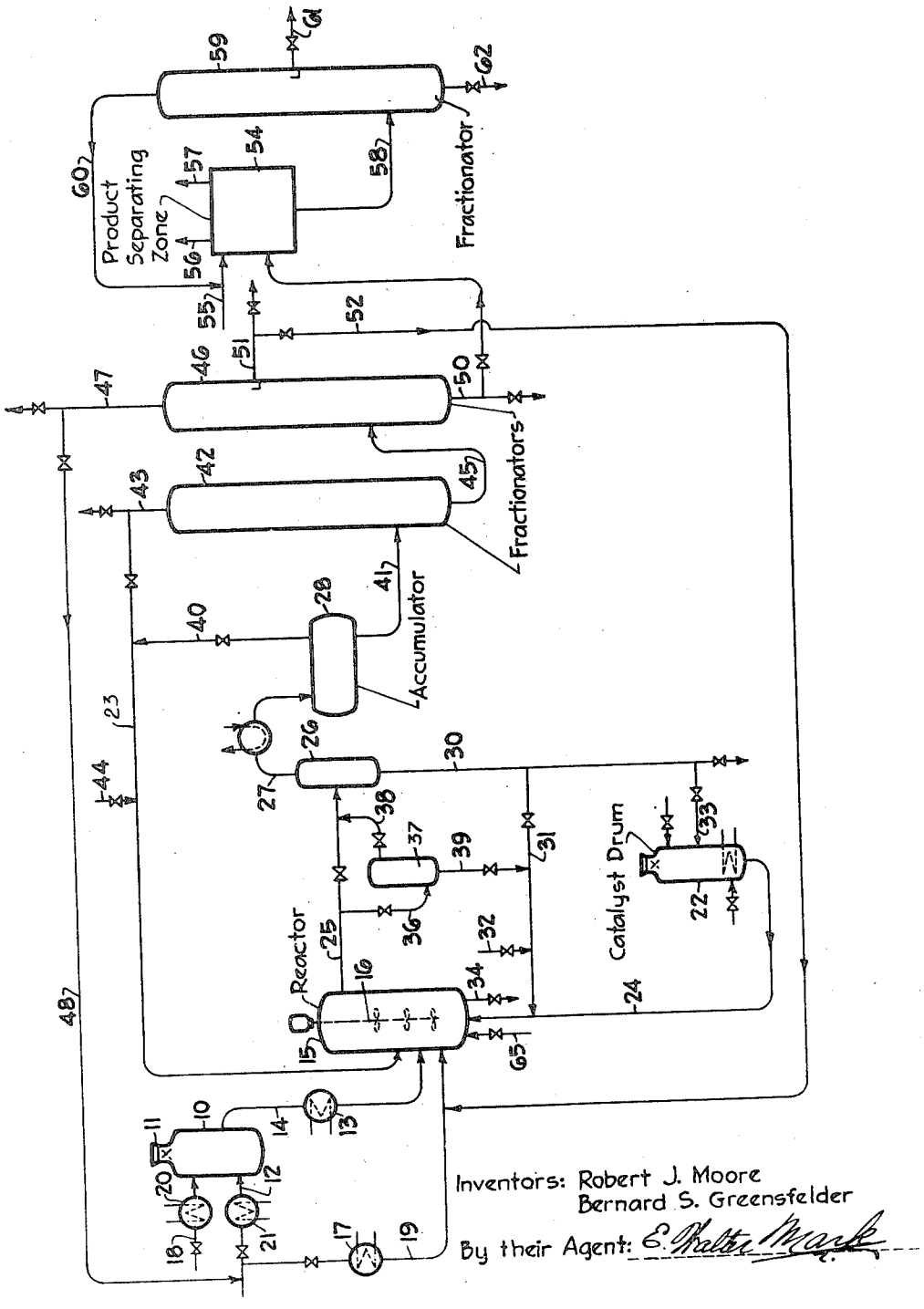
July 5, 1949. R. J. MOORE ET AL 2,475,358

HYDROCARBON CONVERSION

Filed Sept. 3, 1946



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Patented July 5, 1949 2,475,358

UNITED STATES PATENT OFFICE

2,475,358

HYDROCARBON CONVERSION

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Application September 3, 1946, Serial No. 694,532

3 Claims. (Cl. 260—683.5)

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This invention relates to the conversion of normally solid hydrocarbons. The invention relates more particularly to a process for the conversion of straight and branched chain normally solid paraffin hydrocarbons to branched and more highly branched chain paraffin hydrocarbons respectively. A particular aspect of the invention relates to the conversion of normally solid paraffin hydrocarbons to normally liquid hydrocarbons of branched structure having substantially the same molecular weight as the solid paraffin hydrocarbons charged.

Processes disclosed heretofore directed to the treatment of normally solid hydrocarbons, such as paraffin wax, and producing a purely hydrocarbon product, generally involve either a refining operation to remove undesirable impurities, resulting in a normally solid material of improved characteristics, or a more drastic conversion treatment resulting in the obtaining of a normally liquid product. The former usually comprise such steps as solvent extraction, fractional crystallization, clay treatment and the like, in which the structure of the hydrocarbon is unaltered, whereas the latter involve a step in which hydrocarbon decomposition resulting in a wide range of reaction products comprising normally gaseous and normally liquid products as well as solid hydrocarbons and carbonaceous materials is a generally predominant reaction. The primary decomposition, or cracking, of the normally solid hydrocarbons is effected thermally with or without aid of a catalyst. Catalysts disclosed as promoting the hydrocarbon decomposition reaction include aluminum chloride, but, although aluminum chloride is known also to promote such reactions as the conversion or normal butane to isobutane in the absence of any substantial hydrocarbon decomposition at certain conditions, the effect of this catalyst in the presence of a higher paraffin is to favor the cracking reaction over the isomerization reaction. Thus, in the presence of normal pentane, aluminum chloride will cause the cracking reaction to predominate, and in the presence of still higher paraffins, the cracking reaction will generally prevail to an increasing degree over the isomerization reaction. Recourse is therefore had in the isomerization of normal pentane with aluminum chloride to the use of agents capable of suppressing the cracking reaction. The agents suppressing the cracking of the lower boiling paraffins, however, also suppress to some degree the isomerization of these materials. Since cracking proceeds at a progressively greater rate with increase of molecular

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weight of the paraffins, the inordinately large amount of cracking suppressor required to inhibit effectively the cracking of, for example, a C_8 paraffin, results in a concomitant suppression of the isomerization reaction to a degree rendering the isomerization on a practical scale of such more readily cracked paraffins very uneconomical. Normally solid hydrocarbons and waxes in particular are completely converted to lower molecular weight hydrocarbons and tarry complex sludges by a combination of cracking and polymerization, condensation and addition reactions. Therefore, the treatment of paraffins of such high molecular weights with aluminum chloride on a practical scale without substantial extent of cracking has until now been held unfeasible.

