Oct. 21, 1941.

E. L. D'OUVILLE ET AL

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CATALYTIC CONVERSION OF HYDROCARBONS

Filed Dec. 21, 1938

3 Sheets-Sheet 1

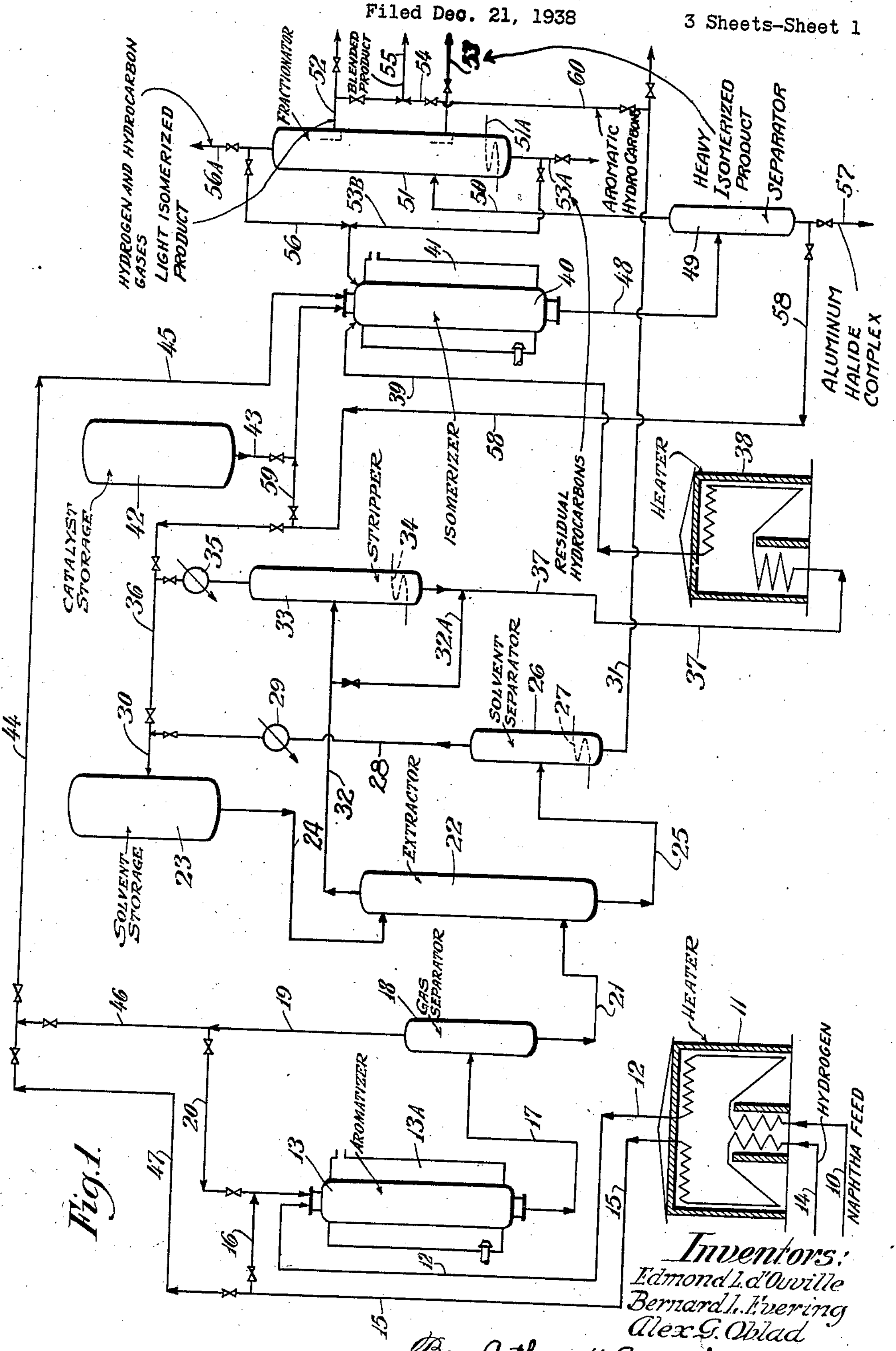

Fig. 1.

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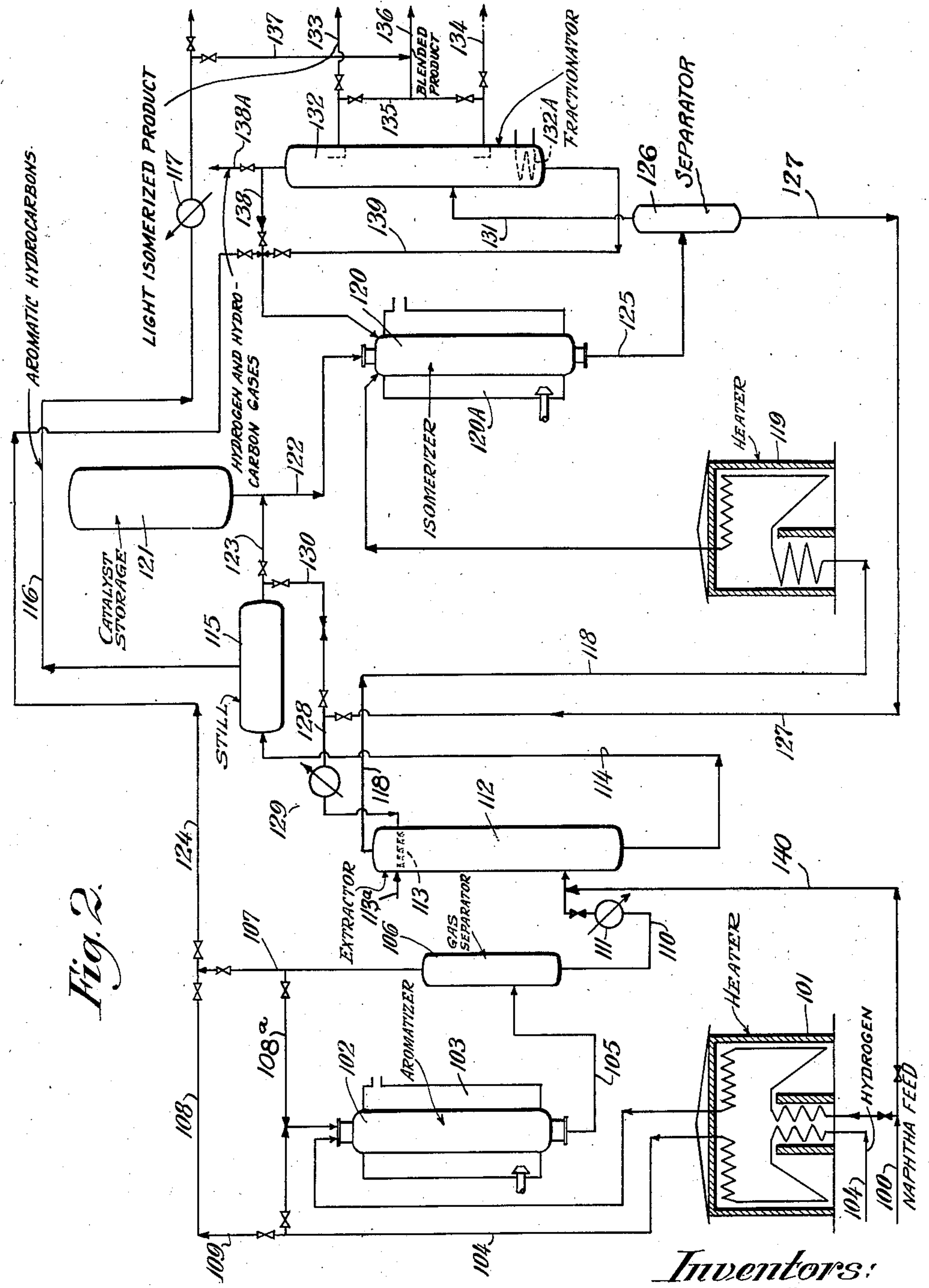

