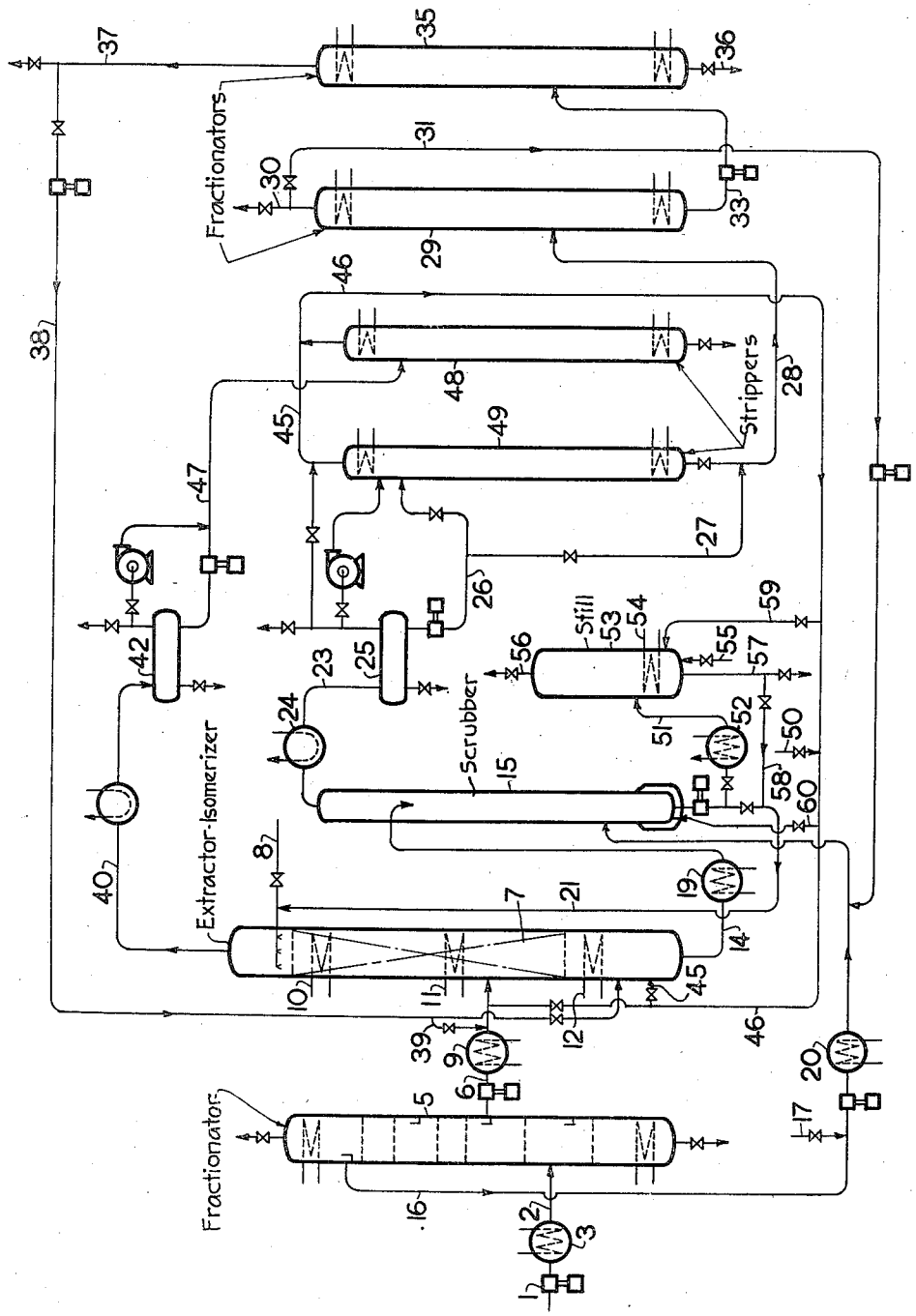
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CYCLOPARAFFIN PRODUCTION

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CYCLOPARAFFIN PRODUCTION

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This invention relates to an improved process for the separation of cycloparaffins from hydrocarbon mixtures comprising cycloparaffins in admixture with open chain paraffins. The invention relates more particularly to an improved process for the production of cycloparaffins of hydroaromatic structure from hydrocarbon mixtures of wide boiling range such as naphthenic gasolines comprising open chain paraffins and cycloparaffins of non-hydroaromatic structure.

The cycloparaffins have become of exceeding importance as starting materials and intermediates in the production of a wide variety of organic products. The most fertile source of these highly desirable materials resides in the hydrocarbon mixtures obtained in the natural state as petroleum, and in the products obtained in the thermal or catalytic treatment of petroleum or distillate fractions thereof, and in the thermal or catalytic treatment such as, for example, hydrogenation of carbonaceous materials, etc. As is well known, the cycloparaffins in these readily available hydrocarbon mixtures are found therein in admixture with open chain paraffins. Realization of the full advantages inherent in the many chemical processes relying upon the cycloparaffins as starting or intermediate materials has heretofore been seriously handicapped by the lack of a process enabling the efficient separation on a practical scale of the cycloparaffins from the open chain paraffins in admixture with which they are generally encountered. Thus, separation of the cycloparaffins from open chain paraffins having the same, or approximately the same, number of carbon atoms to the molecule by such methods as fractional distillation, if at all possible, is often rendered so complex and delicate an operation as to render it impractical.

Of the cycloparaffins, those of hydroaromatic structure are presently of particular value and find application in the production of an exceedingly wide range of valuable organic products. The production of the cycloparaffins of hydroaromatic structure in a state of required purity is rendered even more difficult since, to the difficulty of their separation from open chain paraffins is added the often equally vexing problem of their separation from isomeric non-hydroaromatic cycloparaffins and other hydrocarbons of close boiling range or capable of forming azeotropes therewith. By the term "hydroaromatic cycloparaffins" as used throughout this specification and appended claims is meant the cycloparaffins having a hexamethylene ring such as, for example, cyclohexane and the alkyl cyclohexanes, to distinguish them from cycloparaffins of non-hydroaromatic structure comprising those having pentamethylene rings such as, for example, methylcyclopentane and the alkyl cyclopentanes.

