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HYDROCARBON SEPARATIONS

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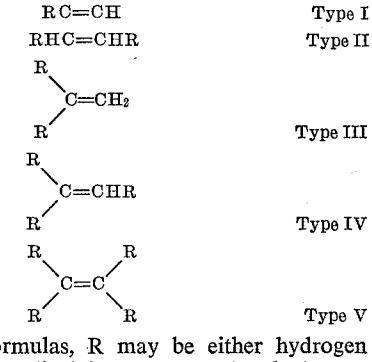
ABSTRACT OF THE DISCLOSURE

A process for the separation of olefin hydrocarbons according to structure and type by contacting a mixture of at least two olefin hydrocarbons of different structure or type with a complex of a cuprous fluoroborate or cuprous fluorophosphate.

BACKGROUND OF THE INVENTION

The present invention relates to a process for the separation, purification and recovery of certain hydrocarbons. More particularly, the present invention relates to a process for the separation and recovery of olefin hydrocarbons of differing skeletal structure.

The separation of olefin hydrocarbons according to structure and type has long been a problem. The structural and type configuration of olefins include branched-chain and straight-chain as well as cyclic. Additionally, even as to straight-chain, the olefin may have a cis and trans isomer having different molecular dimensions. Still further olefins may be of different types according to the point of unsaturation within the olefin molecule. The possible positions of the ethylenic unsaturation of olefin hydrocarbons gives rise to five types of olefins represented by the following structural formulas:



In the structural formulas, R may be either hydrogen or a hydrocarbonyl radical in Type I and a hydrocarbonyl radical in Types II, III, IV and V. In general, prior art processes for the separation of olefins from olefins have been directed to the separation of straight-chain olefins from branched-chain olefins or to the separation of internally unsaturated olefins from terminally unsaturated olefins. Few of these processes have proposed means for separating the cis and trans olefin isomers or separation of the various olefin types from one another.

SUMMARY OF THE INVENTION

The present invention which fulfills the above and other objects is a process for the separation of olefin hydrocarbons according to structure and type, said process comprising contacting an olefin hydrocarbon mixture containing at least two olefin hydrocarbons of different structure or type with a first complex which comprises a complex of a cuprous salt selected from the group consisting of cuprous fluoroborate and cuprous fluorophosphate and a hydrocarbon selected from the group

consisting of aromatic hydrocarbons, olefin hydrocarbons of a molecular weight different from those of said olefin hydrocarbon mixture and combinations of such aromatic hydrocarbons and olefin hydrocarbons, thereby forming an extract phase and a raffinate phase, separating said extract and raffinate phase, recovering from said extract phase an olefin hydrocarbon fraction substantially richer in one of said two olefin hydrocarbons than the original olefin hydrocarbon mixture, and recovering from said raffinate phase an olefin hydrocarbon fraction substantially richer in the other of said two olefin hydrocarbons than said original olefin hydrocarbon mixture.

The present invention provides for the separation of the cis-olefin isomers from the trans-olefin isomers. Additionally, Type I olefin hydrocarbons can be separated from admixture with Type II and/or Type III and/or Type IV and/or Type V olefin hydrocarbons. Also, in accordance with the present invention, Type II olefin hydrocarbons may be separated from admixture with Type III and/or Type IV and/or Type V olefin hydrocarbons and Type III olefin hydrocarbons may be separated from Type IV and/or Type olefin hydrocarbons.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In order to further describe the present invention, the following examples are presented.

Example I

A $CuBF_4$ first complex was formed as follows: 63.5 grams of powdered metallic copper and 127.5 grams of $CuF_2 \cdot 2H_2O$ were dispersed in 644 grams of toluene. Gaseous BF_3 was continuously introduced into the dispersed medium until all of the solids had solubilized. The mixture was maintained at a temperature of approximately 110° C. and continuously agitated during addition of the BF_3, the agitation continuing until the product had cooled back to ambient temperatures (73–75° F.). Water generated during the mixing period was continuously removed.