In contrast to the methods resorted to heretofore in the treatment of normally solid paraffin hydrocarbons, and notwithstanding the increasingly unfavorable behavior of the lower boiling paraffins of progressively increasing molecular weight in the presence of aluminum chloride and a cracking suppressor, it has now been found that normally solid hydrocarbons, such as, for example, paraffin wax, can be catalytically converted to normally solid and/or normally liquid hydrocarbons of improved properties having the same molecular weight as the normally solid hydrocarbon charge, in the absence of any substantial degree of hydrocarbon decomposition, with the aid of certain catalysts comprising a modified metal halide of the Friedel-Crafts type in the presence of a cracking suppressor under the conditions fully described herein.

It is an object of the present invention to provide an improved process for the efficient conversion of normally solid hydrocarbons.

Another object of the invention is the provision of an improved process for the efficient conversion of normally solid hydrocarbons to normally liquid hydrocarbons having the same molecular weight as the normally solid hydrocarbons charged.

Another object of the invention is the provision of an improved process for the efficient conversion of normally solid paraffin hydrocarbons of straight or branched chain structure to normally solid paraffin hydrocarbons of branched and more highly branched chain structure, respectively, having the same molecular weight as the normally solid hydrocarbon charge.

Still another object of the invention is the provision of an improved process for the efficient conversion of normally solid paraffin hydrocarbons of straight and branched chain struc-

ture to normally liquid paraffin hydrocarbons of branched and more highly branched chain structure, respectively, having the same molecular weight as the normally solid paraffin hydrocarbons charged.

A further object of the invention is the provision of an improved process for the efficient conversion of normally solid paraffin hydrocarbons to branched chain normally liquid paraffin hydrocarbons having the same molecular weight as the normally solid paraffin hydrocarbon charged, and comprising high quality lubricants and diesel engine fuels.

Still another object of the invention is the provision of improved high quality lubricants consisting essentially of branched chain paraffins combining a high viscosity index with a low pour point.

Still another object of the invention is the provision of improved high quality diesel engine fuels combining low pour point with relatively high ignition values.

A still further object of the invention is the provision of high quality microcrystalline wax. Further objects and advantages of the invention will become apparent from the following detailed description thereof.

In accordance with the process of the invention, normally solid hydrocarbons comprising, for example, at least one straight or branched chain paraffin having at least seventeen carbon atoms to the molecule and which is solid at room temperature, is dissolved in a suitable solvent. The resulting solution is contacted with a catalyst comprising a modified metal halide of the Friedel-Crafts type in the presence of a cracking suppressor under conditions converting normally solid hydrocarbons to reaction products comprising normally solid and/or normally liquid hydrocarbons of branched and more highly branched structure, respectively, having the same molecular weight as the normally solid hydrocarbons charged, in the absence of any substantial hydrocarbon decomposition. By the term "decomposition" as used in the present specification and appended claims is meant the rupture of carbon to carbon bonds of the hydrocarbon molecule to result in the formation of hydrocarbons of substantially lower molecular weight than the normally solid hydrocarbon charged, or recombination of hydrocarbon fragments to form higher molecular weight tars and sludges.

In order to set forth more fully the nature of the invention, it will be described in detail with reference to the accompanying drawing, wherein the single figure illustrates more or less diagrammatically one form of apparatus suitable for executing the process of the invention.

The normally solid hydrocarbons converted in accordance with the process of the invention comprise, for example, the paraffin hydrocarbons of normal or branched structure having at least seventeen carbon atoms to the molecule which are normally solid at room temperature. The normally solid hydrocarbon charge to the system may consist predominantly of a single hydrocarbon or a mixture of two or more normally solid hydrocarbons obtained from any suitable source. They comprise, for example, the hydrocarbon waxes, such as the paraffin waxes separated from naturally occurring petroleum, or other waxy material such as petrolatum, slop wax, ozokerite wax, wax from asphaltic or bituminous substances, or other hydrocarbon waxes. A desirable charge to the system comprises the normally solid

hydrocarbons, such as the paraffin waxes produced synthetically in any of the known processes for the synthesis of hydrocarbons such as, for example, the normally solid hydrocarbon materials obtained in the synthesis of hydrocarbons from carbon monoxide and hydrogen by the Fischer-Tropsch process or modifications thereof. A particularly suitable normally solid hydrocarbon charge comprises, for example, one or more paraffin hydrocarbons having from seventeen to about 200 carbon atoms to the molecule which are solid at a temperature of about 20° C. The invention is furthermore not limited to the conversion of only the normally solid open chain paraffin hydrocarbons, but comprises within its scope the conversion of any isomerizable normally solid hydrocarbon such as, for example, the normally solid hydrocarbons comprising an isomerizable alkyl group linked to an alicyclic or aromatic ring.

Referring to the drawing, the normally solid hydrocarbon charge may be introduced into a suitable enlarged chamber such as, for example, chamber 10, provided with a suitable inlet for the solid hydrocarbons such as a hopper 11.