It has been suggested heretofore to subject the hydrocarbon mixtures comprising open chain paraffins and cycloparaffins of non-hydroaromatic structure to isomerizing conditions effecting the conversion of non-hydroaromatic cycloparaffins to hydroaromatic cycloparaffins and thereafter subject the entire hydrocarbon mixture to fractionation to separate fractions comprising desired cycloparaffins. Although such a procedure enables the concentration on a practical scale of certain of the cycloparaffins such as, for example, cyclohexane, it still does not enable the attainment of desired yields in even such specific instances. It furthermore does not eliminate to a sufficient degree the difficulties of separation. Thus, for example, in the production of cyclohexane from hydrocarbon mixtures comprising C_6 paraffins and methylcyclopentane, the available raw material must first be subjected to a fractionation resulting in the production of a methylcyclopentane concentrate. In so doing, a considerable amount of valuable cyclohexane originally present in the available raw material, as well as a certain amount of methylcyclopentane, is left in the higher boiling fraction from which the methylcyclopentane concentrate is separated. Such methods furthermore offer limited advantages in only such specific cases. They do not provide a practical answer, for example, to the production of hydrocarbons predominating in methyl cyclohexane from the readily available hydrocarbon mixtures comprising the non-hydroaromatic cycloparaffins having seven carbon atoms to the molecule in admixture with close boiling open chain paraffins having seven and eight carbon atoms to the molecule. In such case the problem of separation is in no wise overcome by isomerizing the mixture as a whole under conditions resorted to heretofore.

In its broadest aspect, the object of the present invention is to provide an improved process enabling the more efficient separation of cycloparaffins from hydrocarbon mixtures comprising cycloparaffins and open chain paraffins.

A more particular object of the invention is the provision of a process enabling the more efficient separation of cycloparaffins from hydrocarbon mixtures boiling in the gasoline boiling range and containing cycloparaffins and open

chain paraffins having substantially the same number of carbon atoms to the molecule.

Another object of the invention is the provision of an improved process enabling the more efficient separation of cycloparaffins of non-hydroaromatic structure from hydrocarbon mixtures in the gasoline boiling range comprising cycloparaffins and open chain paraffins with simultaneous conversion of the cycloparaffins of non-hydroaromatic structure to cycloparaffins of hydroaromatic structure during the separation.

A further object of the invention is the provision of an improved process for the production of hydrocarbons comprising cyclohexane from naphthenic hydrocarbon mixtures of relatively wide boiling range comprising methylcyclopentane.

Still another object of the invention is the provision of an improved process for the more efficient production of methylcyclohexane from naphthenic hydrocarbon mixtures having a relatively wide boiling range and containing non-hydroaromatic cycloparaffins having seven carbon atoms to the molecule. Other objects and advantages of the invention will become apparent from the following description thereof.

It is known that unsaturated hydrocarbons such as olefins and aromatic hydrocarbons which react readily with aluminum chloride, are removed from hydrocarbon mixtures containing them by treatment with aluminum chloride. It has now been found that saturated hydrocarbons of cyclic structure comprising the cycloparaffins can be separated efficiently by extraction under suitable conditions with a preformed complex obtained by the interaction of a metal halide of the Friedel-Crafts type and an organic compound. It has been found that by selection of suitable conditions the cycloparaffins of non-hydroaromatic structure present in the hydrocarbon mixture treated are converted to, and separately recovered, as cycloparaffins of hydroaromatic structure.

In accordance with the process of the invention, a hydrocarbon mixture of relatively wide boiling range comprising paraffins and cycloparaffins such as, for example, a naphthenic gasoline, is introduced into a feed fractionating zone. Within the feed fractionating zone there are separated a fraction of intermediate boiling range and a fraction of lower boiling range. The fraction of intermediate boiling range is passed into an extraction zone wherein it is contacted with a preformed organo-metal halide complex, obtained by the interaction of a metal halide of the Friedel-Crafts type and an organic compound, under suitable conditions resulting in the formation of a raffinate phase comprising paraffins and an extract phase comprising organo-metal halide complex and cycloparaffins. A suitable extraction zone comprises, for example, an enlarged chamber or packed tower containing suitable packing material through which the hydrocarbon charge is passed countercurrent to a descending stream of the organo-metal halide complex. The extract phase is passed into a scrubbing zone wherein it is scrubbed with a scrubbing medium comprising the lower boiling fraction separated in the feed fractionating zone. In passing through the scrubbing zone the cycloparaffins in the extract phase are separated from the organo-metal halide complex. The organo-metal complex is recycled from the scrubbing zone to the extraction zone. The hydrocarbon mixture eliminated from the scrubbing zone, comprising the lighter boiling fraction of the charge separated in the feed fractionating zone and the cycloparaffins of intermediate boiling range, is passed into a fractionating zone. Within the fractionating zone the cycloparaffins of intermediate boiling range are separated as a final product from the lower boiling scrubbing medium. The lower boiling scrubbing medium is recycled, at least in part, from the fractionating zone to the scrubbing zone.

By maintaining suitable cycloparaffin isomerizing conditions within the extraction zone, comprising the introduction therein of hydrogen halide or a material affording a hydrogen halide, and the maintenance of temperature conditions defined more fully below, the isomerization of cycloparaffins such as, for example, the conversion of cycloparaffins of non-hydroaromatic structure to cycloparaffins of hydroaromatic structure is accomplished simultaneously with the extraction operation.

When the extraction zone is maintained under cycloparaffin isomerizing conditions the raffinate phase eliminated therefrom comprising paraffins in the intermediate boiling range, and the hydrocarbon mixture comprising lighter boiling paraffins and cycloparaffins of intermediate boiling range removed from the scrubbing zone, are passed in separate streams to separate stripping zones wherein the hydrogen halide admixed therewith is separated as gaseous fractions. The gaseous fractions comprising the hydrogen halide promoter are recycled to the extraction zone.