A mixture of C_5 hydrocarbons consisting of 31.27% by weight pentene-1, 31.93% by weight trans-pentene-2 and 36.80% by weight cis-pentene-2 was agitated with an amount of the above described first complex sufficient to cause a mole ratio of $CuBF_4$ to C_5 hydrocarbons of 1:6. Temperature during the agitation was approximately 25° C. To this mixture was added 2,3-dimethyl butane to aid in inducing phasing. After several minutes, agitation was stopped and an extract and raffinate phase allowed to form. The extract and raffinate phases were then separated and each analyzed. The C_5 hydrocarbon composition in weight percent of each of these phases was as follows:

Component: pentene-1; extract, 45.27; raffinate, 27.64. Component: trans-pentene-2; extract, 13.80; raffinate, 37.01. Component: cis-pentene-2; extract, 40.93; raffinate, 35.34.

The above results illustrate the preferential selectivity of the first complex for Type I olefin hydrocarbons and in addition, the preference for the cis-isomer over the trans-isomer.

Example II

To further demonstrate the separation of the cis and trans isomers of olefin hydrocarbons in accordance with the present invention, a first complex prepared as in Example I above was agitated with a C_5 hydrocarbon mixture consisting of 47.8% by weight of trans-pentene-2 and 52.2% by weight of cis-pentene-2. The mole ratio of $CuBF_4$ in the first complex to C_5 hydrocarbons was 1:6.5. Temperature during the agitation which continued for several minutes was approximately 25° C. To aid in inducing phase formation, 2,3-dimethyl butane was added.

On stopping agitation, extract and raffinate phases formed and were separated and separately analyzed. The C_5 hydrocarbon composition in weight percent of each phase was as follows:

Component: trans-pentene-2; extract 24.4; raffinate, 52.4. Component: cis-pentene-2; extract, 75.6; raffinate, 47.6.

Example III

A cuprous fluoroborate first complex prepared as described in Example I above is agitated at a temperature of 25° C. and at autogenous pressure with a C_5 hydrocarbon mixture consisting of hexene-1 (Type I) and 2-methyl pentene-1 (Type III) in a 1:1 weight ratio. The mole ratio of $CuBF_4$ in the first complex to the C_6 hydrocarbon mixture is 0.25:1. To aid in phasing, n-heptane is added to the agitating mass. On ceasing agitation, extract and raffinate phases form and are separated. On analysis, the extract phase is found to contain a substantially higher weight ratio of hexene-1 to 2-methyl pentene-1 than in the original C_6 hydrocarbon mixture whereas the raffinate phase is found to contain a substantially higher weight ratio of 2-methylpentene-1 to hexene-1 than in the original C_6 hydrocarbon mixture.

Example IV

To demonstrate the recovery of separated olefins from an extract phase using an olefin hydrocarbon of a different molecular weight, a hexene-1 containing extract such as that obtained in Example III above was intimately contacted with pentene-1 at a temperature of 25° C. The amount of pentene-1 used was in a weight ratio of 2:1 to the hexene-1 in the extract phase. An extract and a raffinate phase formed and were separated and the extract phase again contacted with pentene-1 in a weight ratio of 2:1. Again, an extract and raffinate phase formed and were separated. The final extract phase was found to contain only 27.4% by weight of the hexene-1 present in the original hexene-1 containing extract.

Example V

A cuprous fluoroborate first complex prepared substantially as described in Example I above is agitated at a temperature of 25° C. and at autogenous pressures with a mixture of C_6 hydrocarbons consisting of 2-ethylbutene-1 (Type III) and 2-methylpentene-2 (Type IV) in a 1:1 weight ratio. An amount of n-heptene equal in weight to the amount of C_6 hydrocarbons is also agitated with the first complex and the C_6 hydrocarbons. The mole ratio of $CuBF_4$ in the first complex to the C_6 hydrocarbon mixture is the same as in Example III above. On ceasing agitation, extract and raffinate phases form and are separated. On analysis, the extract phase is found to contain a substantially higher weight ratio of 2-ethylbutene-1 to 2-methylpentene-2 than in the original C_6 hydrocarbon mixture whereas the raffinate phase is found to contain a substantially higher weight ratio of 2-methylpentene-2 to 2-ethylbutene-1 than in the original C_6 hydrocarbon mixture.

