

# UNITED STATES PATENT OFFICE

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## ISOMERIZATION OF PARAFFINIC HYDROCARBONS

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This invention relates to the conversion of hydrocarbons and has to do with the isomerization of hydrocarbons to form branched chain hydrocarbons. It is applicable particularly with respect to the isomerization of saturated gasoline hydrocarbons.

Broadly, the invention contemplates effecting the reaction by subjecting the feed hydrocarbon to contact with an isomerizing catalyst in the presence of an alicyclic hydrocarbon in amount sufficient to substantially inhibit cracking of the feed hydrocarbon and deterioration of the catalyst.

One problem involved in isomerizing hydrocarbons to a relatively high yield of branched chain hydrocarbons by conversion at relatively higher temperatures is that of avoiding the occurrence of substantial cracking, and other undesirable side reactions, with formation of hydrocarbons both of lower and of higher molecular weight than the feed hydrocarbon undergoing conversion. Such cracking may also involve the formation of unsaturated hydrocarbons which readily react with the catalyst to form undesirable complex compounds.

We have discovered that by effecting the isomerizing reaction in the presence of a naphthene hydrocarbon such as the cyclopentanes and cyclohexanes, it is possible to carry out the reaction at relatively higher temperatures than heretofore so as to obtain relatively higher conversion to branched chain hydrocarbons without substantial occurrence of cracking or other side reactions.

In accordance with this invention, normal paraffin gasoline hydrocarbons, such as butane, pentane, hexane and heptane, etc., are subjected to contact with an active metallic halide catalyst, such as aluminum chloride, in a reaction zone or zones maintained under isomerizing conditions and the reaction is effected in the presence of at least a substantial proportion of a saturated alicyclic hydrocarbon having, for example, about 3 to 20 carbon atoms per molecule, such as cyclohexane, methylcyclohexane, dimethylcyclopentane, decahydronaphthalene, etc. If desired, a mixture of alicyclic hydrocarbons may be employed such as a naphthenic fraction segregated from naphtha derived from a coastal or naphthene base crude, or such as obtained in the re-

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fining of naphthene base petroleum or fractions thereof.

The feed hydrocarbon may comprise an isoparaffin such as 2-methylpentane, for example, where it is desired to convert the hydrocarbon to a more highly branched form such as 2,2-dimethylbutane (neohexane).

It is also contemplated that the invention may be employed to treat straight run gasoline rich in aliphatic hydrocarbons for the purpose of improving its antiknock qualities. In such case the paraffinic gasoline is advantageously blended with a suitable proportion of naphtha or fraction relatively rich in naphthenic hydrocarbons. The resulting blend is then subjected to contact with an isomerization catalyst maintained under isomerizing conditions whereby substantial conversion of the paraffinic gasoline hydrocarbons to branched chain hydrocarbons is secured without the occurrence of substantial cracking and formation of undesirable products.

In applying the invention to the treatment of individual hydrocarbons, such as butane, pentanes, hexanes and heptanes or gasoline fractions of relatively narrow boiling range, it is advantageous to effect the isomerization reaction in the presence of a naphthene hydrocarbon of substantially different boiling temperature range, namely, in the presence of a naphthene hydrocarbon boiling either below or above the feed hydrocarbon or hydrocarbon mixture undergoing conversion. This facilitates separating the naphthene hydrocarbon from the reaction product by fractionation so that the naphthene hydrocarbon can be recycled to the reaction.

An advantageous modification of the invention involves carrying out the reaction in a fluid type of operation wherein a substantial body of fluid containing the catalyst dissolved or suspended therein is maintained in a reaction zone with provision for continuous withdrawal of a stream of the reaction mixture and continuous recycling of the withdrawn stream to the reaction zone. Sufficient of the liquid mixture is recycled to impart thorough agitation to the reaction mixture within the reaction zone and also to permit maintaining a relatively high ratio of naphthene hydrocarbon to entering feed hydrocarbon. In this way the ratio of naphthene hydrocarbon to feed hydrocarbon at the point of introduction of the

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fresh feed to the reaction zone may range from 1 to as high as 1000 or more by volume.