It is to be noted that in the process of the invention a raffinate phase comprising open chain paraffins, and an extract phase comprising organo-metal halide complex in admixture with cycloparaffins, are separately removed from the extraction zone, and that such operation in no wise approximates the practice resorted to heretofore in the isomerization of hydrocarbons wherein hydrocarbons and catalyst are drawn in single stream from the reaction zone, and wherein hydrocarbons separated from catalyst drawn from the reaction zone are recombined with the total hydrocarbon effluence from the reaction zone before or during product separation.

In order to set forth more clearly the nature of the invention it will be described herein in detail with reference to the attached drawing in which the single figure represents a more or less diagrammatic elevational view of one form of apparatus suitable for executing the process of the invention.

A hydrocarbon mixture of relatively wide boiling range comprising cycloparaffins and open chain paraffins such as, for example, a naphthenic gasoline is forced by means of pump 1 through line 2 into a feed fractionating zone. Suitable heating means such as, for example, a hydrocarbon fluid heater or indirect heat exchanger 3 is positioned in line 2. The feed fractionating zone is depicted in the drawing by a single fractionator 5 for the purpose of simplicity. It will be understood that in actual practice more than one such fractionator will generally be employed to effect the desired feed fractionation. Within feed fractionator 5 there is separated a fraction of intermediate boiling range and a fraction of lower boiling range. The fraction of intermediate boiling range may suitably comprise hydrocarbons having six carbon atoms to the molecule, such as a hexane fraction comprising open chain hexanes, methylcyclopentane, and cyclohexane. Although a hexane fraction is chosen in the present illustrative description, it is to be understood

that the invention is in no wise limited to the separation of a hexane fraction as the fraction of intermediate boiling range. Thus, the intermediate boiling range fraction may comprise hydrocarbons having seven carbon atoms to the molecule; a hydrocarbon mixture of wider boiling range comprising both C_6 and C_7 hydrocarbons, or a hydrocarbon mixture comprising or predominating in hydrocarbons having more than seven carbon atoms to the molecule.

The hexane fraction is passed from fractionator 5 through line 6 into an extraction zone. The extraction zone may comprise an elongated chamber or column 7 containing inert solid contact material such as, for example Raschig rings, crushed brick, silica stone, etc. The hydrocarbon charge is introduced into the column at an intermediate point along the length thereof.

A preformed fluid organo-metal halide complex is introduced into the top of the column by means of a valved line 8. The fluid organo-metal halide complex is prepared by mixing a metal halide of the Friedel-Crafts type, for example, a halide of aluminum such as aluminum chloride and/or aluminum bromide with an organic compound under suitable conditions resulting in the interaction of the metal halide with the organic compound and/or decomposition products thereof. Suitable organic compounds with which the metal halide may be combined under conditions resulting in the obtaining of a desired organo-metal halide complex comprising, for example, aromatic hydrocarbons such as benzene, toluene; hydrocarbon fractions such as an aromatic kerosene extract; cyclic olefins such as cyclohexane, cyclopentene, and alkyl derivatives thereof; paraffinic and olefinic hydrocarbons of straight or branched chain structure; phenols; organic acids; ethers, etc. Of the suitable organo-metal halide complexes, those comprising the aluminum chloride-hydrocarbon complex are somewhat preferred.

By means of heat exchanger 9 and optionally heating or cooling means, such as closed coils 10, 11 and 12 within column 7 the hydrocarbons and complex are maintained in the temperature range of from about 20° C. to about 140° C., and preferably from about 20° C. to about 70° C. Atmospheric or superatmospheric pressures are maintained within column 7. The pressure is, however, kept sufficiently high to maintain the hydrocarbons in the liquid phase. Under these conditions cycloparaffins in the hydrocarbon mixture passing upward through the column will be selectively removed from open chain paraffins resulting in the formation of a raffinate phase in the upper part of the column consisting essentially of paraffinic hydrocarbons, and an extract phase in the lower part of the column consisting essentially of complex and cycloparaffins.

The extract phase comprising aluminum chloride-hydrocarbon complex and cycloparaffins is passed from the lower part of column 7 through valved line 14 into the upper part of a scrubbing zone. The scrubbing zone may comprise a column 15 provided with suitable packing material, baffle plates, or the like.

The lower boiling fraction separated in feed fractionator 5 and comprising, for example, a pentane fraction, is passed from fractionator 5 through line 16 into the lower part of scrubber 15. Although a pentane fraction has been chosen as the fraction of lower boiling range passed from fractionator 5 to the scrubbing tower, any suitable hydrocarbon fraction lower boiling than the intermediate fraction passed into extraction column 7 may suitably be separated in the feed fractionator 5 and passed therefrom to scrubbing column 15. Thus, instead of a pentane fraction, a butane fraction, or a fraction comprising both butane and pentane, may be passed from fractionator 5 to scrubber 15. Additional hydrocarbons lower boiling than the fraction of intermediate boiling range passed into the extraction column 7, may be introduced into the system by means of valved line 17. In passing downwardly through scrubbing tower 15, the cycloparaffins contained in the extract phase are separated from the aluminum chloride-hydrocarbon complex by solution in the upward flowing, lower boiling hydrocarbons comprising pentane. A temperature favorable to separation of the cycloparaffins from the complex is maintained within scrubbing tower 15. The temperature within column 15 is maintained by heat input in heat exchangers 19 and 20, and optionally by additional heating means maintained within or about the scrubbing column itself. Suitable temperatures to be maintained within scrubbing column 15 comprise a temperature in the range of, for example, from about 20° C. to about 140° C. and preferably from about 20° C. to about 80° C. The pressure within column 15 is always kept sufficiently high to maintain at least a substantial part of the hydrocarbons passing therethrough in the liquid phase. Under these conditions aluminum chloride-hydrocarbon complex, free of any substantial amount of cycloparaffins, will settle in the lower part of scrubber 15 whence it is continuously withdrawn and forced through line 21 into line 8 entering the top of extraction column 7. Hydrocarbons comprising pentanes, methylcyclopentane, and cyclohexane, free of any substantial amount of aluminum chloride-hydrocarbon complex, are taken from the top of scrubber 15 and passed through line 23 containing cooler 24 into accumulator 25.