Within chamber 10 the normally solid hydrocarbon is dissolved in a suitable solvent. Preferred solvents comprise a normally gaseous or normally liquid material functioning also as the hydrocarbon cracking suppressor in the conversion zone of the process. Such solvent and cracking suppressor is introduced into chamber 10 from any suitable outside source by means of a valved line 12. Suitable cracking suppressors comprise any materials capable of suppressing the cracking of hydrocarbons in the presence of the catalysts comprising a modified metal halide of the Friedel-Crafts type, under the conditions of execution of the reaction. The cracking suppressors employed may be normally gaseous materials as well as normally solid materials which are liquid at the temperature of reaction or which can be adequately dissolved in materials liquid at the temperature of reaction. Suitable cracking suppressors comprise, for example, the butanes, the cycloparaffins and alkyl substituted cycloparaffins, such as cyclopentane, methylcyclopentane, ethylcyclopentane, dimethylcyclopentane, cyclohexane, methylcyclohexane, dimethylcyclohexane and ethylcyclohexane, binuclear alicyclic hydrocarbons such as decahydronaphthalene, hydrindan, methylhydrindan, bicyclopentyl, cyclopentylcyclohexane, bicyclohexyl, dimethylbicyclopentyl, dimethylbicyclohexyl, dicyclo alkyl methanes, dicycloalkylethanes, perhydroanthracene, tricyclopentyl, dicyclopentylcyclohexane, cyclopentylbicyclohexyl, dicyclohexylcyclopentane, tricyclohexyl, and homologs thereof. Other suitable cracking suppressors include saturated terpenes, saturated dicyclopentadienes, adamantane, spirocycloparaffins, and homologs thereof.

A single cracking suppressor or a mixture of two or more cracking suppressors may be employed. The cracking suppressors need not necessarily be introduced into the system in pure or concentrated form, but may comprise other materials such as hydrocarbon diluents, or solvents for the cracking suppressor or wax charge, having no deleterious effect under the conditions of execution of the process. The cycloparaffin cracking suppressors, for example, may be introduced into the system in the form of cycloparaffin concentrates obtained by separating a cycloparaffin-containing fraction of narrow boiling range from naturally occurring or synthetically produced

hydrocarbon mixtures. Thus, a dimethylcyclopentane fraction containing approximately 70% cycloparaffins was found to be effective as a cracking inhibitor under the conditions employed in the process of the invention.

From chamber 10, the normally solid hydrocarbon in solution in a cracking suppressor, for example, methylcyclohexane, is passed through line 14 into the conversion zone. The conversion zone may comprise any suitable reactor, or plurality of reactors, connected in series or in parallel, optionally in combination with soaking vessels or a zone of restricted cross-sectional area such as a coil. In the drawing, the reaction zone is represented by reaction chamber 15 provided with suitable stirring means 16. Though the invention is in no wise limited by the type of reactor or reactors employed, those providing intimate contact of catalyst and reactant are preferred. It has been found that efficient execution of the process is materially aided by intimate contact, preferably in the form of an emulsion or dispersion of catalyst and reactants.

Although the use of a normally gaseous or normally liquid cracking inhibitor is preferred for simplicity as the sole solvent medium for the normally solid hydrocarbon charge, the use of a solvent which is not necessarily a suppressor of the cracking reaction may be resorted to in addition to the cracking inhibitor. Such additional solvent is employed to facilitate solution of the solid hydrocarbon wax in a mixture of inhibitor and solvent or to enable the use of an inhibitor possessing little if any solubility for the normally solid hydrocarbon charge. Such additional solvents comprise any suitable normally liquid solvent or normally gaseous solvent which is liquid under the operating conditions, capable of dissolving the normally solid hydrocarbon charge and having no adverse effect upon the execution of the reaction. Suitable solvents which may be employed in addition to the cracking suppressor comprise, for example, the paraffins such as propane, normal pentane, isopentane, neopentane, and hexanes.

The solvent, or solvents, employed in addition to the cracking suppressor, are introduced into chamber 10 by means of valved line 18. When thus introducing solvent through line 18 into chamber 10, all or part of the cracking suppressor may be passed from line 12, through valved line 19 to reactor 15. The solvent other than the cracking inhibitor is generally introduced into the system in an amount not substantially in excess of that necessary to maintain the normally solid hydrocarbon in solution in the system.

To aid in dissolving the solid hydrocarbon charge, heating means such as, for example, indirect heat exchangers 20 and 21 are provided to raise the temperature of the streams entering chamber 10 through lines 12 and/or 18.

The rate of introduction of cracking suppressor into the system is controlled to effect the suppression of any substantial amount of hydrocarbon decomposition within reactor 15. The proportion of suppressor introduced will vary within the scope of the invention, depending upon the particular suppressor employed as well as the conditions and particular catalyst maintained in reactor 15. A ratio of inhibitor to normally solid hydrocarbon charge of from about 3:1 to 5:1 by by weight and higher may be employed. It is preferred, however, particularly when employing hydrocarbons as cracking suppressors, to maintain the ratio of suppressors to normally solid hydrocarbon in excess of about 1:1 by weight and preferably in the range of from about 2:1 to about 8:1 by weight. Excellent results are obtained with the cycloparaffin cracking suppressors employed in the ratio of suppressor to solid hydrocarbon charge of from about 3:1 to 5:1 by weight.