As a further means of insuring a high ratio of naphthene to paraffin, the entering fresh feed advantageously contains naphthene hydrocarbon ranging from about 1 to 90% by volume of the paraffin feed hydrocarbon.

Also, it is of advantage to introduce the paraffin feed in the form of a large number of separate streams simultaneously to the mass of reaction mixture in such a way as to distribute them uniformly within and throughout the depth and cross section of the fluid mass within the reaction zone.

As an example of catalyst mixture, finely divided aluminum chloride dissolved or suspended in aluminum chloride-hydrocarbon complex may be mentioned.

The reaction vessel or vessels may be of any suitable design and may, for example, comprise vessels having provision for internal circulation of the reaction mixture such as to realize the desired conditions of high turbulence and high ratio of naphthene hydrocarbon to feed hydrocarbon undergoing conversion. These and other modifications will be apparent upon reference to the further description of the invention.

The accompanying drawing comprises a flow diagram illustrating one method of carrying out the reaction. Thus, referring to the drawing a feed hydrocarbon, such as n-pentane, is continuously drawn from a source not shown and passed through a heater 1 wherein it is heated to a temperature in the range about 160 to 300° F. or higher. The heated hydrocarbon is then conducted through a pipe 2 to a reactor 3. Likewise a naphthene hydrocarbon, such as cyclohexane, is withdrawn from a source not shown and introduced to the heater 1.

The reactor 3 comprises a vessel which may be provided with internal mechanical mixing means and is of sufficient capacity to hold a substantial body of reaction mixture.

The reaction vessel is maintained substantially filled with hydrocarbons including the catalyst, which latter may comprise anhydrous aluminum chloride, for example. Provision is made for the contiguous or intermittent introduction of make-up catalyst through an inlet 4.

A suitable promoter such as hydrogen chloride is also introduced to the reaction from a source not shown through a pipe 5.

A stream of reaction mixture is continuously drawn off from the reactor through a pipe 6 to a settling vessel 7 wherein a layer of catalyst mixture collects and is continuously withdrawn therefrom through a pipe 8. Advantageously an additional quantity of reaction mixture is continuously drawn off and recycled through pipe 6a to the reaction vessel 3.

The upper layer accumulating in the settling vessel 7 comprises reacted and unreacted hydrocarbons and cyclohexane. This mixture is drawn off through a pipe 9 to a fractionator 10 wherein the cyclohexane and unreacted normal pentane is separated as a liquid fraction drawn off from the bottom of the fractionator 10 through a pipe 11. Instead of recycling this residual fraction, an intermediate fraction comprising naphthene hydrocarbon may be drawn off as a sidestream from fractionator 10 through pipe 11a and be recycled to the reaction, while the heavier material is discharged from the system.

Means, not shown, may be provided intermediate the settler 7 and the fractionator 10 for

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withdrawing aluminum chloride and promoter.

The isopentane and any lighter hydrocarbon material including promoter is drawn off from the top of the fractionator 10 and conducted to a fractionator 12 wherein the gaseous material is removed as a vapor fraction and discharged through pipe 13. A liquid fraction is drawn off from the bottom of the fractionator 12 through a pipe 14 and will comprise essentially isopentane.

The promoter discharged through the pipe 13 is advantageously recycled to the reaction vessel. Suitable provision, not shown, may be made for discharging from the system light gases or other materials tending to accumulate therein. For example, it is advantageous to separate a butane fraction from the light material accumulating from the reaction, either consisting essentially of isobutane or consisting of a mixture of iso- and normal butane, and recycle this butane fraction, all or in part, through the isomerization reaction.

Likewise any hydrogen formed in the reaction may be recycled, all or in part, to the isomerization reaction.

As indicated in the drawing the liquid fraction drawn off from the fractionator 10 through the pipe 11 and comprising cyclohexane and unreacted pentane is continuously recycled by a pump 15 to the reaction vessel 3. In addition, all or a portion of the catalyst mixture drawn off from settler 7 through the pipe 8 is recycled by a pump 16 to the reaction vessel 3.