Liquid hydrocarbons are drawn from accumulator 25 and forced through lines 26, 27 and 28 into a fractionator 29. Within fractionator 29 the lower boiling hydrocarbons comprising pentane, which are readily separable from the cycloparaffins comprising methylcyclopentane and cyclohexane, are separated as a vapor fraction. The vapor fraction is eliminated overhead through valved line 30. At least a part of the hydrocarbons passing through valved line 30 are recycled through lines 31 and 16 to the lower part of scrubber 15. The amount of lighter hydrocarbons comprising pentane thus recycled is maintained sufficiently high so that a sufficiently high ratio of pentane to extract phase is continuously passed through scrubber 15 to effect the substantially complete separation therein of the cycloparaffins from the aluminum chloride-hydrocarbon complex.

By thus scrubbing the cycloparaffins from the extract phase with a hydrocarbon fraction comprising hydrocarbons which are readily separable from the cycloparaffins contained in the extract phase, substantial advantages are obtained over such methods as separation by distillation. The use of scrubbing instead of distillation not only obviates the disadvantageous effect upon the useful life of the complex occasioned by continuous passage through a zone maintained at distillation temperatures, but greatly facilitates the flow of the complex through the system.

Cycloparaffins comprising methylcyclopentane and cyclohexane are passed from fractionator 29

through line 33 into a fractionator 35. Within fractionator 35 a vapor fraction comprising methylcyclopentane is separated from a liquid fraction comprising methylcyclohexane. The liquid fraction is eliminated from fractionator 35 through valved line 36 as a final product. The vapor fraction is eliminated from fractionator 35 through valved line 37 and at least a part thereof is recycled through line 38 into extraction column 7 and introduced therein at a point below the introduction of the hydrocarbon charge. This, it has been found, adds materially in the separation of cycloparaffins from paraffins under the operating conditions. A by-pass 39 is provided for the introduction of recycled methylcyclopentane into line 6.

The raffinate phase comprising open chain hexanes is taken overhead from column 7 and passed through line 40 into accumulator 42.

A particular advantage of the invention resides in the ability to recover the naphthenic hydrocarbons of non-hydroaromatic structure, originally present in the charge, in the form of naphthenic hydrocarbons of hydroaromatic structure. Thus, in the treatment of a naphthenic hexane fraction containing methylcyclopentane, maintenance of suitable cycloparaffin isomerizing conditions within column 7 enables the conversion of the methylcyclopentane to cyclohexane during the extraction operation. To attain these objectives of the invention, temperatures within column 7 are maintained within the range of, for example, from about 30° C. to about 140° C. and preferably from about 70° C. to about 100° C. A hydrogen halide promoter such as, for example, hydrogen chloride or a material affording the hydrogen halide under the conditions maintained in column 7 is introduced into the lower part of the column through valved line 45 at a point below the introduction of the charge. A part of the hydrogen halide introduced into column 7 may be introduced directly into line 6 from line 46. The hydrogen halide promoter is introduced into the column at such a rate as to maintain a concentration of the hydrogen halide in the column in the range of from about 0.1% to about 2.0% and preferably from about 0.1% to about 0.5% by weight of the hydrocarbons in the column.

The following examples are indicative of the degree to which isomerization of cycloparaffins is accomplished, with simultaneous separation of cycloparaffins, from admixture with open chain paraffins in accordance with the process of the invention.

Example I

A methylcyclopentane concentrate having the following composition

	Per cent volume
Methyl pentane	4.5
Normal hexane	40.0
Methylcyclopentane	55.0
Undetermined	0.5

was contacted in a single stage operation with an aluminum chloride-hydrocarbon complex under the following conditions:

Ratio of complex to hydrocarbon	2:1
Time of contact, minutes	30
Temperature, ° C.	70

Hydrogen chloride was bubbled through the liquid throughout the operation to maintain a concentration of HCl equal to 0.1% of the hydrocarbons charged. A raffinate phase and an extract phase were separately withdrawn. The raffinate phase contained 70% by volume of the hydrocarbons charged whereas the extract phase contained 30% of the hydrocarbons charged. A conversion of methylcyclopentane to cyclohexane of 40% was obtained. The degree of separation of cycloparaffins from open chain paraffins is exemplified by the following ratios of naphthenes to paraffins:

Ratio of naphthenes to paraffins in charge	1.25
Ratio of naphthenes to paraffins in raffinate	1.06
Ratio of naphthenes to paraffins in extract	1.62

Example II

A methylcyclopentane concentration having the following composition:

	Percent volume
Methyl pentane	4.0
Normal hexane	37.0
Methylcyclopentane	51.0
Benzene	8.0

was contacted in a single stage operation with an aluminum chloride-hydrocarbon complex under the following conditions:

Ratio of complex to hydrocarbon	2:1
Time of contact, minutes	30
Temperature	70° C.

Hydrogen chloride was bubbled through the liquid throughout the operation to maintain a concentration of HCl equal to 0.1% of hydrocarbons charged. A raffinate phase and an extract phase were separately withdrawn. The raffinate phase contained 70% by volume of the hydrocarbons charged whereas the extract phase contained 30% of the hydrocarbons charged. A conversion of methylcyclopentane to cyclohexane of 35% was obtained. The separation of cycloparaffins from open chain paraffins is exemplified by the following ratios of naphthenes to paraffins:

Ratio of naphthenes to paraffins in charge	1.24
Ratio of naphthenes to paraffins in raffinate	0.84
Ratio of naphthenes to paraffins in extract	1.64

It is to be pointed out that the above examples are single stage extraction operations wherein the complex and hydrocarbons are contacted with one another in a single operation. After equilibrium is established the two phases are separated from each other and withdrawn from the contacting zone. As such they are indicative of the substantially complete separation of cycloparaffins from admixed open chain paraffins obtainable when operating in a multiple stage or continuous flow operation. It is also evident from the foregoing examples that high conversions of the non-hydroaromatic cycloparaffin to hydroaromatic cycloparaffin is accomplished during the execution of the process within the specified conditions.