Within reactor 15 the reactants are contacted with a modified isomerization catalyst which in the presence of the cracking suppressor will effect the conversion of normally solid hydrocarbons. Suitable catalysts comprise an isomerization catalyst comprising a modified metal halide of the Friedel-Crafts type. Modification of the catalyst is essential to the attainment of the objects of the invention. Thus the use of $AlCl_3$ per se in the absence of inhibitor at a temperature of about 100° C. resulted in complete destruction of a paraffin wax with which it was contacted. Addition of sufficient methylcyclohexane to suppress the cracking of the wax, on the other hand, will generally substantially completely suppress any conversion of the paraffin wax in the presence of aluminum chloride per se under the usual operating conditions. Of the catalysts comprising a modified metal halide of the Friedel-Crafts type, those comprising a halide of aluminum, such as the chloride or bromide or mixtures thereof are preferred. By the term "modified metal halide" employed throughout the specification and attached claims, is meant a metal halide which has been modified by combining a portion of it with a reactive material to form a fluid medium in which the remaining metal halide and added HCl can be dissolved or suspended in a catalytically active state. The isomerization catalysts, comprising the modified metal halide, employed in the process of the invention, are obtained by combining a metal halide of the Friedel-Crafts type with a suitable modifying agent under conditions resulting in a combination of the metal halide with the modifying agent. The resulting combination may be in the form of an actual complex compound of the metal halide and the modifying agent or in the form of a loose combination in which no actual compound formation between the metal halide and modifier occurs, and the actual compositions and structures of which, because of their complexity, do not lend themselves to ready determination. Suitable modifying agents which are combined with metal halides of the Friedel-Crafts type to result in isomerization catalysts comprising the modified metal halide include, for example, the aromatic hydrocarbons as exemplified by benzene, toluene, dimethyl benzene, trimethyl benzene, ethyl benzene, triethyl benzene, propyl benzene, ethyl propyl benzene, the isopropyl benzenes, the normal butyl benzenes, the tertiary butyl benzenes, the amyl benzenes, the mixed alkyl benzenes, such as ethyl toluene, dipropyl toluene, etc.; aromatic hydrocarbon fractions such as kerosene extracts obtained by the extraction of kerosene with a solvent possessing preferential solvent action for aromatics; aromatic extracts derived from thermally or catalytically cracked, reformed, or dehydrogenated petroleum or synthetic petroleum fractions, cyclic olefins such as cyclopentene or cyclohexene; paraffinic and olefinic hydrocarbons of straight or branched chain structure; halogen substituted paraffin hydrocarbons such as propyl chloride and butyl chloride, organic carboxylic acids of the fatty acid series, such as formic, acetic, propionic, butyric, oleic, napthoic and the like; ethers such as diethyl

ether, ethyl phenyl ether, and the like; the esters, such as isobornyl acetate, pyroboric acetate, ethyl benzoate, and the like; organic nitro compounds of which the nitro-paraffins, the nitro-aralkyl and the nitro-isocyclic compounds such as nitrobenzene, nitronaphthalene, nitromethane, nitroethane, nitrocyclohexane and the like, are representative; alcohols such as isobornyl, glycerine, phenol, ethyl alcohol, propyl alcohol, isopropyl alcohol, dodecanol and the like; the ketones of aliphatic, aralkyl, aromatic or mixed character, such as acetone, methyl ethyl ketone, methyl propyl ketone, acetophenone, ethyl phenyl ketone, benzophenone and the like, their homologues and substitution products; aliphatic, aralkyl or aromatic carboxylic acid halides, particularly the aromatic carboxylic acid halides as benzoyl chloride, benzoyl bromide, etc.; organic sulphones, such as the aryl and the aralkyl sulphones as diphenyl sulphone, benzyl sulphone; organic compounds broadly possessing a dipole moment and capable of reacting with aluminum halides, such as aluminum chloride.

The catalysts comprising a modified metal halide are obtained by combining one or more of the above catalyst modifiers with the metal halide, such as aluminum chloride, and allowing the mixture to stand at room temperature or at an elevated temperature up to, for example, about 150° C., generally in the presence of an added hydrogen halide, for a sufficient length of time to result in the formation of a liquid, or sludge, consisting essentially of an organo-metal halide complex. Although the above modified catalysts consisting of complex reaction product containing the metal halide are preferred, the invention in in no wise limited in the manner in which the activity of the metal halide is modified.

Thus suitable modified metal halide-containing catalysts are obtained by contacting a metal halide, such as aluminum chloride, with a portion of the normally solid hydrocarbon charge in the absence of a cracking suppressor, thereby obtaining a complex reaction product comprising modified aluminum chloride. Another source of modified metal halide catalysts comprises the metal halide-containing complex reaction products obtained during the isomerization of lower boiling paraffins with a metal halide of the Friedel-Crafts type such as aluminum chloride. The aluminum chloride-containing complex mixtures or sludges thus rejected from processes isomerizing lower paraffins which are completely spent with respect to their ability to promote the isomerization reaction are converted to suitable modified aluminum chloride catalysts for use in the present invention by the addition thereto of fresh aluminum chloride.

Other methods of modifying the metal halides to render them suitable in the process of the invention comprise their combination with at least one other metal halide. Thus suitable catalysts comprise a solution of $AlCl_3$ in molten $SbCl_3$; the melts consisting of $AlCl_3$ in combination with a halide of one or more of the following elements: Na, K, or other alkali metals, Zn, etc.

The modified catalyst may be prepared, for example, by the introduction of the modifying agent and the metal halide of the Friedel-Crafts type, such as $AlCl_3$, into a chamber **22**. From chamber **22** the modified aluminum chloride is passed to reactor **15** by means of line **24**. The ratio of catalyst to hydrocarbon within reactor **15** may vary within the scope of the invention. Catalyst to normally solid hydrocarbon ratios

may range, for example, from about 1:20 to about 10:1, and preferably from about 1:4 to 4:1 by volume. Higher or lower proportions of catalyst may, however, be employed within the scope of the invention.

The reaction is preferably executed in the presence of added hydrogen halide such as, for example, hydrogen chloride, which is introduced into reactor **15** by means of line **23**. The hydrogen chloride is preferably added in sufficient amount to saturate the reactants in reactor **15** therewith. A lesser or greater amount of hydrogen halide promoter may be employed, however.

The temperature within reactor **15** is maintained in the range of from about 20° C. to about 150° C. and preferably from about 50° C. to about 120° C. Optimum results are generally obtained by effecting the reaction in the range of from about 70° C. to about 110° C. The temperature within reactor **15** is maintained by suitable heating means such as for example heat exchangers **13** and **17** in lines **14** and **19**, respectively. Additional temperature controlling means not shown in the drawing to effect the addition or removal of heat from reactor **15** may be employed. Subatmospheric, atmospheric or superatmospheric pressures up to, for example, about 100 atmospheres may be maintained in reactor **15**. Pressures ranging, for example, from about atmospheric to about 25 atmospheres are generally preferred. The contact time of catalyst and normally solid hydrocarbon charge may vary considerably within the scope of the invention. Thus, contact times may range from about 5 minutes to about 2 hours. Optimum results are, however, obtained by maintaining a contact time in the range of from about 15 minutes to about 30 minutes. Higher or lower contact times may, however, be applied within the scope of the invention.