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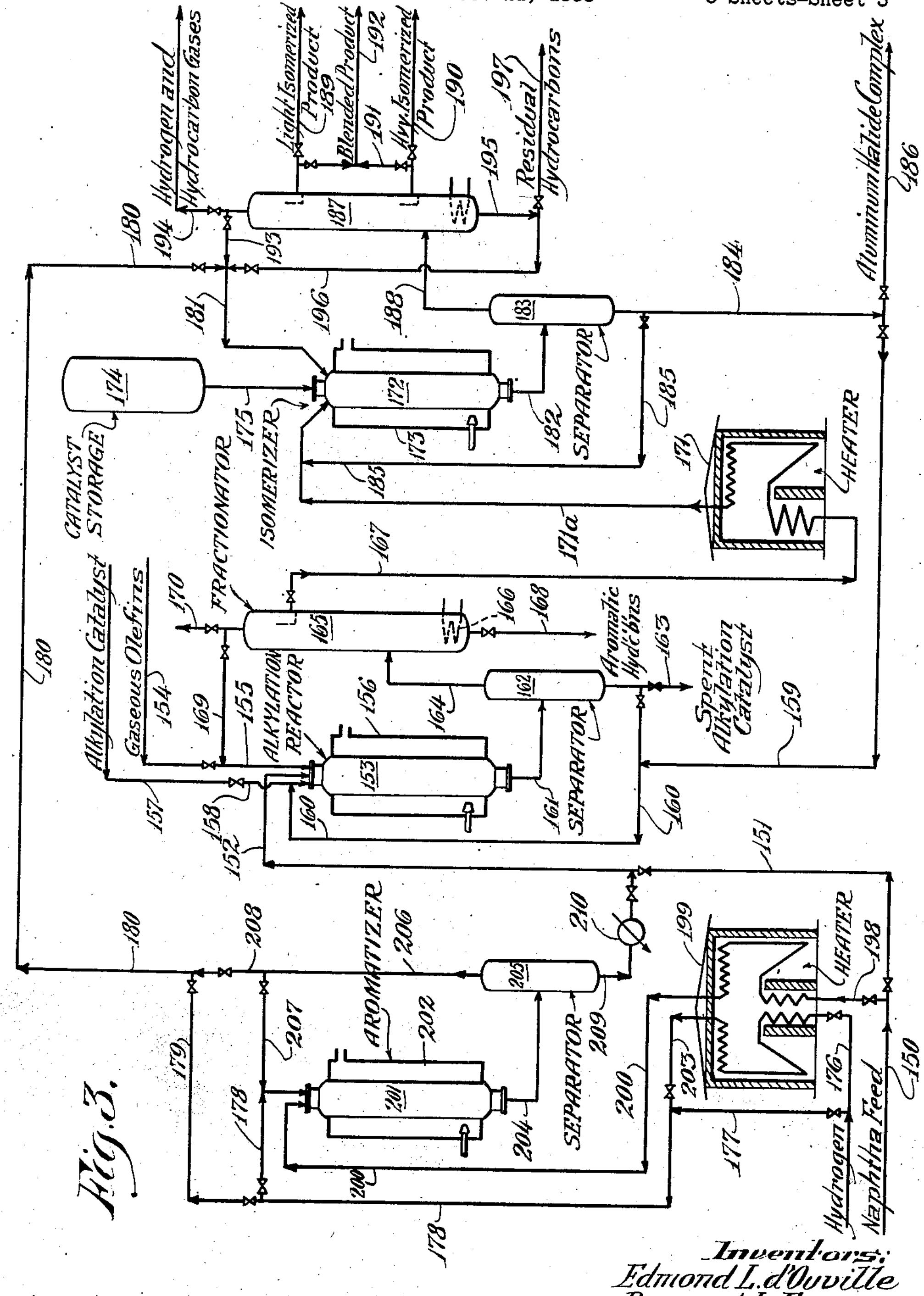
Fig. 3.



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CATALYTIC CONVERSION OF HYDROCARBONS

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20 Claims. (Cl. 196—9)

This invention relates to the preparation of saturated branched-chain hydrocarbons from hydrocarbon mixtures containing aliphatic hydrocarbons, naphthenes and aromatic hydrocarbons. In particular, the invention relates to the preparation of motor fuel products containing large quantities of branched-chain saturated hydrocarbons and to the preparation of high solvency naphthas.