If desired the hydrocarbons recycled through pipes 11 or 11a may be subjected to a separate treatment to concentrate the naphthenes and eliminate non-naphthenic hydrocarbons from the mixture prior to return to the reactor 3.

During the operation, the naphthene may undergo isomerization, for example, cyclohexane will be converted to methyl cyclopentane. Therefore in continuous operation with recycle of the naphthenes an equilibrium mixture of the naphthenes will ultimately result and hence an equilibrium mixture would ordinarily be recycled.

As already explained it is advantageous to adjust the operation so that the amount of recycled hydrocarbon and particularly the recycled naphthene hydrocarbon is relatively large as compared with the amount of entering feed hydrocarbon, thereby maintaining turbulent conditions within the reactor 3 and likewise maintaining a high ratio of naphthene to feed hydrocarbon undergoing treatment.

While a single reaction vessel 3 is shown in the drawing, it is contemplated that a plurality of reaction vessels may be employed or a plurality of reaction and settling stages. In such case the feed hydrocarbon may flow through each stage in succession or portions of the feed may be separately introduced to succeeding stages in the system. Likewise provision may be made for continuous concurrent or countercurrent flow of feed hydrocarbon and catalyst mixture.

It is understood, of course, that the arrangement of fractionators illustrated in the drawing may be altered depending upon the particular hydrocarbons undergoing treatment and upon the type of fractionation required. For example, when isomerizing a relatively high boiling gasoline hydrocarbon or hydrocarbon mixture in the presence of a relatively lower boiling naphthene hydrocarbon it is necessary to rearrange the fractionators so as to segregate the naphthene hydrocarbon which is more volatile than the resulting isomerization product.

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It is intended also that the reaction may be effected in a reaction zone packed with a solid catalyst in lump or particle form. In such case the surplus naphthene hydrocarbon may be recirculated through a vertical reaction vessel packed with the solid catalyst or a catalyst supported upon a suitable supporting material.

Also, if desired a fluid suspension of powdered aluminum chloride in naphthene hydrocarbon or in aluminum chloride-hydrocarbon complex may be employed with a reaction tower packed with a solid inert packing material such as Raschig rings, through which tower the fluid suspension of catalyst is continuously recycled.

Besides aluminum chloride, other metallic halide catalysts may be used such as aluminum bromide, zirconium chloride, antimony chloride, or mixtures of halides such as  $AlCl_3-SbCl_3$ . The

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sults obtained by isomerizing hydrocarbons such as pentane and hexane by contact with aluminum chloride in the presence of naphthene hydrocarbons such as cyclohexane, methylcyclohexane and dimethylcyclopentane.

A series of batch liquid phase experiments was made for the purpose of isomerizing normal pentane at a temperature of 160° F. with a reaction time of 4 hours. In each case powdered anhydrous aluminum chloride of about 200 mesh was charged to the reaction vessel to the extent of 10% by weight of the feed hydrocarbon, the reaction being promoted by the addition of a small amount of hydrogen chloride. One run was made in the absence of any naphthene, while two runs were made in which a quantity of cyclohexane was added to the reaction mixture as follows.

| Run   | 1                        | 2                       | 3                       |
|---|--------------------------|-------------------------|-------------------------|
| Per cent hydrogen chloride, by weight of feed hydrocarbon                                   | 0.6                      | 0.7                     | 0.5                     |
| Per cent cyclohexane, by weight of feed hydrocarbon   | 0                        | 10                      | 25                      |
| Composition of Hydrocarbon Reaction Mixture by Fractional Distillation, per cent by weight: |                          |                         |                         |
| Hydrocarbons of lower molecular weight than isobutane                                       | 0                        | 0                       | 0                       |
| Isobutane   | 47.4                     | 10                      | 0                       |
| Normal butane   | 2.4                      |                         | 0                       |
| Isopentane  | 25.0                     | 36                      | 16.4                    |
| Normal pentane  | 7.6                      | 45                      | 59.3                    |
| Hydrocarbons of higher molecular weight than normal pentane including naphthene             | 17.6                     | 9                       | 24.3                    |
| Pentane converted to isopentane and other materials, weight per cent                        | 92.6                     | 52.3                    | 23.3                    |
| Pentane converted to isopentane, weight per cent  | 24.3                     | 38.2                    | 21.1                    |
| Weight ratio of isopentane to normal pentane converted                                      | 4.26                     | 78                      | 89                      |
| Appearance of used catalyst   | Red-brown liquid complex | Dry yellow brown powder | Light yellow wet powder |