Under the above-defined conditions, straight and branched chain normally solid hydrocarbons are converted to normally solid and normally liquid hydrocarbons of branched or more highly branched structure possessing the same molecular weight as the normally solid hydrocarbon charge from which they are derived, in the absence of substantial hydrocarbon decomposition. Thus the paraffinic hydrocarbons having at least seventeen carbon atoms to the molecule which are normally solid at room temperature are converted to normally solid paraffins comprising microcrystalline waxes and normally liquid products comprising high quality lubricating oils and Diesel fuels having the same number of carbon atoms, but of more highly branched structure, than the normally solid paraffin charge, in the absence of any substantial hydrocarbon decomposition. Without intent to limit the scope of the invention by any theories advanced herein to set forth more fully the nature of the invention, it is believed that the effect of the conversion carried out in reactor **15** is to increase the number of alkyl side chains of the normally solid hydrocarbons treated and that the products obtained consist essentially of branched chain hydrocarbons in which the alkyl side chains formed during the reaction consist substantially exclusively of methyl groups.

Effluent from reactor **15** comprising dissolved normally solid hydrocarbons, normally liquid hydrocarbons in the lubricating oil and Diesel fuel boiling range, cracking suppressor, catalyst and hydrogen chloride promoter, is passed through valved line **25** into a separating zone,

for example a chamber 26. Within chamber 26 a lower liquid layer comprising catalyst is separated from an upper liquid layer comprising hydrocarbons. The upper layer comprising hydrocarbons, as well as any normally gaseous materials such as hydrogen chloride, is passed from chamber 26 through line 27 into accumulator 28.

Liquid comprising catalyst is drawn from chamber 26 and returned through valved lines 30, 31 and 24 to reactor 15. Inlet 32 is provided for the addition of make-up aluminum chloride to the recirculating catalyst. Such addition is preferably controlled to provide sufficient aluminum chloride to the system to combine with any excess catalyst modifier present. Catalyst withdrawn from chamber 26 through line 30 is passed in part through valved line 33 into drum 22 wherein it is subjected to reactivation or employed as a component in production of additional modified catalyst. Removal of spent catalyst from the system may be effected by continuous or intermittent withdrawal from valved line 30.

In a modified form of operation at least a portion of the reactor effluent is diverted from line 25 through valved line 36 into a chamber 37, wherein at least partial separation of catalyst from hydrocarbons is effected. Hydrocarbons, at least partially freed of catalyst, are passed from chamber 37 through valved lines 38 and 25 into chamber 26. Liquid comprising catalyst is withdrawn from chamber 37 and passed through valved line 39 into valved line 31. The use of at least two separating chambers is advantageous in view of the desirability of maintaining intimate contact of reactants and catalyst in reactor 15. The maintenance of such a high degree of contact, preferably in the state of an emulsion, may require the use of the plurality of separators enabling a rapid partial separation, under conditions favorable to such separation, in the first of the separators.

Normally gaseous materials comprising hydrogen chloride may be flashed intermittently or continuously from accumulator 28 and passed through valved line 40 into line 23 leading to reactor 15.

Liquid comprising unreacted charge and reaction products, as well as cracking suppressor and dissolved hydrogen chloride, may be taken from accumulator 28 and passed to any suitable separating zone capable of effecting the separation of normally liquid and/or normally solid reaction products therefrom. Any conventional methods involving one or more such steps as fractionation, solvent extraction, fractional crystallization, filtration, etc., may be employed therein. The particular method of product separation will of course be governed to some degree by the properties such as boiling ranges of the components present in the reactor effluent. In the present illustrative presentation of the invention, product separation is shown for conditions in which the cracking suppressor, and the additional solvent, if employed, are lower boiling than the products of the reaction. Liquid is drawn for accumulator 28 and passed through line 41 into fractionator 42. Within fractionator 42 a fraction comprising normally gaseous material such as hydrogen chloride and optionally at least a part of the cracking suppressor, and solvent, if present, is taken overhead through valved line 32 and passed, at least in part, through valved line 23 to reactor 15. A valved line 44 leading into line 23 is provided for the introduction of make-up hydrogen chloride into the system. Bottoms comprising normally solid hydrocarbons in solution in normally liquid hydrocarbons are taken from fractionator 42 and passed through line 45 into a fractionator 46. Within fractionator 46 a fraction comprising the cracking suppressor is taken overhead through valved line 47 and passed at least in part through valved line 48 into the cracking suppressor charge line 12. A liquid fraction comprising hydrocarbons in the diesel fuel boiling range and higher is removed from the lower part of fractionator 46 through valved line 50. Any material boiling between the overhead and bottoms, which may have been introduced into, or formed within the system, is withdrawn from fractionator 46 through valved line 51 and eliminated from the system, or passed in part or entirely through valved line 52 into line 19.

Bottoms from fractionator 46 withdrawn through line 50 are passed through valved line 53 into a separating zone, such as, for example, a fractional crystallization zone 54. Within the fractional crystallization zone the hydrocarbon stream is fractionally crystallized in conventional manner, for example in the presence of a suitable solvent such as, for example, methylethyl ketone introduced through valved line 55. Within fractional crystallization zone 54 there is separated from the hydrocarbon stream a normally solid fraction comprising unreacted normally solid hydrocarbons, which is eliminated through line 56 and recycled to the reaction zone by means not shown in the drawing. Within fractional crystallization zone 54 there is also separated a normally solid reaction product comprising normally solid hydrocarbons having the same molecular weight as the normally solid hydrocarbon charge but possessing a more branched structure. This normally solid reaction product is removed from crystallization zone 54 through line 57. The normally solid reaction product may be recycled in part or entirely into reactor 15, by means not shown in the drawing, to undergo further conversion therein to a normally liquid product having the same molecular weight as the normally solid hydrocarbon charge. Remaining liquid products comprising hydrocarbons in the diesel oil and lubricating oil boiling range and ketone solvent are taken from fractional crystallization zone 54 and passed through line 58 into a fractionator 59. Within fractionator 59 there is separated a fraction comprising the ketone solvent which is taken overhead and recycled through line 60 to the fractional crystallization zone. Within fractionator 59 there is also separated an intermediate fraction boiling in the diesel fuel boiling range and a fraction boiling in the lubricating oil range, which fractions are removed therefrom through valved lines 61 and 62, respectively.