Saturated branched-chain hydrocarbons are very useful as motor fuels because of their non-detonating properties and high heating values. Furthermore, the saturated branched-chain hydrocarbons have lower boiling points than the corresponding straight-chain paraffins so that motor fuels containing substantial quantities of the former have better starting characteristics than motor fuels containing large quantities of the straight-chain paraffins. In addition, branched-chain paraffin hydrocarbons are very useful as raw materials in the preparation of many chemical products.

It is known that normal paraffins can be isomerized to saturated branched-chain hydrocarbons in the presence of suitable catalysts, notably an aluminum halide in the presence of an activator, preferably a hydrogen halide, or a compound which will yield a hydrogen halide.

We have found that the catalytic conversion of normal paraffins to saturated branched-chain hydrocarbons is materially inhibited by the presence of even small amounts of aromatic hydrocarbons. For example under certain conditions the presence of as little as about 0.4% (by volume) of aromatics in the isomerization feed stock will reduce the ratio of moles of normal paraffins converted to moles of aluminum chloride catalyst used from about 66 to about 10, while about 5% (by volume) of aromatics will further depress the ratio to about 6. Effective conversion of normal paraffins to saturated branched-chain hydrocarbons therefore requires a feed stock substantially free of aromatics.

One object of the present invention is to process an admixture of paraffins together with naphthenes and/or aromatics by a series of steps whereby two main products are formed, namely a product containing predominantly aromatic hydrocarbons and a product containing predominantly saturated branched-chain hydrocarbons to be used in motor fuels having high octane numbers. Another object of our invention is to secure improved yields of branched-chain paraffins per pound of catalyst in an aluminum halide catalytic hydrocarbon conversion process. A further object of the invention is to provide a process of converting a hydrocarbon mixture containing at least normal paraffins, naphthenes and aromatics into products rich in aromatic hydrocarbons and products rich in saturated branched-chain hydrocarbons by a process involving the selective catalytic aromatization of the naphthenes to aromatics, the removal of the aromatics, that is, those present in the original feed stock and also those formed by the aromatization of the naphthenes, and the catalytic conversion of the aromatic-free residue to produce saturated branched-chain hydrocarbons.

Other objects and advantages of the present invention will become apparent from the following description thereof read in conjunction with the accompanying drawings which form a part of the present specification and in which:

Figure 1 is a general flow diagram of one arrangement for carrying out the invention;

Figure 2 is a schematic flow diagram of a modified method of carrying out the invention;

Figure 3 is a schematic flow diagram of another modification according to our invention wherein aromatic hydrocarbons are removed from the isomerization feed stock by alkylation followed by fractional distillation.

Since the feed stocks employed generally comprise mixtures containing at least normal paraffins, aromatics and naphthenes, it is advantageous to convert naphthenes to aromatics by catalytic aromatization in the presence of hydrogen prior to the removal of aromatics from the isomerization feed stock. We therefore will describe and illustrate our invention as applied to a combination aromatization and isomerization process, although it is to be understood that the invention is not so limited.

For the purpose of clarity several of the terms used in the present specification and claims are defined as follows: "Aromatization" means the catalytic conversion of naphthenes, such as cyclohexane and its derivatives, to the corresponding aromatic hydrocarbons; "isomerization" means the catalytic conversion of normal paraffins to saturated branched-chain hydrocarbons; "space velocity" means the volume of cold liquid, per volume of gross space occupied by the catalyst, passed through the catalyst per hour.

Referring to Figure 1 a petroleum fraction having a boiling range from about 60° F. to about 400° F., preferably from about 150° F. to about 300° F., and containing at least normal paraffins, naphthenes and aromatic hydrocarbons, is passed through a line **10**, a heater **11** and a line **12** to a catalytic reactor 13, hereinafter referred to as aromatizer 13. Hydrogen from a line 14 is passed through the heater 11, and lines 15 and 16 to the aromatizer 13. The aromatizer 13 is packed with a suitable aromatization catalyst, for example 90 Al_2O_3; 10 Cr_2O_3 (a mixture of 90 parts aluminum oxide by weight and 10 parts chromic oxide by weight), platinum on magnesium chromite, nickel on magnesium chromite, platinum black, palladium, nickel or reduced copper suitably supported, or other suitable catalysts. By maintaining the catalyst in the aromatizer 13 at a temperature ranging from about 500° F. to about 1000° F., and preferably about 850° F., by suitable means such as the jacket heater 13A, and passing the feed stock therethrough under a hydrogen pressure of about 0.2 to about 10 atmospheres, at a space velocity of about 0.05 to about 5.0 substantially all of the naphthenes capable of aromatization in the feed stock will be converted to aromatics. Under the conditions prevailing in the aromatizer 13 substantially no olefins are formed from paraffins, the reaction being almost exclusively a conversion of naphthenes to aromatics. This is of particular advantage in that the absence of olefins materially prolongs the life of the aromatization catalyst, and furthermore permits a more effective separation of the aromatics from the normal paraffins in the manner hereinafter described.

The products in the aromatizer 13 are removed therefrom through a line 17 to a gas separator 18 wherein hydrogen is separated and removed overhead through a line 19 to be either recycled to the aromatizer 13 through a line 20 or utilized in a subsequent isomerization stage as hereinafter described.

The gas-free stock from the gas separator 18 is removed therefrom through a line 21, and introduced into an extractor 22 wherein the aromatic hydrocarbons undergo substantially complete removal by countercurrent contact with a suitable selective solvent from a solvent storage tank 23 introduced into the upper portion of the extractor 22 through a line 24. As the selective solvent we may use liquefied SO_2, an aluminum chloride-complex, to which further reference will be made hereinafter, other solvents such as furfural, nitrobenzene, nitromethane, or other solvents selected with respect to the distillation characteristics of the feed stock employed and the boiling point of the solvent. The temperature employed in the extraction stage will depend upon the solvent used, but in general this temperature will be between about −40° F. and 120° F.

