to 125° C. for toluene, (suitable other temperature ranges for fractions containing benzene or di- or other polyalkyl benzenes) may be distilled with an organic nitrite or a mixture of organic nitrites having a boiling point in the aforementioned desired boiling range. The non-aromatic hydrocarbon components form azeotropes with the organic nitrite and distill first leaving the aromatic hydrocarbon as a residue.

My invention is further illustrated by the following examples:

In carrying out the separation of butadiene from other hydrocarbon components of a closely

fractionated C_4 fraction of cracked petroleum according to the principles of my invention, to 100 parts of the C_4 fraction containing approximately 50 parts by weight of butadiene, 40 parts by weight of butene-1 and isobutene and 10 parts by weight of butanes is added approximately 130 parts by weight of methyl nitrite and the resulting mixture is distilled under ordinary atmospheric pressures. The first produced distillate is the butane azeotrope which vaporizes at between −20° C. and −17° C. The azeotrope containing butene-1 and isobutene is then distilled at about −16° C. followed by any remaining methyl nitrite which vaporizes at approximately the same temperature. The distillation temperature rises abruptly to approximately −4.7° C. when relatively pure butadiene is produced as a distillate.

In another example, to 100 parts of the above mentioned closely fractionated C_4 fraction of cracked petroleum is added 20 parts by weight of methyl nitrite and the mixture is distilled under ordinary atmospheric pressure until the added component has substantially all distilled at which time the temperature which has been in the order of −20° C. to −17° C. abruptly begins to rise. The azeotropic distillate is extracted with a solvent to separate and recover the methyl nitrite and the hydrocarbon component separated consists primarily of butanes. An additional 110 parts of methyl nitrite is then added to the residue from the above distillation which comprises a mixture of butene-1, isobutene and butadiene. The distillation is continued until the temperature which has been in the order of −16° C. again rises abruptly indicating that all of the butene-1 azeotrope, isobutene azeotrope and excess azeotrope former has been distilled over leaving relatively pure butadiene as a distillation residue. This azeotrope is then treated to separate therefrom the monoolefin hydrocarbon components and the azeotrope former. If the distillation residue contains relatively small amounts of higher boiling hydrocarbons which were originally present in the hydrocarbon fraction or which formed during the azeotropic distillation the distillation may be continued without further addition of methyl nitrite to produce as a distillate a relatively pure butadiene leaving the impurities as a distillation residue.

The treatment of a C_4 fraction of cracked petroleum containing approximately 60 parts by weight of butadiene, 10 parts by weight of butene-2s, 20 parts by weight of butene-1 and isobutene and 10 parts by weight of butanes is effected by combining 100 parts by weight of the C_4 fraction with 70 parts by weight of methyl nitrite and distilling the resulting mixture at ordinary atmospheric pressures. The distillation temperature rises slowly from about −20° C. when the butane azeotrope starts to distill to about −16° C.

When all of the methyl nitrite, butanes, butene-1 and isobutene have distilled the distillation temperature rises abruptly to approximately −4.7° C. at which temperature the relatively pure butadiene distills leaving butene-2 as a residue.

In the treatment of a butadiene fraction containing approximately 70 parts by weight of butadiene, 20 parts by weight of butene-1 and 10 parts by weight of isobutene, the said butadiene fraction is mixed with an equal weight of methyl nitrite and the mixture is distilled under ordinary atmospheric pressures. The azeotrope containing the butenes vaporizes at about −16° C. and distills first and the excess methyl nitrite then distills at approximately the same temperature leaving the relatively pure butadiene as a residue.