For the purpose of clarity, parts of apparatus, such as, for example, pumps, valves, accumulators, reboilers, reflux circuits and auxiliary equipment not essential to a full and complete description of the invention have been omitted from the drawing. The separation indicated above as effected within certain fractionators shown in the drawing, may in practical operation involve the utilization of a greater number of fractionators.

The normally solid hydrocarbons comprised in the reaction products of the invention will vary to some extent with the molecular weight of the normally solid hydrocarbon charge. Thus,

the use of normally solid hydrocarbons of higher molecular weight enables the attainment of relatively larger amounts of normally solid reaction products. The proportion of normally solid reaction products obtained is, however, reduced in a controllable manner by increasing the contact time employed or by recycling the normally solid reaction product to the reaction zone. Thus, sufficiently long contact times and/or continuous recycling of the normally solid reaction products will result in the obtaining of reaction products consisting predominantly, or substantially completely, of only normally liquid hydrocarbons having the same molecular weight as the normally solid original hydrocarbon charge in the absence of substantial hydrocarbon decomposition.

The production of a more highly branched product from the normally solid hydrocarbon charge in accordance with the process of the invention therefore enables the efficient conversion of the normally solid hydrocarbons to normally solid hydrocarbons of substantially different and improved properties. Thus a paraffin hydrocarbon wax of straight or only moderately branched chain structure is converted to a normally solid hydrocarbon product comprising high quality microcrystalline wax. The microcrystalline waxes thus produced posses highly improved properties rendering them eminently desirable for use as coating, impregnating and waterproofing materials, for rubber compounding, polishes, molding waxes, and other uses where a plastic wax of improved tensile or binding strength is desirable.

A particularly valuable aspect of the process of the invention resides in its ability to convert normally solid hydrocarbons whose presence is detrimental to the physical properties of the fractions or products in which they occur into exceptionally valuable normally liquid products which may be returned to the parent fraction with great benefit thereto or which may be used separately to obtain the full application of their special properties. Thus the process of the invention enables the substantially complete conversion of normally solid hydrocarbons such as paraffin wax to normally liquid branched paraffins comprising high quality Diesel engine fuels and lubricating oils. The normally liquid products in the Diesel engine fuel boiling range obtained in accordance with the process of the invention possess the highly advantageous characteristics of combining a high heating value with low pour point and high ignition quality. Thus Diesel engine fuels having a cetane number of about 80 to 100 are readily obtainable in accordance with the process of the invention. The pour point of these materials can be controlled by increasing the degree of branching of the product. Thus the pour point of a liquid reaction product can be decreased materially with only a relatively slight lowering of cetane number, by recycling it through the reaction zone. As an example, a normally liquid hydrocarbon product in the Diesel engine fuel boiling range having a pour point as low as −60° C. is readily obtainable from normally solid hydrocarbons by means of the invention.

Normally liquid products of the process of the invention in the lubricating oil range combine a high viscosity index with a low pour point, thereby rendering them of particular value as lubricants or as components of lubricating oils and compositions. Oils having a viscosity index of about 150 are readily produced in accordance with the process of the invention. Their pour point is also controllable within a wide range as in the case of Diesel fuels. Thus the pour point of liquid products in the lubricating oil range may be reduced further by recycling through the reaction zone without decreasing the molecular weight of the hydrocarbon and in the absence of any substantial hydrocarbon decomposition. Normally liquid hydrocarbons in the lubricating oil range having a pour point of about −20° C. are readily obtained in accordance with the process of the invention from normally solid hydrocarbons.

The liquid products of the invention are, however, of value not only as Diesel engine fuels, lubricants, and as components for such compositions, but are suitably employed wherever a branched chain hydrocarbon of high molecular weight is used. They are of particular value as spray oils and components of insecticides. A further particularly advantageous aspect of the invention resides in the obtaining of branched chain hydrocarbons of high molecular weight in relatively pure form from readily available materials by a method in which control of the degree of branching of the final product is possible over an unusually wide range.

The following examples are illustrative of the process and products of the invention:

Example I

A modified aluminum chloride catalyst was prepared by reacting 66.4 parts of anhydrous aluminum chloride with 46 parts by weight of toluene resulting in a fluid sludge. One part of a purified hydrocarbon wax, comprising only n-$C_{25}H_{52}$ was dissolved in one part by weight of decahydronaphthalene. The resulting solution was contacted with a portion of the modified catalyst at a temperature of 100° C., a contact time of four hours and a ratio of catalyst to wax of 1:1 by weight. The reactants were stirred at a rate to form an emulsion while passing a slow stream of hydrogen chloride therethrough. At the conclusion of this operation, the two phases were allowed to separate. The hydrocarbon layer was decanted and washed with hot water. Decahydronaphthalene was flashed off and unreacted wax separated from the oil by crystallization from methyl ethyl ketone. The properties of the starting wax and the oil obtained are as follows:

	Oil Product	Wax Charge
Distillation range, °C. at 6 mm. Hg	180 to 209	
Refractive index, n_D^{70}	1.4329	1.4303
Refractive index, n_D^{20}	1.4529	
Gravity, d^{70}	0.778	0.770
Pour point, °C	−10	[1] 53.5
Molecular weight	366	352
Kinematic viscosity, 100° F. cs	10.84	
Kinematic viscosity, 210° F. cs	2.88	3.08
Viscosity index	130	

[1] Melting point.