The extract from the extractor 22 is removed therefrom through a line 25 and introduced into a separator 26, wherein the aromatic hydrocarbons are separated from the solvent. The separator 26 may be heated by suitable means, such as a steam coil 27. The separated solvent is removed from the separator 26 through a line 28, condensed in cooler 29, and returned to the solvent storage tank 23 through line 30. The aromatic hydrocarbons are removed from the separator 26 through a line 31 to be utilized as a high solvency naphtha or blended with an isomerized motor fuel as hereinafter described.

We have described the separation of the solvent from the aromatic hydrocarbons in which the solvent is removed as an overhead. It will be appreciated by those well versed in the art that, dependent upon the boiling point of the solvent chosen, the solvent will be removed from the separator 26 either as an overhead or as a bottom, and that the routing of the separated solvent and the separated aromatics must be modified accordingly.

The raffinate from the extractor 22, containing not more than about 2%, and preferably less than 0.5% of aromatic hydrocarbons, is removed therefrom through a line 32 and introduced into a stripper 33, heated by suitable means, such as a heating coil 34, wherein any solvent in the raffinate is separated from it, and returned through condenser 35 and lines 36 and 30 to solvent storage tank 23. The solvent-free raffinate, comprising substantially paraffinic hydrocarbons, is removed from the stripper 33 through a line 37 and passed through a preheater 38 and a line 39 to a catalytic isomerizer 40 wherein the normal paraffinic hydrocarbons are converted to saturated branched-chain hydrocarbons as hereinafter described.

While we have shown the removal of solvent from the raffinate in stripper 33, if the solvent employed is the aluminum chloride-hydrocarbon complex, the raffinate may be sent directly to the preheater 38 through the line 32A, since a small amount of the aluminum chloride-hydrocarbon complex in the raffinate is not detrimental to the conversion of normal paraffins to the saturated branched-chain hydrocarbons.

We have described the removal of solvent from the raffinate in which the boiling point of the former is lower than that of the latter. It will be appreciated by those well versed in the art that, dependent upon the boiling point of the solvent chosen, the solvent will be recovered from the stripper 33 either as an overhead or as a bottom, and that the routing of the separated solvent and the raffinate must be modified accordingly.

As aforementioned the raffinate passes from the stripper 33 through a preheater 38 to a catalytic isomerizer 40 maintained at the desired temperature by suitable means such as a jacket heater 41, wherein it is intimately contacted with HCl-activated aluminum chloride, or other aluminum halides activated by a hydrogen halide, introduced into the isomerizer 40 from a catalyst storage tank 42 through a line 43. Contact of the raffinate with the catalyst is preferably made in the presence of hydrogen introduced into the isomerizer 40 through lines 44 and 45. The hydrogen used in the isomerizer 40 may be that obtained from the gas separator 18 and introduced into line 44 through lines 19 and 46, and/or that obtained from the hydrogen storage tank (not shown) and introduced into line 44 through lines 14, 15 and 47. To substantially reduce the degradation of the product formed in the isomerizer 40 to C_3 and/or C_4 hydrocarbons, it is desirable to introduce C_3 and/or C_4 gases, from a fractionator as hereinafter described, into the isomerizer 40.

When the reaction is carried out in the presence of hydrogen the isomerizer 40 is maintained at a temperature within the range of about 180° F. to about 450° F. by suitable means, such as the jacket heater 41 and under a hydrogen pressure from about 800 to about 4000 pounds per square inch. However, at times it may be desirable to carry out the conversion of the raffinate in the absence of extraneous hydrogen or under a relatively low hydrogen pressure, in which case the isomerizer 40 is operated within the temperature range of about 180° F. to about

450° F. under a pressure ranging from about 50 pounds to about 800 pounds per square inch.

Under the conditions prevailing in the isomerizer **40** the normal paraffins are converted to saturated branched-chain hydrocarbons. The products from the isomerizer **40**, comprising substantialy saturated branched-chain hydrocarbons and an aluminum chloride-hydrocarbon complex, are removed therefrom through a line **48** and introduced into a separator **49** wherein the products from the isomerizer are permitted to separate, the aluminum chloride-hydrocarbon complex forming the lower layer. The upper stratum comprising substantially hydrocarbons is removed from the separator **49** through a line **50** and introduced into a fractionator **51**, provided with a heating coil **51A** wherein by effective fractionation the saturated branched-chain hydrocarbons are separated and removed from the system through lines **52** and **53** as side streams. If desired the streams may be blended by lines **54** and **55**. Bottoms from the fractionator **51**, comprising substantially partially converted products are removed through a line 53A, and may be recycled to the isomerizer **40** through a line 53B. The unconverted low-boiling hydrocarbons, particularly propane and butane, and hydrogen are removed as an overhead from the fractionator **51** through a line **56** and recycled to the isomerizer **40** as hereinbefore described, or removed from the system through line **56A**.

The aluminum chloride-hydrocarbon complex separated in the separator **49** is removed therefrom through a line **57**. When the complex is employed as the solvent for the removal of aromatic hydrocarbons from the paraffins following the aromatization stage, it may be transferred from the separator **49** to the extractor **22** through lines **58**, **36**, **30**, solvent storage tank **23** and line **24**. A portion of the complex may also be recycled to the isomerizer **40** through line **59**.

If desired the aromatic hydrocarbons, or a portion thereof, removed from the separator **26** through the line **31**, may be blended with the saturated branched-chain hydrocarbons through a line **60**.

The partly spent aluminum chloride catalyst used in the conversion of normal paraffins to saturated branched-chain hydrocarbons forms an aluminum chloride-hydrocarbon complex, hereinafter called aluminum chloride-complex, having substantially the following composition:

	Per cent
Aluminum	8 to 14
Chlorine	30 to 50
Hydrocarbon	30 to 60

This aluminum chloride complex is substantially immiscible with paraffins but is an excellent solvent for aromatics, thereby making it an excellent reagent for the removal of aromatics from the feed stock going to the isomerizer. In the description of the process of Figure 1 we have alluded to the use of the aluminum chloride complex as the solvent for the removal of aromatic hydrocarbons from the feed stock going to the isomerizer. In the following paragraphs we will describe in more detail the embodiment of our invention using the aluminum chloride-complex as the selective solvent.