The foregoing description is not to be taken as in any way limiting but merely as illustrative of my invention for many variations may be made by those skilled in the art without departing from the spirit or scope of the following claims:

I claim:

1. A method for the treatment of a complex hydrocarbon fraction to separate chemically similar components from other chemically similar components, different from said first named chemically similar components contained in said complex hydrocarbon fraction, which components distill from said complex hydrocarbon fraction at approximately the same temperature, which comprises distilling said complex hydrocarbon fraction in the presence of a sufficient amount of an alkyl nitrite to vaporize chemically similar components together with said alkyl nitrite, thereby leaving chemically similar components different from said vaporized chemically similar components in the residue, said alkyl nitrite having a boiling point within 25° C. above to 50° C. below the average boiling point of the said complex hydrocarbon fraction.

2. A method for the treatment of a complex hydrocarbon fraction to separate chemically similar components from other chemically similar components, different from said first named chemically similar components contained in said complex hydrocarbon fraction, which components distill from said complex hydrocarbon fraction at approximately the same temperature, which comprises distilling said complex hydrocarbon fraction in the presence of a sufficient amount of an alkyl nitrite to vaporize chemically similar components together with said organic nitrite, thereby leaving chemically similar components different from said vaporized chemically similar components in the residue, said alkyl nitrite containing from 1 to 8 carbon atoms in the organic radical.

3. A method for the treatment of a complex hydrocarbon fraction to separate chemically similar components from other chemically similar components, different from said first named chemically similar components contained in said complex hydrocarbon fraction, which components distill from said complex hydrocarbon fraction at approximately the same temperature, which comprises distilling said complex hydrocarbon fraction, under pressures in the order of from 0 to 300 pounds per square inch absolute in the presence of a sufficient amount of an alkyl nitrite to vaporize chemically similar components together with said alkyl nitrite, thereby leaving chemically similar components different from said vaporized chemically similar components in the residue, said alkyl nitrite containing from 1 to 8 carbon atoms in the organic radical and having a boiling point within 25° C. above to 50° C. below the average boiling point of the said complex hydrocarbon fraction.

4. A method for the treatment of an olefinic hydrocarbon fraction to separate relatively olefinic hydrocarbons from relatively non-olefinic hydrocarbons which distill from said olefinic hydrocarbon fraction in the same temperature range as said relatively non-olefinic hydrocarbons distill therefrom which comprises distilling said olefinic hydrocarbon fraction in the presence of a sufficient amount of an alkyl nitrite to distill said relatively non-olefinic hydrocarbons

together with said alkyl nitrite thereby leaving said relatively olefinic hydrocarbons in the residue substantially completely separated from said relatively non-olefinic hydrocarbons, said alkyl nitrite having a boiling point within 25° C. above to 50° C. below the average boiling point of said olefinic hydrocarbon fraction.

5. A method for the treatment of an olefinic hydrocarbon fraction to separate relatively olefinic hydrocarbons from relatively non-olefinic hydrocarbons which distill from said olefinic hydrocarbon fraction in the same temperature range as said relatively non-olefinic hydrocarbons distill therefrom which comprises distilling said olefinic hydrocarbon fraction, under absolute pressures in the order of from 0 to 300 pounds per square inch, in the presence of a sufficient amount of an alkyl nitrite to distill said relatively non-olefinic hydrocarbons together with said alkyl nitrite thereby leaving said relatively olefinic hydrocarbons in the residue substantially completely separated from said relatively non-olefinic hydrocarbons, said alkyl nitrite having a boiling point within 25° C. above to 50° C. below the average boiling point of said olefinic hydrocarbon fraction.

6. A method for the treatment of an olefinic hydrocarbon fraction to separate relatively olefinic hydrocarbons from relatively non-olefinic hydrocarbons which distill from said olefinic hydrocarbon fraction in the same temperature range as said relatively non-olefinic hydrocarbons distill therefrom which comprises distilling said olefinic hydrocarbon fraction, under absolute pressures in the order of from 15 mm. of mercury to 100 pounds per square inch, in the presence of a sufficient amount of an alkyl nitrite to distill said relatively non-olefinic hydrocarbons together with said alkyl nitrite thereby leaving said relatively olefinic hydrocarbons in the residue substantially completely separated from said relatively non-olefinic hydrocarbons, said alkyl nitrite containing from 1 to 8 carbon atoms in the alkyl radical and having a boiling point within 25° C. above to 50° C. below the average boiling point of said olefinic hydrocarbon fraction.