catalyst may also comprise a solid material impregnated with metallic halide such as Porocel and aluminum chloride, charcoal and aluminum chloride, or alumina and aluminum chloride.

Also other halogen halides besides hydrogen chloride may be used as the promoter. The promoter may be generated in situ if desired.

It is frequently desirable to remove impurities from the feed hydrocarbon prior to contact with the catalyst in order to avoid catalyst deterioration. This may be accomplished by subjecting the feed hydrocarbon to a suitable pretreatment. For example, it may be subjected to treatment with caustic in order to remove sulfur compounds. On the other hand, the pretreatment may in-

Comparing runs 1 and 2 above, it is seen that by effecting the reaction in the presence of cyclohexane a materially higher conversion to isopentane was realized with a greatly reduced amount of cracking, and at the same time the catalyst had apparently suffered no deterioration. The results of run 3 indicate that with a sufficiently large percentage of naphthene present the converted pentane consists almost entirely of the desired isoparaffin.

A similar series of experiments was made in which the reaction was effected at a higher temperature, namely, 200° F., using the same proportion of aluminum chloride to pentane charge and with the following results.

| Run   | 4                    | 5                       | 6                        |
|---|----------------------|-------------------------|--------------------------|
| Per cent hydrogen chloride, by weight of feed hydrocarbon                                   | 0.5                  | 0.6                     | 0.7                      |
| Per cent cyclohexane, by weight of feed hydrocarbon   | 0                    | 10                      | 25                       |
| Composition of Hydrocarbon Reaction Mixture by Fractional Distillation, per cent by weight: |                      |                         |                          |
| Hydrocarbons of lower molecular weight than isobutane                                       | 0.5                  |                         | 0                        |
| Isobutane   | 51.2                 | 1.7                     | 1.6                      |
| Normal butane   | 4.5                  |                         | 0.5                      |
| Isopentane  | 22.7                 | 65.6                    | 55.7                     |
| Normal pentane  | 6.1                  | 28.7                    | 27.8                     |
| Hydrocarbons of higher molecular weight than normal pentane                                 | 15.0                 | 4.0                     | 14.4                     |
| Pentane converted to isopentane and other materials, weight percent                         | 94.2                 | 75.0                    | 69.0                     |
| Pentane converted to isopentane, weight percent   | 21.4                 | 72.2                    | 67.2                     |
| Weight ratio of isopentane to normal pentane converted                                      | 4.23                 | 96                      | 97                       |
| Appearance of used catalyst   | Brown liquid complex | Light brown gummy solid | Light brown sticky solid |

volve contact with weak sulfuric acid, or treatment with a solid adsorbent clay in the vapor phase or in the liquid phase to remove diolefins and also to remove sulfur compounds. Aromatic constituents may be removed from the feed hydrocarbon by treatment with sulfuric acid or with a suitable solvent. For example, the feed hydrocarbon may be subjected to contact with water at elevated temperature and pressure in order to selectively extract aromatic constituents from the feed prior to the isomerization reaction.

The following data illustrate the improved re-

As indicated by the foregoing experiments substantially better conversion yields to isopentane are realized by carrying out the reaction in the presence of the cyclohexane at a temperature of 200° F. Again the results reveal that cracking is substantially eliminated by effecting the reaction in the presence of cyclohexane. So much so that the converted normal pentane is substantially entirely isopentane.