Referring to Figure 2, a petroleum fraction, containing at least paraffins, and naphthenes, and having a boiling range between about 60° F. and about 400° F., and preferably between about 150° F. and 300° F., from a source (not shown) is passed through a line **100**, and a heater **101** to a catalytic aromatizer chamber **102** containing a suitable aromatization catalyst, and maintained at the desired temperature by suitable means such as a jacket heater **103**, wherein the naphthenes are converted to aromatics in the presence of hydrogen introduced into the aromatizer **103** through line **104** which passes through the heater **101**.

As suitable aromatization catalysts we mention by way of example, $90Al_2O_3:10Cr_2O_3$ (a mixture of 90 parts aluminum oxide by weight, and 10 parts chromic oxide by weight) platinum on magnesium chromite, nickel on magnesium chromite, palladium, nickel, and reduced copper suitably supported. The aromatization is carried out at a temperature of about 500° F. to about 1000° F., and preferably about 850° F. under a hydrogen pressure of about 0.2 to about 10 atmospheres and at a space velocity of about 0.05 to about 5.0.

The products from the aromatizer **102** are removed therefrom through a line **105** to a gas separator **106** wherein the hydrogen is separated from the products from the aromatizer. The hydrogen separated in the gas separator **106** is removed therefrom through a line **107** and either recycled to the aromatizer **102** through line **108***a* or used for the isomerization of the normal paraffins as hereinafter described. The hydrogen-free products from the gas separator **106** are removed therefrom through a line **110** and a cooler **111** and introduced into the bottom of an extractor **112**, wherein they are countercurrently contacted at a temperature of from about 40° F. to about 120° F. with a descending stream of aluminum chloride-complex, obtained from an isomerization stage as hereinafter described and introduced into the extractor **112** through a spray **113**. If desired aluminum chloride complex from an extraneous source may be introduced into the extractor **112** through spray **113** by means of line **113***a*. The aromatics formed in the aromatization stage, together with the aromatics which may be present in the original stock, are dissolved in the aluminum chloride-complex to form an extract phase comprising substantially aromatic hydrocarbons and aluminum chloride-complex and a raffinate phase comprising substantially paraffins. The extract from the extractor **112** is removed therefrom through a line **114** and introduced into a still **115**, wherein the aromatics dissolved therein are removed by distillation and passed through a line **116** to a condenser **117** wherein the vaporized aromatic hydrocarbons are condensed and removed to a suitable storage container (not shown), or blended with isomerized products as hereinafter referred to.

The raffinate from the extractor **112** is removed therefrom through a line **118**, heated in a preheater **119**, and introduced into an isomerizer **120** maintained at the desired temperature by a jacket heater **120A**, or other suitable means, wherein it is catalytically converted in the presence of a hydrogen halide-activated aluminum halide, but preferably HCl-activated aluminum chloride and/or a mixture of aluminum chloride and aluminum chloride-complex to form saturated branched-chain hydrocarbons. The aluminum chloride catalyst is introduced from a storage tank **121** through a line **122** into the isomerizer **120**. Instead of using fresh aluminum chloride catalyst we may use in combination therewith the aluminum chloride-complex separated from the aromatics in the still **115**. The aromatic-free aluminum chloride-complex from the still **115** is removed therefrom through a line **123** which communicates with fresh aluminum chloride catalyst line **122**.

The raffinate from the extractor **112** comprising substantially normal paraffins is converted in the isomerizer **120** in the presence of aluminum chloride and/or aluminum chloride-complex at a temperature of about 180° F. to about 450° F., preferably from about 210° F. to about 250° F., and at a pressure of from about 500 pounds to about 4000 pounds per square inch when hydrogen is employed in the isomerization step, or at a pressure of about 50 pounds to about 500 pounds per square inch when hydrogen is used at low pressures or not at all, in the isomerization stage. It is preferred, however, to employ hydrogen in the isomerization stage since we have found that its presence prolongs the catalyst life. Hydrogen for the isomerization stage may be hydrogen from the gas separator **106** which is introduced into the isomerizer **120** through lines **107** and **124** or it may be hydrogen obtained from the external source (not shown) through lines **104**, **109**, **108** and **124**.

The products from the isomerizer **120** comprising substantially saturated branched-chain hydrocarbons and aluminum chloride-complex are removed therefrom through a line **125** and introduced into a separator **126** wherein the withdrawn products separate into an upper layer comprising substantially saturated branched-chain hydrocarbons and a lower layer comprising substantially aluminum chloride-complex. The aluminum chloride-complex used to extract the aromatic hydrocarbons from the products obtained from the aromatization stage is withdrawn from the bottom of the separator **126** through lines **127**, **128**, cooled in a cooler **129**, and introduced into the upper portion of the extractor **112** through the aforementioned spray **113**. A portion of the aluminum chloride-complex from the separator **126** may be by-passed through a line **130** and combined with the aluminum chloride-complex from the still **115**, or if desired, a portion of the aluminum chloride-complex recovered from the still **115** may be by-passed to the extractor **112** through the line **130**.

The hydrocarbons separated in the separator **126** are removed therefrom through a line **131** and introduced into a fractionator **132** heated by suitable means such as a coil **132A** wherein the products from the isomerizer **120** are fractionated from the light paraffins, such as the C_3 and C_4 hydrocarbons. The isomerized products are removed as side cuts from fractionator **132** through lines **133** and **134**, and may be blended by means of lines **135** and **136**. If desired, a portion of the aromatic hydrocarbons being removed from the system through the line **116** may be by-passed through a line **137** and blended with the isomerized products in line **136**.

The C_3 and C_4 hydrocarbons and hydrogen removed as an overhead from the fractionator **132** may be recycled to the isomerizer **120** through line **138** together with partially isomerized products removed from the lower portion of the fractionator **132** through a line **139**. By recycling the C_3 and C_4 hydrocarbons to the isomerizer degradation of paraffins to C_3 and C_4 hydrocarbons is materially inhibited. If desired a portion of the overhead from the fractionator **132** may be removed from the system through a line **138A**.

The processes just described provide economical and efficient means of obtaining aromatic rich naphthas which are suitable as a source of high solvency naphthas and naphthas having a high content of saturated branched-chain hydrocarbons which are suitable for high anti-knock motor fuels.