Example II

A paraffin hydrocarbon wax consisting essentially of a normal paraffin hydrocarbon having 25 carbon atoms to the molecule, having a molecular weight of 352, and a melting point of 53.4° C., was contacted with a modified aluminum chloride catalyst under conditions substantially as set forth in the foregoing example. Hydrocarbons were separated from the catalyst, washed with hot water and lighter materials comprising

the cracking inhibitor employed removed therefrom by distillation. Unconverted hydrocarbon wax was removed from the normally solid and normally liquid reaction products obtained by low temperature extraction thereof with methyl ethyl ketone. Remaining normally liquid and normally solid hydrocarbon reaction products were further separated by successive low temperature extraction by methyl ethyl ketone at the temperatures indicated in the following table. The boiling range of the oil before extraction was about 160° C. to about 203° C. at 4 mm. of Hg and had the following characteristics:

Viscosity index	130
Pour point, °C.	−6.7
Gravity, d_4^{20}	0.8134
Refractive index n_D^{20}	1.4522
Molecular weight	350
Kinematic viscosity, at 100° F. ——cs——	10.84
Kinematic viscosity, at 210° F. ——cs——	2.88

Separation of the reaction products by the low temperature extraction resulted in the obtaining of a normally solid hydrocarbon fraction consisting of microcrystalline wax, and three normally liquid hydrocarbon fractions having the following properties:

Extraction Temp., °C.	Per cent of Total Oil Extracted	Pour point, °C.	Refractive Index, n_D^{20}	Coefficient of Friction at—	
				80° C.	130° C.
−50	26	below −51	1.4597	0.070	0.066
−50	39	−46	1.4548	0.076	0.062
−20	23	−4	1.4501		
Residue	12	37 (melting point).		0.064	0.064

The hydrocarbons comprised in each of the four fractions indicated above were found to have a molecular weight corresponding substantially to that of the paraffin wax charged to the process, namely 352. Infra-red examination of the products revealed the presence of groups identifiable as 2-, 3- and other methyl and the absence of any geminate or neo-type dimethyl groups. Excellent values for the coefficient of friction were obtained with a four-ball machine according to the test as described in Lubrication Engineering, vol. 1, No. 2, page 35 (1945).

Example III

A modified aluminum chloride catalyst was prepared by reacting 2 parts of anhydrous aluminum with 5 parts by weight of tertiary butyl chloride at room temperature and allowing the mixture to stand 8 hours. To the resulting sludge there was added an additional 1 part by weight of aluminum chloride to 3 parts by weight of the catalyst sludge. The resulting modified aluminum chloride catalyst had a specific gravity of 1.4.

A paraffin wax averaging 25 carbon atoms per molecule with a molecular weight of 350 and a melting point of 53° C. was contacted in a series of separate runs with portions of the above-prepared modified aluminum chloride catalyst in the presence of a hydrocarbon cracking suppressor. The wax was dissolved in the cracking suppressor prior to contact with the catalyst. The reactions were executed with a ratio of catalyst to hydrocarbon of 1:2 by volume. The reactants were stirred vigorously during the execution of the conversion and a stream of hydrogen chloride was passed continuously through the reaction zone. The time of contact, nature and amount of cracking inhibitor employed, and conversion to normally liquid hydrocarbons obtained for each run are indicated in the following Table A:

Table A

Run No.	Temp., °C.	Contact Time, hrs.	Cracking Suppressor	Weight Ratio of Cracking Suppressor to Wax	Conversion to Normally Liquid Hydrocarbons, per cent wt.
1	100	4	Methylcyclohexane	1:1	21.0
2	100	1	do	1:1	10.0
3	100	1	do	2:1	28.0
4	100	0.25	do	4:1	21.0
5	100	0.50	do	4:1	28.9
6	100	1.0	do	4:1	29.1
7	100	1.0	do	8:1	30.0
8	50	4	Decahydronaphthalene	1:1	18.5
9	50	4	Dimethylcyclopentanes	1:1	18.0
10	100	3	Decahydronaphthalene	1:1	21.0

Unconverted wax was separated from the normally liquid hydrocarbon reaction products by crystallization in methylethyl ketone. The oil thus obtained was stabilized by distillation, in which material boiling up to 100° C. at 2 mm. of mercury was removed from the liquid hydrocarbon product. The oils obtained had the same molecular weights as the paraffin wax employed as charge to the runs. The observed physical properties of the composited oil thus obtained had the following properties:

Density d_4^{20}	0.806
Refractive index, n_D^{20}	1.4542
Pour point, °C.	−9
Viscosity at 100° F. ——cs——	8.679
Viscosity at 210° F. ——cs——	2.705
Viscosity index	135

Example IV

A high melting California wax averaging 35 carbon atoms to the molecule, having a melting point of 77° C. and a molecular weight of 500, was converted by contact with a portion of the modified $AlCl_3$ catalyst prepared as in Example III. The conversion was carried out at a temperature of 100° C. with a contact time of 3 hours in the presence of 1 part of methylcyclohexane to 1 part of wax charge by weight. A stream of hydrogen chloride was passed through the reaction zone and the reactants were stirred throughout the contact time. A conversion to normally liquid hydrocarbons of 18% was obtained in the absence of any substantial hydrocarbon decomposition. Low boiling materials in the oil thus obtained were flashed therefrom.

Properties of the normally liquid hydrocarbon product thus obtained were as follows:

S. A. E. viscosity number	10
Kinematic viscosity at 100° F. ---------cs--	36.4
Kinematic viscosity at 130° F.	19.9
Kinematic viscosity at 210° F.	7.2
Viscosity index	150
Molecular weight	500
Pour point, °C.	0

EXAMPLE V

A modified aluminum chloride catalyst indicated in the following table by the letter "A" was prepared by fusing together $AlCl_3$, $ZnCl_2$, KCl and NaCl in the following proportions by weight, respectively, 75.15:7.5:7.5.