When thus maintaining cycloparaffin isomerizing conditions within column 7, the raffinate phase eliminated through line 40 as well as the hydrocarbon mixture comprising pentane and cycloparaffins emanating from scrubber 15 through line 23 will comprise hydrogen chloride. The hydrocarbons comprising hydrogen chloride within accumulator 42 are forced through line 47 into a stripping column 48. Hydrocarbons comprising pentane and cycloparaffins and containing hydrogen chloride are taken from accumulator 25 and forced through line 26 into a separate stripping column 49. Within stripping columns 48 and 49 conditions are maintained to effect the removal of the hydrogen chloride from

the hydrocarbons. The hydrogen chloride thus separated in columns 48 and 49 is passed therefrom through lines 46, 45 and 6 into column 7. Make-up HCl is introduced into the system by means of valved line 50.

Paraffinic hydrocarbons comprising open chain hexanes are eliminated from the lower part of stripping column 48 as a final product. Hydrocarbons comprising pentane, cyclohexane and unconverted methylcyclohexane are passed from stripping column 49 through valved line 28 into fractionator 29.

In a further modification of the invention hydrogen halide, for example, hydrogen chloride, is introduced into the lower part of column 15 through valved line 60, but no hydrogen halide is introduced into column 7. Column 7 will then function as described above to effect separation of cycloparaffins from paraffins in the absence of any substantial cycloparaffin isomerization, whereas in scrubber 15 isomerization of cycloparaffins, for example, conversion of cycloparaffins of non-hydroaromatic structure to cycloparaffins of hydroaromatic structure will take place.

Available hydrocarbon mixtures comprising naphthenic hydrocarbons often contain, in addition to the open chain paraffins, a certain amount of aromatic hydrocarbons. Thus, the naphthenic hexane and/or heptane fractions will generally comprise a certain amount of benzene and/or toluene. This material may be removed from the charge by suitable pretreatments prior to introduction into column 7. The aluminum chloride-hydrocarbon complex, it has been found however, is far more selective as a solvent for aromatic hydrocarbons than for naphthenic hydrocarbons. Distillation of the extract under conditions effecting the separation of cycloparaffins from the complex will generally result in a retention in the complex of at least a substantial amount of the aromatics originally present in the charge. In a modification of the invention, when the charge to the system comprises aromatic hydrocarbons, at least a part of the complex eliminated from the lower part of scrubber 15 is passed through line 51 containing heat exchanging means 52 into a second distillation zone comprising, for example, still 53. Within still 53 the complex, substantially free of cycloparaffins but still containing aromatic hydrocarbons, which in the treatment of naphthenic hexane fractions will comprise benzene, is subjected to more drastic distillation conditions to effect the separation of substantially all of the benzene. The more drastic conditions may be obtained by distillation at a higher temperature by means of heat input into heating means 52 and closed heating coil 54, by prolonged residence time in the still, by use of subatmospheric pressure, by the introduction of stripping gases such as hydrogen, methane, ethane, nitrogen, etc., through valved line 55 or HCl through line 59, or any two or more of these expedients. Vapors comprising benzene are eliminated from still 53 through valved line 56. Aluminum chloride-hydrocarbon complex, now free of any substantial amount of benzene, is passed from still 53 through valved line 57 and recycled at least in part through lines 58, 21 and 8 into the upper part of column 7.

The degree to which aromatic hydrocarbons can be separately recovered in the process of the invention is exemplified by the following example.

Example III

The complex remaining after separating the extracted cycloparaffins from the extract phase in the operation of Example II was subjected to distillation at a temperature of 70° C., under a subatmospheric pressure of 150 mm. for a period of 2 hours. The resulting vapors were condensed and recovered. Upon analysis 33% by volume of the distillate was found to be aromatic hydrocarbon.

Example IV

A hydrocarbon fraction boiling in the range of from 65° C. to 85° C., containing normal hexane, methylcyclopentane, cyclohexane and 7% by weight of benzene was contacted countercurrently in continuous operation with an $AlCl_3$ hydrocarbon complex thereby forming a paraffinic raffinate phase and an extract phase containing the complex, cycloparaffins and benzene. The extract phase was stripped at 90° to 110° C., and atmospheric pressure for 30 minutes to remove cycloparaffins therefrom. The remaining complex was thereafter subjected to further stripping, with the aid of hydrogen chloride, at a temperature of 90° to 100° C. for a period of one hour. Properties of the distillate product from the second stripping operation indicated it to contain above 90% of benzene.

The separate removal of the aromatics from the recycled complex is resorted to not only to maintain the efficiency of the aluminum chloride-hydrocarbon complex as the extracting medium and/or isomerization catalyst, but also to separately recover the aromatic hydrocarbons as a valuable by-product of the process.

The invention as described is capable of modifications without departing from the spirit and scope thereof. Thus, though a packed column has been chosen as a preferred extraction or extraction-isomerizing zone, other types of apparatus enabling intimate contact between the hydrocarbon charge and the organo-metal halide complex, resulting in the formation of an extract phase, and a raffinate phase may suitably be used. Thus, column 7 may suitably be replaced by a plurality of chambers connected in series provided with suitable stirring means through which the hydrocarbon fraction of intermediate boiling range is passed, and in which operation raffinate may be removed from one or more of the chambers.

We claim as our invention:

1. The process for the production of cyclohexane from a hydrocarbon mixture boiling in the gasoline boiling range comprising open chain hexanes and methylcyclopentane, which comprises, fractionating said hydrocarbon mixture in a feed fractionating zone to separate a fraction of intermediate boiling range comprising open chain hexanes and methylcyclopentane and a fraction of lower boiling range comprising pentane, subjecting said fraction of intermediate boiling range and a hydrocarbon-aluminum chloride complex to continuous counter-current contact in the presence of added hydrogen chloride in a contacting zone at a temperature of from about 70° C. to about 100° C. to effect the conversion of methylcyclopentane to cyclohexane while forming a raffinate phase comprising open chain hexanes and an extract phase comprising said complex, cyclohexane and unconverted methylcyclopentane, removing the raffinate phase from one end of said contacting zone, separately removing said extract phase from the opposite end of said contacting

zone, contacting said extract phase in a scrubbing zone with said hydrocarbon fraction of lower boiling range separated in said feed fractionating zone, thereby separating cycloparaffins from said complex in the scrubbing zone, passing hydrocarbons comprising cyclohexane, methylcyclopentane and said lower boiling hydrocarbons from said scrubbing zone into a product fractionating zone, and separating hydrocarbons comprising cyclohexane in said product fractionating zone.