Example VI

A cuprous fluoroborate first complex prepared substantially as described in Example I above is agitated at a temperature of 25° C. and at autogenous pressures with a mixture of C_{10} hydrocarbons consisting of decene-5 (Type II) and 4-methylnonene-3 (Type III) in a 1:1 weight ratio. The mole ratio of $CuBF_4$ in the first complex to the C_{10} hydrocarbon mixture is the same as in Example III above. Normal octane is added to the agitating mixture to aid in phase formation. On ceasing agitation, extract and raffinate phases form and are separated. The extract phase is found to contain a substantially higher weight ratio of decene-5 to 4-methylnonene-3 than in the original C_{10} hydrocarbon mixture whereas the raffinate phase is found to contain a substantially higher weight ratio of the 4-methylnonene-3 to decene-5 than in the original C_{10} hydrocarbon mixture.

Example VII

A cuprous fluorophosphate containing first complex was prepared as follows: about 68.8 grams of $CuF_2 \cdot 2H_2O$ and 37 grams of powdered metallic copper were dispersed in 460 grams of toluene with continuous agitation. Temperature during agitation was 80 to 110° C. Phosphorous pentafluoride was introduced continuously until all solids were solubilized. To the resulting complex was added approximately 240 grams of sulfolane. On addition of the sulfolane, two phases formed and were separated. The extract phase represents the first complex and has a composition of 31.2% by weight $CuPF_6$, 39% by weight sulfolane and 29.8% by weight toluene.

A first complex prepared as above described is contacted at a temperature of 25° C. with agitation and at autogenous pressures with a C_5 hydrocarbon mixture consisting of pentene-1 and cis-pentene-2 in a 1:1 weight ratio. The mole ratio of $CuPF_6$ in the first complex to the C_5 hydrocarbon mixture is 0.25:1. Normal hexane is added to the agitating mixture to aid in phase formation. On ceasing agitation, extract and raffinate phases form and are separated. The extract phase is found to contain a substantially higher weight ratio of pentene-1 to cis-pentene-2 than in the original C_5 hydrocarbon mixture whereas the raffinate phase is found to contain a substantially higher weight ratio of cis-pentene-2 to pentene-1 than in the original C_5 hydrocarbon mixture.

Example VIII

To demonstrate operation of the process of the present invention as a continuously operating process, a mixture of C_5 olefin hydrocarbons consisting of 50% by weight of cis-pentene-2 and 50% by weight of trans-pentene-2 is continuously separated in an extraction column having approximately 24 perforated trays, each tray capable of operating at approximately 50% theoretical tray efficiency. A first complex is continuously introduced onto the top of the 24th tray (from bottom) of the first column. This first complex is one prepared as follows: Powdered metallic copper and $CuF_2 \cdot 2H_2O$ are dispersed in toluene, the weight ratio of Cu to $CuF_2 \cdot 2H_2O$ to toluene being 1:2,17:14.5, and then gaseous BF_3 is passed through the mixture until it is completely in liquid phase. The reaction mass is maintained at a temperature of approximately 110° C. and continuously agitated throughout addition of the BF_3 with continuous removal of the water generated. The agitation is continued for several minutes beyond the period of BF_3 addition and the product cooled to ambient temperatures (73–75° F.). Concurrently with introduction of this first complex phase into the top of the first column, the above defined C_5 olefin hydrocarbon feed mixture is continuously introduced into the column between the 12th and 13th tray and n-heptane is continuously introduced below the 1st tray. The column is operated at substantially ambient temperatures and at autogenous pressure. The weight ratio of first complex to feed mixture to n-heptane is 1:0.53:0.47. A raffinate, termed the first raffinate, is continuously taken overhead from the extraction column and an extract, termed the first extract, is continuously taken from the bottom. The first raffiniate contains trans-pentene-2 and cis-pentene-2 in a weight ratio of 17.75:1. The first extract contains trans-pentene-2 and cis-pentene-2 in a weight ratio of 1:8.87. This first extract is continuously introduced into a second column also of 24 trays wherein it is countercurrently contacted with hexene-1 at ambient temperatures and pressures. The amount of hexene-1 used is in molar excess over the amount of pentene-2 in the extract phase. An extract phase, termed the second extract, is continuously taken from the bottom of this second column and a raffinate phase, termed the second raffinate, is continuously taken from the overhead of this second column. The second raffinate contains trans-pentene-2 and cis-pentene-2 in a weight ratio of 1:8.78. The second extract from the second column is