A second modified aluminum chloride catalyst indicated in the following table "B" was prepared by melting together $AlCl_3$, KCl and NaCl in the following proportions by weight, respectively, 8:1:1.

A third modified aluminum chloride catalyst was prepared by dissolving 5 parts of $AlCl_3$ in 95 parts by weight of $SbCl_3$. The catalyst is indicated in the table by the letter "C."

Each of the modified aluminum chloride catalysts thus prepared was contacted with a separate portion of an n-paraffin wax, consisting essentially of normal paraffin hydrocarbons having 25 carbon atoms to the molecule, at a temperature of 100° C. in the presence of added hydrogen chloride and for a time of contact indicated in the following table. Prior to contact with the catalyst the wax was dissolved in an equal amount, by weight, of decahydronaphthalene. The reactants were stirred throughout the conversion period. No evidence of any substantial hydrocarbon decomposition was observed throughout the runs. The conversion of wax charged to normally liquid products is indicated in the following table:

Catalyst	Contact Time, hrs.	Percent Conversion to Liquid Hydrocarbons
A	2	15.2
B	4	17.3
C	4	7.6

EXAMPLE VI

One part of paraffin wax was dissolved in four parts by weight of methylcyclohexane. The wax employed consisted essentially of a mixture of normal paraffins having an average of 25 carbon atoms per molecule, a melting point of 53° C., and a molecular weight of 350.

In a series of separate operations, carried out under substantially identical conditions except for the reaction temperature employed, separate portions of the solution of wax in methylcyclohexane were contacted with a modified aluminum chloride catalyst. The catalyst was prepared as described in Example III. A contact time of one-half hour was used in each run and the reactants were stirred vigorously throughout the conversion period while passing a stream of hydrogen chloride therethrough. Upon completion of each run, catalyst was separated from the hydrocarbon layer by stratification and decantation. Methylcyclohexane was removed from the hydrocarbon layer by distillation. Normally solid hydrocarbons comprising unconverted wax and wax having a lower melting point, but having the same molecular weight as the starting material, were separated from the normally liquid hydrocarbon reaction products. The normally liquid reaction products consisted of a branched chain saturated paraffinic oil having substantially the same molecular weight as the wax charged and properties similar to those shown for the oil in Example III. Low temperature fractional crystallization of this oil from methyl-ethyl ketone resulted in the following three fractions:

Extract Fraction	Temperature of Extraction, °C.	Weight-percent of total oil extracted	Pour Point, °F.	n^{20} D	Viscosity Index
1	−50	42	−60	1.4508	132
2	−36	24	−27	1.4494	139
3	residue at −36	34	+45	1.4492	160

The temperature at which the reaction was executed, the total amount of wax reacted, and the amount of wax converted to hydrocarbon oil for each run are indicated in the following table:

Reaction Temp., °C.	Total Amount of Wax Reacted, Per cent	Conversion of Wax to Oil, Per Cent
30	2	2
50	5.2	5.2
75	18.0	18.0
80	21.0	20.8
85	33.0	24.8
90	40.5	28.8
100	40.0	28.9

EXAMPLE VII

Twenty-five percent of liquid paraffinic oil produced as in Example III was blended with a Diesel fuel of 42 cetane number and tested. The cetane number for the blend was 51.5 and the calculated cetane number of the added paraffinic oil made in accordance with the process of this invention was, therefore, 80.

The invention claimed is:

1. The process for isomerizing paraffin wax which comprises dissolving paraffin wax in an amount of decahydronaphthalene at least equal to about an added 100% by weight of said paraffin wax, contacting said solution with a preformed toluene-aluminum chloride complex in a reaction zone at a temperature of about 80 to 110° C. while agitating the reactants vigorously to maintain them in a state of emulsion, said preformed toluene-aluminum chloride complex being obtained by the interaction of hydrocarbons comprising toluene with anhydrous aluminum chloride, thereby converting paraffin wax to reaction products consisting essentially of paraffin wax and normally liquid hydrocarbons which are isomeric in structure to said charged paraffin wax in said reaction zone, and separating paraffin wax and normally liquid hydrocarbons isomeric in structure to said charged paraffin wax from the effluence of said reaction zone.

2. The process for isomerizing paraffin wax which comprises dissolving paraffin wax in an amount of decahydronaphthalene equal to from about an added 200% to about 800% by weight of said paraffin wax, contacting said solution with a preformed hydrocarbon-aluminum chloride complex in a reaction zone at a temperature of from about 20 to about 150° C. while agitating the reactants vigorously to maintain them in a state

of emulsion, said preformed hydrocarbon-aluminum chloride complex being obtained by the interaction of a hydrocarbon with anhydrous aluminum chloride, thereby converting paraffin wax to reaction products consisting essentially of paraffin wax and normally liquid hydrocarbons which are isomeric in structure to said charged paraffin wax in said reaction zone, and separating paraffin wax, and normally liquid hydrocarbons isomeric in structure to said charged paraffin wax from the effluence of said reaction zone.

3. The process for isomerizing paraffin wax which comprises dissolving paraffin wax in an amount of cycloparaffinic hydrocarbon solvent equal to from about an added 50% to about 1000% by weight of said paraffin wax contacting said solution with a preformed hydrocarbon-aluminum chloride complex in a reaction zone at a temperature of from about 20 to about 150° C. while agitating the reactants vigorously to maintain them in a state of emulsion, said preformed hydrocarbon-aluminum chloride complex being obtained by the interaction of a hydrocarbon with anhydrous aluminum chloride, thereby converting paraffin wax to reaction products consisting essentially of paraffin wax and normally liquid hydrocarbons which are isomeric in structure to said charged paraffin wax in said reaction zone, and separating paraffin wax and normally liquid hydrocarbons isomeric in structure to said charged paraffin wax from the effluence of said reaction zone.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,404,436	Crawford et al.	July 23, 1946
2,406,868	Tongberg et al.	Sept. 3, 1946
2,408,941	Mavity et al.	Oct. 8, 1946
2,414,371	Fragen et al.	Jan. 14, 1947
2,417,698	McAllister et al.	Mar. 18, 1947