2. The process for the production of cyclohexane from a hydrocarbon mixture boiling in the gasoline boiling range comprising open chain hexanes and methylcyclopentane which comprises, fractionating said hydrocarbon mixture in a feed fractionating zone to separate a fraction of intermediate boiling range comprising open chain hexanes and methylcyclopentane and a fraction of lower boiling range comprising pentane, subjecting said fraction of intermediate boiling range and a hydrocarbon-aluminum halide complex to continuous counter-current contact in the presence of an added hydrogen halide in a contacting zone at a temperature of from about 30° C. to about 140° C. to effect the conversion of methylcyclopentane to cyclohexane while forming a raffinate phase comprising open chain hexanes and an extract phase comprising said complex, cyclohexane and unconverted methylcyclopentane, removing the raffinate phase from one end of said contacting zone, separately removing said extract phase from the opposite end of said contacting zone, contacting said extract phase in a scrubbing zone with said hydrocarbon fraction of lower boiling range separated in said feed fractionating zone, thereby separating cycloparaffins from said complex in the scrubbing zone, passing hydrocarbons comprising cyclohexane, methylcyclopentane and said lower boiling hydrocarbons from said scrubbing zone into a product fractionating zone, and separating hydrocarbons comprising cyclohexane in said product fractionating zone.

3. The process for the production of cycloparaffins of hydroaromatic structure from a hydrocarbon mixture boiling in the gasoline boiling range comprising open chain paraffins and cycloparaffins of non-hydrocaromatic structure which comprises, fractionating said hydrocarbon mixture in a feed fractionating zone to separate a fraction of intermediate boiling range comprising open chain paraffins and cycloparaffins of non-hydroaromatic structure and a fraction of lower boiling range, subjecting said fraction of intermediate boiling range and a hydrocarbon-aluminum halide complex to continuous countercurrent contact in the presence of an added hydrogen halide in a contacting zone at a temperature of from about 70° C. to about 100° C. to effect the conversion of cycloparaffins of non-hydroaromatic structure to cycloparaffins of hydroaromatic structure while forming a raffinate phase comprising open chain paraffins and an extract phase comprising said complex and cycloparaffins, removing the raffinate phase from one end of said contacting zone, separately removing said extract phase from the opposite end of said contacting zone, contacting said extract phase in a scrubbing zone with said hydrocarbon fraction of lower boiling range separated in said feed fractionating zone, thereby separating cycloparaffins from said complex in the scrubbing zone, passing hydrocarbons comprising cycloparaffins and said lower boiling hydrocarbons from said scrubbing zone into a product fractionating zone, and separating hydrocarbons comprising cycloparaffins of hydroaromatic structure in said product fractionating zone.

4. The process for the production of cycloparaffins of hydroaromatic structure from a hydrocarbon mixture boiling in the gasoline boiling range comprising open chain paraffins and cycloparaffins of non-hydroaromatic structure which comprises, fractionating said hydrocarbon mixture in a feed fractionating zone to separate a fraction of intermediate boiling range comprising open chain paraffins and cycloparaffins of non-hydroaromatic structure and a fraction of lower boiling range, subjecting said fraction of intermediate boiling range and an organo-aluminum halide complex to continuous countercurrent contact in the presence of an added hydrogen halide in a contacting zone at a temperature of from about 30° C. to about 140° C. to effect the conversion of cycloparaffins of non-hydroaromatic structure to cycloparaffins of hydroaromatic structure while forming a raffinate phase comprising open chain paraffins and an extract phase comprising said complex and cycloparaffins, removing the raffinate phase from one end of said contacting zone, separately removing said extract phase from the opposite end of said contacting zone, contacting said extract phase in a scrubbing zone with said hydrocarbon fraction of lower boiling range separated in said feed fractionating zone, thereby separating cycloparaffins from said complex in the scrubbing zone, passing hydrocarbons comprising cycloparaffins and said lower boiling hydrocarbons from said scrubbing zone into a product fractionating zone, and separating hydrocarbons comprising cycloparaffins of hydroaromatic structure in said product fractionating zone.

5. The process for the production of cycloparaffins of hydroaromatic structure from a hydrocarbon mixture boiling in the gasoline boiling range comprising open chain paraffins and cycloparaffins of non-hydroaromatic structure which comprises, fractionating said hydrocarbon mixture in a feed fractionating zone to separate a fraction of intermediate boiling range comprising open chain paraffins and cycloparaffins of non-hydroaromatic structure and a fraction of lower boiling range, subjecting said fraction of intermediate boiling range and an organo-metal halide complex to continuous countercurrent contact in the presence of an added promoter affording a hydrogen halide in a contacting zone at a temperature of from about 30° C. to about 140° C. to effect the conversion of cycloparaffins of non-hydroaromatic structure to cycloparaffins of hydroaromatic structure while forming a raffinate phase comprising open chain paraffins and an extract phase comprising said complex and cycloparaffins, separately removing the raffinate phase and the extract phase from said contacting zone, contacting said extract phase in a scrubbing zone with said hydrocarbon fraction of lower boiling range separated in said feed fractionating zone thereby separating cycloparaffins from said complex, passing hydrocarbons comprising cycloparaffins and said lower boiling hydrocarbons from said scrubbing zone into a product separating zone, and separating hydrocarbons comprising cycloparaffins of hydroaromatic structure in said product fractionating zone.