recycled back to the first extraction column as a part of the first complex. The first raffinate phase is subjected to fractional distillation in a distillation column having approximately 30 trays, and an overhead fraction obtained which is substantially richer in the trans-pentene-2 than is the original feed mixture to the extraction column. Also, a second fraction containing hexene-1 is obtained from this distillation which fraction is recycled to the second column. The second raffinate is also subjected to fractional distillation in a column having approximately 30 trays and a fraction is obtained from this distillation which is substantially richer in cis-pentene-2 than is the original feed mixture to the first extraction column.

The cuprous salts employed in forming the complexes used in carrying out the process of the present invention are cuprous tetrafluoroborate and cuprous hexafluorophosphate. Generally, these are referred to as cuprous fluoroborate and cuprous fluorophosphate. Both of these salts are relatively unstable and cannot be readily formed as the salt. As a result, the usual practice is to form the salt in the presence of an organic compound with which the salt will complex, thereby forming the salt and the complex of the salt with the organic compound almost concurrently.

The organic compounds in which the cuprous salts may be formed and with which such salts are immediately complexed may include any of a rather large number of such compounds. The choice of the particular organic compound is often dictated by the hydrocarbons in the hydrocarbon mixture to be separated. Generally, however, the organic compounds will be aromatic hydrocarbons. Such aromatic hydrocarbons may contain a single aromatic ring or may contain two or more aromatic rings, either condensed or noncondensed. In addition, the aromatic hydrocarbons may have substituents to the rings or may be condensed with one or more other ring structures which are paraffinic or olefinic in nature. Nonlimiting examples of aromatic hydrocarbons suitable for use in preparing the cuprous salts of the present invention are benzene, toluene, the xylenes, various other polymethylbenzenes, such as mesitylene, isodurene, tri-, tetra-, penta- and hexamethylbenzenes, ethylbenzene and the various polyethylbenzenes, isopropylbenzenes, the various butyl and pentylbenzenes and the like, the substituted benzenes containing two or more different substituents such as ethyltoluene, isopropyltoluene, and ethylxylenes; naphthalene, the various methylnaphthalenes, and polymethylnaphthalenes, ethylnaphthalene and the various polyethylnaphthalenes, the naphthalenes containing propyl, isopropyl, butyl, and pentyl substituents; the substituted naphthalenes containing two or more different substituents such as methylethylnaphthalene, methylpropylnaphthalenes, etc.; the various indanes such as methylindanes, ethylindanes, isopropylindanes, etc.; the dihydronaphthalanes such as methyl, ethyl, propyl, and butyl substituted dihydronaphthalenes; the tetrahydronaphthalenes such as methyl, ethyl, propyl, and pentyl substituted tetrahydronaphthalenes and the like. In the preferred practice of the present invention, the aromatic hydrocarbons most often employed as the organic compound in forming the complexes of the present invention are benzene, naphthalene, partially hydrogenated naphthalenes, and the various alkyl substituted derivatives of these wherein the alkyl substituents have no more than four carbon atoms per substituent. Within this group of preferred aromatic hydrocarbons are such compounds as benzene, ethylbenzene, toluene, the xylenes, naphthalene and the methyl naphthalenes, dihydronaphthalenes and tetrahydronaphthalenes. A particularly useful group of aromatic hydrocarbons for use in forming the complexes is that including such compounds as toluene, ethylbenzene, ethyltoluene, the xylenes and tetrahydronaphthalene.