While we have described our invention as applied to an aromatization stage in combination with an isomerization stage it is to be understood that the invention can be applied to installations having no aromatization stage prior to the isomerization stage. In the latter case the isomerization feed stock containing aromatic hydrocarbons will be passed directly by means of line **140** to the extractor **112** wherein the aromatics are removed from the feed stock by solvent extraction in the manner hereinbefore described.

While we prefer to remove the aromatics from the isomerization feed stock by selective solvent extraction other effective means may be employed. Although it is difficult to separate mixtures of aromatics, naphthenes and normal paraffins by simple fractionation because of the overlapping boiling points of the constituents we have found that an effective method of separating the constituents by fractionation is to alter the relative boiling points thereof by alkylation of the aromatics with low molecular weight olefins, namely the $C_2=$, $C_3=$ and $C_4=$ olefins. Theses low molecular weight olefins may be present in the original feed stock or may be added thereto from an extraneous source. This method of alkylation as a means of separation is especially applicable to the separation of aromatics from a narrow boiling range hydrocarbon cut that is 150° to 250° F. in which case the alkylated aromatics formed will distill outside this distillation range. The alkylation takes place at a temperature of from about 50° F. to about 225° F. under a pressure of from about 15 pounds to about 100 pounds per square inch in the presence of a suitable catalyst, such as aluminum chloride activated with HCl or the aluminum chloride-complex obtained in the isomerization of normal paraffins to saturated branched-chain hydrocarbons. Following the alkylation stage the products are introduced into a fractionating column, wherein the unreacted olefins are removed as an overhead and recycled to the alkylation stage, the paraffins and naphthenes are removed as a side stream, and the alkylated aromatics removed as bottoms. The paraffins and naphthenes removed as a side stream are passed directly to the isomerization stage wherein the normal paraffins are converted to branched-chain paraffins as hereinabove described.

Apparatus suitable for carrying out the modification of our invention last described is schematically shown in Figure 3, to which reference is now made. A petroleum fraction of the type hereinabove specified containing at least paraffin and aromatic hydrocarbons from a source (not shown) is passed through lines **150**, **151** and **152** to an alkylation reactor **153** wherein it is contacted with low molecular weight olefins in the presence of a suitable catalyst under conditions such that these olefins combine with the aromatic hydrocarbons in the charge to form alkylated aromatics. As stated above, these olefins, namely the $C_2=$, $C_3=$, and $C_4=$ olefins, may be present in the feed stock but may be introduced from an extraneous source, for instance, through lines **154** and **155**. The alkylation takes place at a temperature in the range from about 50° F. to about 225° F. maintained by means of jacket heater 156 or other suitable arrangement and under a pressure in the range from about 15 to about 100 pounds per square inch. The catalyst, aluminum chloride activated with HCl for example, can be introduced into reactor 153 through lines 157 and 158, but if the aluminum chloride-complex obtained in the isomerization stage is used, this is introduced into line 158 through lines 159 and 160.

The reaction products are withdrawn from the bottom of reactor 153 through line 161 and introduced into separator 162 wherein the products are permitted to stratify. Regardless of whether aluminum chloride, the hydrocarbon complex formed in the isomerization reaction or both are used as the alkylation catalyst, the catalytic material withdrawn from reactor 153 will be in the form of a fluid hydrocarbon complex and will form a lower layer in separator 162 which can either be recycled through lines 160 and 158 or removed from the system through line 163. The upper stratum comprising unreacted paraffin and naphthene hydrocarbons and alkylated aromatics is removed from separator 162 through line 164 and introduced into fractionator 165 provided with a heating coil 166 wherein by effective fractionation the paraffin hydrocarbons together with the naphthenic hydrocarbons which may be present in the feed stock are separated as a sidestream and withdrawn through line 167. Bottoms from fractionator 165 containing the alkylated aromatics are removed through line 168, while the overhead consisting largely of unreacted gaseous olefins is recycled to reactor 153 through lines 169 and 155. A portion of this overhead may be vented through line 170 to prevent inert gases from building up in the system.

The hydrocarbon fraction rich in normal paraffins flowing through line 167 is introduced into the isomerization stage, which, as shown in Figure 3, is similar to that illustrated in Figure 2. This isomerization feed is heated in preheater 171 and introduced through line 171*a* into isomerizer 172 maintained at the desired temperature by jacket heater 173 or other suitable means, wherein the normal paraffin hydrocarbons are catalytically converted to saturated branched-chain hydrocarbons as already described. The alluminum chloride catalyst is introduced into isomerizer 172 from storage tank 174 through line 175, and when hydrogen is employed, this is supplied through lines 176, 177, 178, 179, 180 and 181.

The products from isomerizer 172 are removed therefrom by means of line 182 and separated in separator 183 into an upper hydrocarbon layer and a lower layer comprising substantially aluminum chloride complex which is withdrawn through line 184. This complex is preferably recycled, at least in part, to isomerizer 172 through line 185, and a portion of it can be used in the alkylation stage as hereinabove set forth by means of line 159. If desired, all or a portion of the complex can be withdrawn from the system through line 186.

The upper layer is introduced into fractionator 187 through line 188, and the isomerized products are removed as sidestream cuts through lines 189 and 190. These cuts may be blended if desired by means of lines 191 and 192. The C_3 and C_4 hydrocarbons and hydrogen removed as an overhead from fractionator 187 may be recycled to isomerizer 172 through lines 193 and 181 to inhibit the degradation of the normally liquid paraffins to gaseous hydrocarbons, or a portion thereof may be removed from the system through line 194. The relatively heavy bottoms may also be recycled for further conversion through lines 195, 196 and 181 or withdrawn by means of line 197.

As an alternative procedure the original feed stock may be first catalytically treated to convert the cyclohexane type naphthenes therein to aromatics and then alkylated in the foregoing manner.