6. The process for the production of cycloparaffins of hydroaromatic structure from a hydrocarbon mixture boiling in the gasoline boiling range comprising open chain paraffins and cycloparaffins of non-hydroaromatic structure, which comprises, fractionating said hydrocarbon mix-

ture in a feed fractionating zone to separate a fraction of intermediate boiling range comprising open chain paraffins and cycloparaffins of non-hydroaromatic structure and a fraction of lower boiling range, subjecting said fraction of intermediate boiling range and an organo-metal halide complex to continuous countercurrent contact in the presence of an added promoter affording a hydrogen halide in a contacting zone at cycloparaffin isomerizing conditions to effect the conversion of cycloparaffins of non-hydroaromatic structure to cycloparaffins of hydroaromatic structure while forming a raffinate phase comprising open chain paraffins and an extract phase comprising said complex and cycloparaffins, separately removing the raffinate phase and the extract phase from said contacting zone, contacting said extract phase in a scrubbing zone with said hydrocarbon fraction of lower boiling range separated in said feed fractionating zone thereby separating cycloparaffins from said complex, passing hydrocarbons comprising cycloparaffins and said lower boiling hydrocarbons from said scrubbing zone into a product separating zone, separating hydrocarbons comprising cycloparaffins of hydroaromatic structure in said product fractionating zone, and recycling complex from said scrubbing zone to said contacting zone.

7. The process for the production of cyclohexane from a hydrocarbon mixture boiling in the gasoline boiling range comprising open chain hexanes and methylcyclopentane which comprises, fractionating said hydrocarbon mixture in a feed fractionating zone to separate a fraction of intermediate boiling range comprising open chain hexanes and methylcyclopentane and a fraction of lower boiling range comprising pentane, subjecting said fraction of intermediate boiling range and a hydrocarbon-aluminum halide complex to continuous countercurrent contact in the presence of an added hydrogen halide in a contacting zone at a temperature of from about 70° C. to about 100° C. to effect the conversion of methylcyclopentane to cyclohexane while forming a raffinate phase comprising open chain hexanes and hydrogen halide and an extract phase comprising said complex, cyclohexane, methylcyclopentane and hydrogen halide, passing the raffinate phase from one end of said contacting zone into a stripping zone, passing said extract phase from the opposite end of said contacting zone into a scrubbing zone, contacting said extract phase with said hydrocarbon fraction of lower boiling range separated in said feed fractionating zone, thereby separating cycloparaffins and hydrogen halide from complex in said scrubbing zone, passing hydrocarbons comprising cycloparaffins and said lower boiling hydrocarbons in admixture with hydrogen halide from said scrubbing zone into a separate stripping zone, separating a gaseous fraction comprising hydrogen halide in each of said stripping zones, and recycling said gaseous fractions from said stripping zones to said contacting zone.

8. The process for the production of cycloparaffins of hydroaromatic structure from a hydrocarbon mixture in the gasoline boiling range comprising open chain paraffins and cycloparaffins of non-hydroaromatic structure which comprises, fractionating said hydrocarbon mixture in a feed fractionating zone to separate a fraction of intermediate boiling range comprising open chain paraffins and cycloparaffins of non-hydroaromatic structure and a lower boiling fraction, subjecting said fraction of intermediate boiling range and an organo-metal halide complex to continuous countercurrent contact in the presence of an added promoter affording a hydrogen halide in a contacting zone at cycloparaffin isomerizing conditions to effect the conversions of cycloparaffins of non-hydroaromatic structure to cycloparaffins of hydroaromatic structure while forming a raffinate phase comprising open chain paraffins and hydrogen halide and an extract phase comprising said complex, cycloparaffins of hydroaromatic structure and hydrogen halide, passing said raffinate phase into a stripping zone, passing said extract phase into a scrubbing zone, contacting said extract phase with said hydrocarbon fraction of lower boiling range separated in said feed fractionating zone, thereby separating cycloparaffins and hydrogen halide from complex in said scrubbing zone, passing hydrocarbons comprising cycloparaffins and said lower boiling hydrocarbons in admixture with hydrogen halide from said scrubbing zone into a separate stripping zone, separating a gaseous fraction comprising hydrogen halide in each of said stripping zones, and recycling said gaseous fractions from said stripping zones to said contacting zone.

9. The process for the production of cyclohexane from a hydrocarbon mixture boiling in the gasoline boiling range comprising open chain hexanes, methylcyclopentane and benzene which comprises, fractionating said hydrocarbon mixture in a feed fractionating zone to separate a fraction of intermediate boiling range comprising open chain hexanes, methylcyclopentane and benzene and a fraction of lower boiling range comprising pentane, subjecting said fraction of intermediate boiling range and a hydrocarbon-aluminum halide complex to continuous countercurrent contact in the presence of an added hydrogen halide in a contacting zone at a temperature of from about 70° C. to about 100° C. to effect the conversion of methylcyclopentane to cyclohexane while forming a raffinate phase comprising open chain hexanes and an extra phase comprising said complex, cyclohexane, methylcyclopentane and benzene, removing the raffinate phase from one end of the contacting zone, passing the extract phase from the opposite end of said contacting zone into a scrubbing zone, contacting said extract phase with said hydrocarbon fraction of lower boiling range separated in said feed fractionating zone, thereby separating cycloparaffins from a residual fraction comprising said complex containing benzene in said scrubbing zone, passing hydrocarbons comprising said hydrocarbons of lower boiling range, cyclohexane and methylcyclopentane from said scrubbing zone into a product separating zone, separating hydrocarbons predominating in cyclohexane in said product separating zone, passing said residual fraction from said scrubbing zone into a distillation zone, separating hydrocarbons comprising benzene as a vapor fraction from a liquid fraction comprising complex in said distillation zone, and recycling said liquid fraction from said distillation zone to the contacting zone.