The method of preparing the cuprous fluoroborate-aromatic hydrocarbon containing complex, referred to herein as the "first complex," which is used for the separation of hydrocarbon mixtures in accordance with the present invention may be any of those methods conventionally used. In U.S. Pat. 2,953,589, the preparation of cuprous fluoroborate-aromatic hydrocarbon complexes by the introduction of powdered copper, BF_3 and anhydrous HF into benzene or other aromatic hydrocarbons is disclosed. This method may be used for the purposes of the present invention. In addition, the cuprous fluoroborate-aromatic hydrocarbon complex may be prepared by dispersing $CuF_2 \cdot 2H_2O$ and metallic copper in an aromatic hydrocarbon an heating the reaction mixture while introducing gaseous BF_3 into the dispersed medium. This method is described in Journal of the American Chemical Society, vol. 74, page 3702, 1952. This latter described method is preferred for the practice of the present invention. In addition to these two methods of preparing the cuprous fluoroborate-aromatic hydrocarbon complex, any other of the methods known to those skilled in the art may be used.

Preparation of the cuprous fluorophosphate-aromatic hydrocarbon complex may be by any of those means known to those skilled in the art. Preferably, however, this complex is prepared by introducing anhydrous CuF_2 or $CuF \cdot 2H_2O$, metallic copper and phosphorous pentafluoride into an aromatic hydrocarbon medium and heating with agitation to an elevated temperature in excess of 75° C. The cuprous fluorophosphate-aromatic hydrocarbon complexes may on occasion be solid at room temperature and therefore, must be maintained at elevated temperatures for use in the process of the present invention or, in the alternative, be used along with a suitable solvent. It is believed that impurities in the system cause these complexes to be solid. A number of solvents suitable for maintaining the cuprous fluorophosphates in solution will be hereinafter discussed. In addition to the above method of preparing the cuprous fluorophosphate-aromatic hydrocarbon complex, any other method known to the art may be used.

In preparing the cuprous salt-organic compound first complexes for use in the separations processes disclosed herein, some care should be exercised in the selection of the organic compound to avoid use of an organic compound which itself will be difficultly separable from hydrocarbons of the mixture to be separated. Each mole of the cuprous salt-organic compound first complexes formed in accordance with the present invention generally will contain at least two moles of organic compound and one mole of the cuprous salt. Separation of hydrocarbon mixtures in accordance with the processes disclosed herein, involves the displacement of one or more of the moles of organic compound from the first complex and substitution therein of at least one of the components of the hydrocarbon mixture to be separated. Since the organic compound displaced from the first complex by the complexible components of the mixture to be separated generally mix freely with the components of the feed mixture which do not complex with the cuprous salt, the organic compound of the first complex should be one which is readily and simply separated from the noncomplexed hydrocarbons of the hydrocarbon mixture to be separated. To illustrate the above, if the hydrocarbon mixture to be separated is one comprised of 2-methyl-octene-1 and nonene-4, it would not be desirable to use ortho-xylene as the organic compound in which the first complex is formed. If, for instance, ortho-xylene was used as the organic compound, the raffinate resulting from contact of the first complex with the mixture of 2-methyloctene-1 and nonene-4 would contain a mixture of 2-methyloctene-1 and ortho-xylene which compounds are difficultly separable from one another.

The amount of the first complex used in carrying out the separation of olefin hydrocarbons in accordance with the process of the present invention may vary considerably depending upon the circumstances. In general, as the mole ratio of available cuprous salt in the first complex

to olefin hydrocarbons goes down, the selectivity of the cuprous salt for certain of the olefin hydrocarbons increases. Therefore, the optimum amount of first complex used will vary according to the olefin hydrocarbon mixture to be separated and upon the particular separation which is desired to carry out. In general, however, the amount of first complex employed will be sufficient to provide a mole ratio of the cuprous salt to the olefin hydrocarbons to be selectively complexed with the cuprous salt of 0.25:1 to 10:1. Preferably, however, this mole ratio is within the range of 0.33:1 to 4:1.