Apparatus for carrying out this modification of our invention is also shown in Figure 3. The fresh feed is passed from line 150 through line 198, heater 199 and line 200 to aromatizer 201 which is maintained at the desired reaction temperature by means of jacket 202. Hydrogen from line 176 is likewise heated in heater 199 and passed to aromatizer 201 through lines 203 and 178. The conversion of naphthenic to aromatic hydrocarbons takes place in aromatizer 201 as already described, and the products pass through line 204 to gas separator 205. The separated hydrogen is removed through line 206 and either returned to aromatizer 201 through lines 207 and 178 or used in the isomerization stage by means of lines 208, 180 and 181. The liquid layer in separator 205, now relatively free from naphthenes and rich in paraffins and aromatics is removed to the alkylation reactor 153 by means of line 209, cooler 210 and line 152. Thereafter the aromatics are removed and the remaining paraffins are isomerized as previously described, giving a good yield of branched-chain paraffin hydrocarbons.

While we have described our invention with specific embodiments thereof, it is to be understood that the same are merely illustrative of the invention and not a limitation thereof, except insofar as the same is defined in the appended claims.

We claim:

1. The process of preparing a motor fuel fraction containing a large proportion of branched-chain paraffin hydrocarbons from a naphtha containing substantial amounts of aromatic and straight-chain paraffin hydrocarbons which comprises treating said naphtha to produce therefrom a hydrocarbon mixture containing straight-chain paraffin hydrocarbons but not more than 2 per cent by volume of aromatic hydrocarbons, and subjecting said hydrocarbon mixture to the action of an aluminum halide catalyst and an activator affording a hydrogen halide under conditions effective to convert straight-chain paraffin hydrocarbons to branched-chain paraffin hydrocarbons.

2. The process of claim 1 wherein said catalyst is aluminum chloride and said activator is hydrogen chloride.

3. The process of preparing a motor fuel fraction containing a large proportion of branched-chain paraffin hydrocarbons from a naphtha containing substantial amounts of aromatic and straight-chain paraffin hydrocarbons which comprises treating said naphtha to produce therefrom a hydrocarbon mixture containing straight-chain paraffin hydrocarbons but substantially free from aromatic hydrocarbons, and subjecting said hydrocarbon mixture to the action of an aluminum halide catalyst and an activator affording a hydrogen halide under conditions effective to convert straight-chain paraffin hydrocarbons to branched-chain paraffin hydrocarbons.

4. The process of preparing a motor fuel fraction containing a large proportion of branched-

chain paraffin hydrocarbons from a naphtha containing substantial amounts of aromatic and straight-chain paraffin hydrocarbons which comprises extracting said naphtha with a selective solvent to produce therefrom a hydrocarbon mixture containing straight-chain paraffin hydrocarbons but not more than 2 per cent by volume of aromatic hydrocarbons, and subjecting said hydrocarbon mixture to the action of an aluminum halide catalyst and an activator affording a hydrogen halide under conditions effective to convert straight-chain paraffin hydrocarbons to branched-chain paraffin hydrocarbons.

5. The process of claim 4 wherein said selective solvent is liquid sulfur dioxide.

6. The process of claim 4 wherein said selective solvent is an aluminum halide-hydrocarbon complex.

7. The process of preparing a motor fuel fraction containing a large proportion of branched-chain paraffin hydrocarbons from a naphtha containing substantial amounts of aromatic and straight-chain paraffin hydrocarbons which comprises treating said naphtha in an extraction zone with an aluminum halide-hydrocarbon complex to remove aromatic hydrocarbons therefrom and produce a raffinate containing straight-chain paraffin hydrocarbons but not more than 2 per cent by volume of aromatic hydrocarbons, subjecting said raffinate in a reaction zone to the action of an aluminum halide catalyst and an activator affording a hydrogen halide under conditions effective to convert straight-chain paraffin hydrocarbons to branched-chain paraffin hydrocarbons, removing said motor fuel fraction and an aluminum halide-hydrocarbon complex from said reaction zone and introducing at least a portion of said complex from said reaction zone into said extraction zone.

8. The process of claim 7 wherein said aluminum halide is aluminum chloride, said aluminum halide-hydrocarbon complex is aluminum chloride-hydrocarbon complex and said activator is hydrogen chloride.

9. The process of preparing a motor fuel fraction containing a large proportion of branched-chain paraffin hydrocarbons from a naphtha containing substantial amounts of aromatic and straight-chain paraffin hydrocarbons which comprises treating said naphtha in an alkylation zone in the presence of olefins having 2 to 4 carbon atoms per molecule with a catalyst under conditions effective to cause alkylation of the aromatic hydrocarbons in said naphtha by said olefins, fractionally distilling the products from said alkylation zone to produce therefrom a hydrocarbon mixture containing straight-chain paraffin hydrocarbons but not more than 2 per cent by volume of aromatic hydrocarbons, and subjecting said hydrocarbon mixture to the action of an aluminum halide catalyst and an activator affording a hydrogen halide under conditions effective to convert straight-chain paraffin hydrocarbons to branched-chain paraffin hydrocarbons.

10. The process of preparing a motor fuel fraction containing a large proportion of branched-chain paraffin hydrocarbons from a naphtha containing substantial amounts of aromatic and straight-chain paraffin hydrocarbons which comprises treating said naphtha in an alkylation zone in the presence of olefins having 2 to 4 carbon atoms per molecule with a catalyst comprising an aluminum halide-hydrocarbon complex under conditions effective to cause alkylation of the aromatic hydrocarbons in said naphtha by said olefins, fractionally distilling the products from said alkylation zone to produce therefrom a hydrocarbon mixture containing straight-chain paraffin hydrocarbons but not more than 2 per cent by volume of aromatic hydrocarbons, subjecting said hydrocarbon mixture to the action of an aluminum halide catalyst and an activator affording a hydrogen halide in an isomerization zone under conditions effective to convert straight-chain paraffin hydrocarbons to branched-chain paraffin hydrocarbons, separting an isomerized hydrocarbon fraction and a catalyst-containing portion comprising an aluminum halide-hydrocarbon complex from the products from said isomerization zone, and introducing at least a portion of said catalyst-containing portion into said alkylation zone.