10. The process for the production of cycloparaffins of hydroaromatic structure from a hydrocarbon mixture boiling in the gasoline boiling range comprising open chain paraffins, cycloparaffins of non-hydroaromatic structure and aromatic hydrocarbons which comprises, fractionating said mixture in a feed fractionating zone to separate a fraction of intermediate boiling range comprising open chain paraffins, cycloparaffins of non-hydroaromatic structure and aromatic hy-

drocarbons and a fraction of lower boiling range, subjecting said fraction of intermediate boiling range and an organo-metal halide complex to continuous countercurrent contact in the presence of an added promoter affording a hydrogen halide in a contacting zone at cycloparaffin isomerizing conditions to effect the conversion of cycloparaffins of non-hydroaromatic structure to cycloparaffins of hydroaromatic structure while forming a raffinate phase comprising open chain paraffins and an extract phase comprising said complex, cycloparaffins and aromatic hydrocarbons, removing the raffinate phase from one end of said contacting zone, passing the extract phase from the opposite end of said contacting zone into a scrubbing zone, contacting said extract phase in the scrubbing zone with said hydrocarbon fraction of lower boiling range separated in said feed fractionating zone, thereby separating cycloparaffins of intermediate boiling range from a residual fraction comprising said complex containing aromatic hydrocarbons in said scrubbing zone, passing hydrocarbons comprising said hydrocarbons of lower boiling range and cycloparaffins of intermediate boiling range from said scrubbing zone into a product separating zone, separating hydrocarbons predominating in cycloparaffins of hydroaromatic structure in said product separating zone, passing said residual fraction from said scrubbing zone into a distillation zone, separating hydrocarbons comprising aromatic hydrocarbons as a vapor fraction from a liquid fraction comprising complex in said distillation zone, and recycling said liquid fraction from said distillation zone to the contacting zone.

11. The process for the production of cycloparaffins from a hydrocarbon mixture boiling in the gasoline boiling range comprising open chain paraffins and cycloparaffins which comprises, fractionating said hydrocarbon mixture in a feed fractionating zone to effect the separation of a fraction of intermediate boiling range comprising open chain paraffins and cycloparaffins and a fraction of lower boiling range, subjecting said fraction of intermediate boiling range and a hydrocarbon-aluminum chloride complex to continuous countercurrent contact at a temperature of from 20° C. to about 70° C. in a contacting zone to form a raffinate phase comprising open chain paraffins and an extract phase comprising said complex and cycloparaffins, removing the raffinate phase from one end of said contacting zone, separately removing said extract phase from the opposite end of said contacting zone, contacting said extract phase in a scrubbing zone with said hydrocarbon fraction of lower boiling range separated in said feed fractionating zone thereby separating cycloparaffins of intermediate boiling range from said complex, passing hydrocarbons comprising said hydrocarbons of lower boiling range and cycloparaffins of intermediate boiling range from said scrubbing zone into a product separating zone, and separating hydrocarbons predominating in cycloparaffins of intermediate boiling range in said product separating zone.

12. The process for the production of cycloparaffins from a hydrocarbon mixture boiling in the gasoline boiling range comprising open chain paraffins and cycloparaffins, which comprises fractionating said hydrocarbon mixture in a feed fractionating zone to effect the separation of a fraction of intermediate boiling range comprising open chain paraffins and cycloparaffins and a fraction of lower boiling range, subjecting said fraction of intermediate boiling range and an organo-aluminum halide complex to continuous countercurrent contact at a temperature of from 20° C. to about 140° C. in a contacting zone to form a raffinate phase comprising open chain paraffins and an extract phase comprising said complex and cycloparaffins, removing the raffinate phase from one end of said contacting zone, separately removing said extract phase from the opposite end of said contacting zone, contacting said extract phase in a scrubbing zone with said hydrocarbon fraction of lower boiling range separated in said feed fractionating zone thereby separating cycloparaffins of intermediate boiling range from said complex, passing hydrocarbons comprising said hydrocarbons of lower boiling range and cycloparaffins of intermediate boiling range from said scrubbing zone into a product separating zone, and separating hydrocarbons predominating in cycloparaffins of intermediate boiling range in said product separating zone.

13. The process for the production of cycloparaffins from a hydrocarbon mixture boiling in the gasoline boiling range comprising open chain paraffins and cycloparaffins, which comprises fractionating said hydrocarbon mixture in a feed fractionating zone to effect the separation of a fraction of intermediate boiling range comprising open chain paraffins and cycloparaffins and a fraction of lower boiling range, subjecting said fraction of intermediate boiling range and an organo-metal halide complex to continuous countercurrent contact at a temperature of from 20° C. to about 140° C. in a contacting zone to form a raffinate phase comprising open chain paraffins and an extract phase comprising said complex and cycloparaffins, removing the raffinate phase from one end of said contacting zone, separately removing said extract phase from the opposite end of said contacting zone, contacting said extract phase in a scrubbing zone with said hydrocarbon fraction of lower boiling range separated in said feed fractionating zone thereby separating cycloparaffins of intermediate boiling range from said complex, passing hydrocarbons comprising said hydrocarbons of lower boiling range and cycloparaffins of intermediate boiling range from said scrubbing zone into a product separating zone, and separating hydrocarbons predominating in cycloparaffins of intermediate boiling range in said product separating zone.

14. The process for the production of cycloparaffins from a hydrocarbon mixture boiling in the gasoline boiling range comprising cycloparaffins in admixture with open chain paraffins and aromatic hydrocarbons which comprises, fractionating said hydrocarbon mixture in a feed fractionating zone to effect the separation of a fraction of intermediate boiling range comprising open chain paraffins, cycloparaffins and aromatic hydrocarbons and a fraction of lower boiling range, subjecting said fraction of intermediate boiling range and an organo-metal halide complex to continuous countercurrent contact at a temperature of from about 20° C. to about 140° C. in a contacting zone to form a raffinate phase comprising open chain paraffins and an extract phase comprising said complex, cycloparaffins and aromatic hydrocarbons, removing the raffinate phase from one end of said contacting zone, removing the extract phase from the other end of said contacting zone, contacting said extract phase in a scrubbing zone with said hydrocarbon fraction of lower boiling range separated in said feed fractionating zone, thereby separating cycloparaffins

of intermediate boiling range from a residual fraction comprising said complex containing aromatic hydrocarbons in said scrubbing zone, passing hydrocarbons comprising said hydrocarbons of lower boiling range and cycloparaffins of intermediate boiling range from said scrubbing zone into a product separating zone, separating hydrocarbons predominating in cycloparaffins of intermediate boiling range in said product separating zone, passing said residual fraction from said scrubbing zone into a distillation zone, separating hydrocarbons comprising aromatic hydrocarbons as a vapor fraction from a liquid fraction comprising complex in said distillation zone, and recycling said liquid fraction from said distillation zone to the contacting zone.

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