It has been found particularly useful in carrying out the separations process of the present invention to use a noncomplexible hydrocarbon diluent or solvent to aid in the formation of extract and raffinate phases and/or for further extraction of the extract phases to remove from such phases hydrocarbons which are not complexed with the cuprous salt. The use of such noncomplexible hydrocarbons as an aid to phase formation is exemplified in the above examples. In most instances, the noncomplexible hydrocarbon employed is an aliphatic hydrocarbon of 3 to 15 carbon atoms. Nonlimiting examples of such hydrocarbons are propane, n-butane, n-pentane, n-hexane, n-heptane, n-octane, n-nonane, n-decane, n-undecane, n-dodecane, n-tridecane, isobutane, isopentanes, isoheptanes, isodecanes, isododecanes, isotridecane, cyclopentane, cyclohexane, methylcyclohexane, cycloheptane, and the like. Most often, the saturated aliphatic hydrocarbons are paraffinic hydrocarbons and may be straight-chain or branched-chain. Petroleum ether is a very practical and useful fraction for use in the present process. The most useful saturated aliphatic hydrocarbons are the paraffinic hydrocarbons of 4 to 7 carbon atoms per molecule.

The amount of noncomplexible hydrocarbon employed in the process of the present invention may vary considerably. The actual amount of such hydrocarbons used will depend to a large extent on the amount of hydrocarbons in the olefin mixture to be separated which will not be complexed with the cuprous salt and on the degree of separation desired. Usually, however, about 0.25 to 5 volumes of the noncomplexible hydrocarbon is used per volume of olefin hydrocarbons in the feed mixture which is to be separated.

Conditions of temperature and pressure whereby the separations process of the present invention may be successfully practiced may vary rather widely. Most often, however, the process of the present invention will be practiced at temperatures within the range of 0 to 195° C., preferably, within the range of 25 to 150° C. The pressures most often employed for practicing the process of the present invention do not appear to be critical and may range from subatmospheric pressures to superatmospheric pressures. As a practical matter, it is usually desirable to operate at or near atmospheric pressure, the pressures ranging from as low as 50 mm. Hg to 250 p.s.i.g.

The separations which may be carried out in accordance with the separations process herein disclosed include the separation of olefin hydrocarbons according to structural configuration and/or olefin type. By the present process cis-olefin hydrocarbons may be separated from trans-olefin hydrocarbons, the cis-olefin hydrocarbons being preferentially extracted by the cuprous salt. Additionally, olefin hydrocarbons may be separated according to type or according to the location of the unsaturated double bonding with respect to the various carbon atoms in the olefin hydrocarbon molecule. For example, Type I olefins may be separated from Type II and/or Type III and/or Type IV and/or Type V olefin hydrocarbons. Type II olefins may be separated from Type II and/or Type IV and/or Type V olefin hydrocarbons. Type III olefins may be separated from Type IV and/or Type V olefin hydrocarbons. In addition combinations of these may be separated. For example, a mixture of Type I, Type II and Type III olefins may be separated by extracting a mixture of the Type I and Type II olefins from the Type III olefins or only Type I olefins may be extracted leaving a mixture of Type II and Type III olefins. In such instances, the particular split in the separations depends upon the mole ratio of the cuprous salt to the olefin mixture. In the mixture of Type I, II and III olefins, a low ratio of cuprous salt to olefin hydrocarbons favors extraction of only the Type I olefins whereas a higher ratio tends to favor extraction of the Type II olefins along with the Type I olefins.

The molecular weight of the olefin hydrocarbons which may be separated in accordance with the present invention includes a wide range of olefin hydrocarbons. The primary consideration is that the olefin hydrocarbons to be separated be liquid or liquefiable under the conditions of the process. By liquefiable is meant that the olefin hydrocarbons can be made liquid either by application of small amounts of heat or by dissolving in a solvent which is substantially inert to the separations process. Most often, the process of the present invention is applied to the separation of olefin hydrocarbons of no greater than 20 carbon atoms per molecule. In the preferred practice of the present invention, the olefin hydrocarbons separated are those having 2 to 15 carbon atoms per molecule.