11. The process of obtaining a solvent naphtha rich in aromatic hydrocarbons and a motor fuel rich in branched-chain paraffin hydrocarbons from a naphtha feed stock containing substantial amounts of aromatic, naphthenic and straight-chain paraffin hydrocarbons which comprises treating said feed stock in a catalytic aromatization step to convert the naphthenic hydrocarbons therein to aromatic hydrocarbons, treating the material from said aromatization step to produce therefrom a fraction rich in aromatic hydrocarbons and a fraction rich in straight-chain paraffin hydrocarbons but containing not more than 2 per cent by volume of aromatic hydrocarbons, and subjecting said fraction rich in straight-chain paraffin hydrocarbons to the action of an aluminum halide catalyst and an activator affording a hydrogen halide under conditions effective to convert straight-chain paraffin hydrocarbons to branched-chain paraffin hydrocarbons.

12. The process of obtaining a solvent naphtha rich in aromatic hydrocarbons and a motor fuel rich in branched-chain paraffin hydrocarbons from a naphtha feed stock containing substantial amounts of aromatic, naphthenic and straight-chain paraffin hydrocarbons which comprises treating said feed stock in a catalytic aromatization step in the presence of hydrogen to convert the naphthenic hydrocarbons therein to aromatic hydrocarbons, contacting the product from said aromatization step with an aluminum halide-hydrocarbon complex to form an extract layer comprising principally aromatic hydrocarbons and aluminum halide-hydrocarbon complex and a raffinate layer rich in straight-chain paraffin hydrocarbons and containing not more than about 2 per cent by volume of aromatic hydrocarbons, heating said extract layer to a temperature sufficient to distill the aromatic hydrocarbons therefrom, and subjecting said raffinate layer to the action of an aluminum halide catalyst and an activator affording a hydrogen halide under conditions effective to convert straight-chain paraffin hydrocarbons to branched-chain paraffin hydrocarbons.

13. The process of claim 12 wherein said aluminum halide catalyst is aluminum chloride and said activator is hydrogen chloride.

14. The process of obtaining a solvent naphtha rich in aromatic hydrocarbons and a motor fuel rich in branched-chain paraffin hydrocarbons from a naphtha feed stock containing substantial amounts of aromatic, naphthenic and straight-chain paraffin hydrocarbons which comprises treating said feed stock in a catalytic aromatization step in the presence of hydrogen at a temperature of about 500° F. to about 1000° F. and

under a hydrogen pressure of about 0.2 to about 10 atmospheres to convert the naphthenic hydrocarbons therein to aromatic hydrocarbons, removing hydrogen from the products from said aromatization step, contacting the substantially hydrogen-free product from said aromatization step with a selective solvent to form an extract layer comprising principally aromatic hydrocarbons and solvent and a raffinate layer rich in straight-chain paraffin hydrocarbons and containing not more than about 2 per cent by volume of aromatic hydrocarbons, heating said extract layer to a temperature sufficient to distill the aromatic hydrocarbons therefrom, removing the solvent from said raffinate layer, subjecting the raffinate in an isomerization step to the action of an aluminum halide catalyst and an activator affording a hydrogen halide in the presence of hydrogen under conditions effective to convert straight-chain paraffin hydrocarbons to branched-chain hydrocarbons, separating a motor fuel fraction and a fraction containing hydrogen and normally gaseous hydrocarbons from the products from said isomerization step, and recycling at least a portion of said last-mentioned fraction to said isomerization step.

15. The process of obtaining a solvent naphtha rich in aromatic hydrocarbons and a motor fuel rich in branched-chain paraffin hydrocarbons from a naphtha feed stock containing substantial amounts of aromatic, naphthenic and straight-chain paraffin hydrocarbons which comprises treating said feed stock in a catalytic aromatization step in the presence of hydrogen at a temperature of about 500° F. to about 1000° F. and under a hydrogen pressure of about 0.2 to about 10 atmospheres to convert the naphthenic hydrocarbons therein to aromatic hydrocarbons, removing hydrogen from the products from said aromatization step, contacting the substantially hydrogen-free product from said aromatization step at a temperature of about 40° F. to about 120° F. with an aluminum chloride-hydrocarbon complex in an extraction step to form an extract layer comprising principally aromatic hydrocarbons and aluminum chloride-hydrocarbon complex and a raffinate layer rich in straight-chain paraffin hydrocarbons and containing not more than about 2 per cent by volume of aromatic hydrocarbons, heating said extract layer to distill aromatic hydrocarbons therefrom, subjecting said raffinate layer in an isomerization step to the action of aluminum chloride and hydrogen chloride in the presence of hydrogen at a temperature of about 180° F. to about 450° F. and a pressure of about 800 to about 4000 pounds per square inch to form branched-chain paraffin hydrocarbons and an aluminum chloride-hydrocarbon complex, and using at least a portion of said aluminum chloride-hydrocarbon complex as solvent for aromatic hydrocarbons in said extraction step.

16. The process of claim 15 including the steps of separating a fraction comprising propane and butane from the products from said isomerization step and recycling said fraction to said isomerization step.

17. The process of claim 15 including the step of introducing at least a portion of the hydrogen removed from the products from said aromatization step into said isomerization step.

18. The process of claim 1 which includes subjecting said hydrocarbon mixture to the action of the aluminum halide catalyst and the activator at a temperature of about 180 to 450° F. and in the presence of hydrogen at a pressure of about 500 to 4000 pounds per square inch.

19. The process of claim 1 which includes subjecting said hydrocarbon mixture to the action of the aluminum halide catalyst and the activator at a temperature of about 210 to 250° F. and in the presence of hydrogen at a pressure of about 500 to 4000 pounds per square inch.

20. The process of preparing a motor fuel fraction containing a large proportion of branched chain paraffin hydrocarbons from a naphtha containing substantial amounts of aromatic and straight chain paraffin hydrocarbons which comprises removing aromatic hydrocarbons from said naphtha to produce therefrom a hydrocarbon mixture containing straight chain paraffin hydrocarbons with not more than 2% by volume of aromatic hydrocarbons and subjecting said hydrocarbon mixture to the action of an aluminum halide catalyst and an activator affording hydrogen halide at a temperature of about 210 to 250° F. and in the presence of hydrogen at a pressure of about 500 to 4000 pounds per square inch to convert straight chain paraffin hydrocarbons to branched chain paraffin hydrocarbons.

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