7. A method for the treatment of a hydrocarbon fraction containing C_4 paraffin, monoolefin and diolefin hydrocarbons to separate the diolefin hydrocarbon from the monoolefin and paraffin hydrocarbons which distill from the said hydrocarbon fraction in the same temperature range as the diolefin hydrocarbon distills therefrom, which comprises distilling said hydrocarbon fraction in the presence of sufficient alkyl nitrite to vaporize the monoolefin and paraffin hydrocarbons together with the alkyl nitrite thereby leaving the diolefin hydrocarbon in the residue substantially completely separated from the hydrocarbons other than diolefin hydrocarbons, said alkyl nitrite having a boiling point within 25° C. above to 50° C. below the average boiling point of said hydrocarbon fraction.

8. A method for the treatment of a butadiene fraction containing hydrocarbons other than butadiene which distill from said butadiene fraction in the same temperature range as said butadiene distills therefrom which comprises distilling said butadiene fraction, under a pressure in the order of from normal atmospheric pressure to 200 pounds per square inch absolute in the presence of a sufficient amount of an alkyl nitrite to vaporize said hydrocarbons other than butadiene together with said alkyl nitrite, thereby leaving butadiene in the residue substantially completely separated from said hydrocarbons other than butadiene, said alkyl nitrite having a boiling point within 25° C. above to 50° C. below the average boiling point of the butadiene fraction.

9. A method for the treatment of a hydrocarbnn fraction containing the butanes, butene-1, isobutene, and butadiene, to separate butadiene therefrom which comprises distilling said hydrocarbon fraction in the presence of sufficient methyl nitrite to vaporize the butanes and the butenes together with the methyl nitrite thereby leaving the butadiene as a residue substantially completely separated from butanes, butene-1 and isobutene.

10. A method for the treatment of a hydrocarbon fraction containing butene-1, isobutene and butadiene, to separate butadiene therefrom which comprises distilling said hydrocarbon fraction under pressures in the order of from about normal atmospheric pressure to about 200 pounds per square inch absolute, in the presence of sufficient methyl nitrite to vaporize the butenes together with the methyl nitrite thereby leaving the butadiene as a residue substantially completely separated from butene-1 and isobutene.

11. A method for the treatment of a butadiene fraction of petroleum containing butanes, isobutene, butene-1, and the butene-2s to separate butadiene therefrom which comprises distilling said butadiene in the presence of a sufficient amount of methyl nitrite to vaporize the butanes, isobutene, and butene-1, together with the methyl nitrite, thereby leaving a distillation residue containing butadiene and the butene-2s substantially completely separated from the butanes, isobutene and butene-1.

12. A method for the treatment of a butadiene fraction of petroleum containing butanes, isobutene, butene-1, and the butene-2s to separate butadiene therefrom which comprises distilling said butadiene in the presence of a sufficient amount of methyl nitrite to vaporize the butanes, isobutene, and butene-1, together with the methyl nitrite, thereby leaving a distillation residue containing butadiene and the butene-2s substantially completely separated from the butanes, isobutene and butene-1 and subsequently separating said butene-2s from said residue of butene-2s and butadiene.

13. A method for the treatment of a butadiene fraction of petroleum containing butanes, isobutene, butene-1, and the butene-2s to separate butadiene therefrom which comprises distilling said butadiene fraction in the presence of a sufficient amount of methyl nitrite to vaporize the butanes, isobutene, and butene-1, together with the methyl nitrite, thereby leaving a distillation residue containing butadiene and the butene-2s substantially completely separated from the butanes, isobutene and butene-1 and subsequently distilling the said distillation residue to distill the butadiene substantially completely separated from the butene-2s thereby leaving the butene-2s as a residue.

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