While the olefin hydrocarbons contained in the extract phase may be recovered therefrom by any means such as heat, reduced pressure, and the like, it is usually preferred to displace these hydrocarbons from the extract phase by means of another hydrocarbon. Such other hydrocarbons which are used to displace the olefin hydrocarbons from the extract phase are vinyl aromatic hydrocarbons and other olefin hydrocarbons, generally of a molecular weight different from the olefin hydrocarbons in the extract phase. Such vinyl aromatic hydrocarbons as styrene, α-methyl styrene, vinyl toluene and the like are useful. The olefin hydrocarbons useful include those having as high as twenty carbon atoms and higher, again generally being those that are liquid or liquefiable at slightly elevated temperatures or by the use of solvents inert to the system or by mutual solubility with the components of the extract phase. Usually, the olefin hydrocarbons employed are those having less than 15 carbon atoms. In choosing the vinyl aromatic hydrocarbon or olefin hydrocarbon, care should be used that the hydrocarbon selected is not one which will itself be difficulty separable from other hydrocarbon components of the system. Also, when employing the olefin hydrocarbons, it may be desirable to consider the relative preference of the complex for the olefin already in the extract and that which is to be used for displacing such olefin. For example, if Type I olefins are in the complex, Type V olefins would not be as effective in displacing the Type I olefins as other Type I olefins would be.

As mentioned above, in many instances to avoid the use of elevated temperatures, it is desirable to use a solvent in the preparation of the cuprous fluorophosphate containing first complex. Such solvent includes a wide range of organic solvents particularly those containing oxygen and/or sulfur. Ethers, ketones, sulfones, disulfides, thioethers, thioureas, nitro alkyl and aryl, trihydrocarbonyl phosphines and the like represent classes of useful solvents. While the particular solvent selected is primarily a matter of individual choice, it is somewhat preferred that the solvent be one selected from the group consisting of the alkyl and aryl sulfones, particularly such compounds as sulfolane and alkyl sulfolanes.

What is claimed is:

1. A process for the separation of monoolefin hydrocarbons according to structure and type, said process comprising contacting a monoolefin hydrocarbon mixture containing at least two monoolefin hydrocarbons of different structure with a first complex which comprises a complex of a cuprous salt selected from the group consisting of cuprous fluoroborate and cuprous fluorophosphate and a hydrocarbon selected from the group consisting of aromatic hydrocarbons, olefin hydrocarbons of a molecular weight different from those of said mono-

olefin hydrocarbon mixture and combinations of such aromatic hydrocarbons and olefin hydrocarbons, thereby forming an extract phase and a raffinate phase, separating said extract and raffinate phase, recovering from said extract phase a monoolefin hydrocarbon fraction substantially richer in one of said two monoolefin hydrocarbons than the original monoolefin hydrocarbon mixture, and recovering from said raffinate phase a monoolefin hydrocarbon fraction substantially richer in the other of said two monoolefin hydrocarbons than said original monoolefin hydrocarbon mixture.

2. The process of claim 1 wherein the cuprous salt is cuprous fluoroborate.

3. The process of claim 2 wherein the first complex comprises cuprous fluoroborate and an aromatic hydrocarbon.

4. The process of claim 3 wherein the aromatic hydrocarbon is selected from the group consisting of benzene, naphthalene, partially hydrogenated naphthalenes, the alkyl substituted derivatives of these wherein the alkyl substituents have no more than 4 carbon atoms per substituent, and mixtures of these.

5. The process of claim 4 wherein the aromatic hydrocarbon is toluene.

6. The process of claim 1 wherein said mixture is contacted with said first complex at a temperature within the range of 0 to 195° C.

7. The process of claim 1 wherein said olefin hydrocarbon mixture contains cis-olefin hydrocarbons and trans-olefin hydrocarbons.

8. The process of claim 1 wherein said olefin hydrocarbon mixture contains a Type I olefin hydrocarbon and another olefin hydrocarbon selected from the group consisting of Type II olefin hydrocarbons, Type III olefin hydrocarbons, Type IV olefin hydrocarbons, Type V olefin hydrocarbons and combinations of these.

9. The process of claim 1 wherein said olefin hydrocarbon mixture contains a Type II olefin hydrocarbon and another olefin hydrocarbon selected from the group consisting of Type III olefin hydrocarbons, Type IV olefin hydrocarbons, Type V olefin hydrocarbons and combinations of these.

10. The process of claim 1 wherein said olefin hydrocarbon mixture contains a Type III olefin hydrocarbon and another olefin hydrocarbon selected from the group consisting of Type IV olefin hydrocarbons, Type V olefin hydrocarbons and combinations of these.

11. The process of claim 1 wherein said olefin hydrocarbons are recovered from said extract phase by contacting said extract phase with vinyl aromatic hydrocarbons, said vinyl aromatic hydrocarbons being in at least molar equivalent with the olefin hydrocarbons within said extract phase.

12. The process of claim 1 wherein said olefin hydrocarbons are recovered from said extract phase by contacting said extract phase with at least a molar equivalent of olefin hydrocarbons of a different molecular weight.

13. The process of claim 1 wherein said olefin hydrocarbon mixture is contacted with said first complex in the presence of a noncomplexible hydrocarbon.

14. The process of claim 13 wherein said noncomplexible hydrocarbon is a saturated aliphatic hydrocarbon of 3 to 15 carbon atoms.

15. The process of claim 1 wherein said first complex is present in an amount such as to provide a mole ratio of cuprous salt to the olefin hydrocarbons to be selectively complexed with said cuprous salt within the range of 0.25:1 to 10:1.

16. The process of claim 1 wherein the olefin hydrocarbons within said olefin hydrocarbon mixture have no greater than 15 carbon atoms per molecule.

17. The process of claim 1 wherein said first complex comprises cuprous fluoroborate, an aromatic hydrocarbon and an olefin hydrocarbon.

18. The process of claim 17 wherein the aromatic hydrocarbon is selected from the group consisting of benzene, naphthalene, partially hydrogenated naphthalenes, the alkyl substituted derivatives of these wherein the alkyl substituents have no more than 4 carbon atoms per substituent, and mixtures of these.

19. The process of claim 17 wherein the olefin hydrocarbon is one having 2 to 15 carbon atoms per molecule.

20. A process for the separation of monoolefin hydrocarbons according to structure, said process comprising introducing a monoolefin hydrocarbon mixture containing at least two monoolefin hydrocarbons of different structure into a first extraction column intermediate the ends thereof, concurrently introducing adjacent the top of said extraction column a first complex comprising a cuprous salt selected from the group consisting of cuprous fluoroborate and cuprous fluorophosphate and a hydrocarbon selected from the group consisting of aromatic hydrocarbons, monoolefin hydrocarbons and mixtures of monoolefin and aromatic hydrocarbons, concurrently introducing into said extraction column adjacent the bottom thereof a non-complexible hydrocarbon, removing overhead from said first extraction column a first raffinate containing a monoolefin hydrocarbon fraction substantially richer in one of said two different olefin hydrocarbons than the original monoolefin hydrocarbon mixture, removing from the bottom of said extraction column a first extract phase, introducing said first extract phase into a second extraction column intermediate the ends thereof, concurrently introducing a hydrocarbon selected from the group consisting of monoolefin hydrocarbons of a molecular weight different from those of said monoolefin hydrocarbon mixture and vinyl aromatic hydrocarbons, said hydrocarbon being introduced in a quantity which is at least in molar equivalent to the monoolefin hydrocarbons in said first extract phase, concurrently introducing noncomplexible hydrocarbons into said second extraction column, removing from the bottom of said second extraction column a second extract phase at least a portion of which is recycled to said first extraction column as at least a portion of said first complex, removing overhead from said second extraction column a second raffinate phase containing a monoolefin hydrocarbon fraction substantially richer in the other of said two different monoolefin hydrocarbons than said original monoolefin hydrocarbon mixture.

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