Another series of experiments was made under conditions similar to those in the preceding group, i. e., employing a temperature of 200° F.

with a reaction time of 4 hours, but isomerizing normal pentane in the presence of three different naphthene hydrocarbons, obtaining the following results.

relatively higher temperatures may be employed when effecting the reaction in the presence of a naphthene such as mentioned above, and thereby enabling the obtaining of a high conversion of

| Run   | 7                           | 8                     | 9   |
|---|-----------------------------|-----------------------|---|
| Naphthene used  | Cyclohexane                 | Methylcyclohexane     | Dimethylcyclopentane concentrate <sup>1</sup> |
| Per cent naphthene by weight of feed hydrocarbon  | 10                          | 10                    | 10  |
| Per cent hydrogen chloride by weight of feed hydrocarbon                                    | 1.2                         | 1.0                   | 1.0   |
| Composition of Hydrocarbon-Reaction Mixture by Fractional Distillation, per cent by weight: |                             |                       |   |
| Hydrocarbons of lower molecular weight than isobutane                                       |                             | 0                     | 0.2   |
| Isobutane   | 3.3                         | 1.0                   | 16.8  |
| Normal butane   |                             | 0                     | 0.5   |
| Isopentane  | 70.2                        | 60                    | 55.5  |
| Normal pentane  | 20.7                        | 39                    | 11.3  |
| Hydrocarbons of higher molecular weight than normal pentane                                 | 5.8                         |                       | 15.7  |
| Pentane converted to isopentane and other materials, per cent by weight                     | 78.4                        | 65.0                  | 75.0  |
| Pentane converted to isopentane, weight percent   | 73.2                        | 60.7                  | 57.7  |
| Weight ratio of isopentane to normal pentane converted                                      | .93                         |                       | .77   |
| Appearance of used catalyst   | Brownish yellow gummy solid | Wet brown lumpy solid | Brown semisolid complex                       |

<sup>1</sup> Dimethylcyclopentane concentrate comprising 70% naphthenes.

In the following example a natural gasoline fraction comprising mixed hexanes and boiling in the range 137 to 156° F. was subjected to isomerization in a batch liquid phase operation using aluminum chloride and hydrogen chloride at a temperature of about 200 to 210° F. The aluminum chloride amounted to 10% by weight of the hexane feed, while the hydrogen chloride amounted to 3% by weight of the feed. Run 11 was made in the presence of cyclohexane amounting to 10% by weight of the hexane feed. Run 10 was made in the absence of the naphthene hydrocarbon. The hydrocarbon product obtained in each run was fractionated to produce a C<sub>6</sub> fraction and the two C<sub>6</sub> fractions were tested for antiknock characteristics with the following results:

| Run                              | 10                          | 11                          |
|----------------------------------|-----------------------------|-----------------------------|
| C. F. R. M. Octane Number—       |                             |                             |
| Without tetraethyl lead addition | 80.5                        | 82.2                        |
| With addition of 2 cc. TEL       | 93.4                        | 96.0                        |
| With addition of 4 cc. TEL       | 99.1                        | Isocetane plus 0.2 cc. TEL  |
| With addition of 6 cc. TEL       | Isocetane plus 0.19 cc. TEL | Isocetane plus 0.53 cc. TEL |

Thus, the product obtained in run 11 exhibited a higher clear octane number and a greater lead susceptibility. For example, with the addition of 4 cc. of tetraethyl lead it possessed an octane number equivalent to that of pure iso-octane containing 0.2 cc. of the lead compound, while the product from run 10 with a similar addition of lead compound had an octane number of only 99.1.

The product from run 11 was found to contain approximately 20 to 22% by weight of 2,2-dimethylbutane (mehexane).

In the foregoing experiments a reaction time of 4 hours was used. However, it is contemplated that a reaction time of 1 hour or less may be employed. For example, in continuous operations the reaction time may be about 5 to 15 minutes and as high as 2 hours or more.

The reaction temperature required will depend upon the character of the hydrocarbon feed undergoing treatment. For example, when isomerizing pentane a temperature in the range above 130° F. may be employed; while with hexanes and heptanes the temperature may be somewhat higher, for example, in the range above 160° F.

Generally speaking, it has been found that

paraffin to isoparaffin without substantial cracking.

The products or any portion thereof produced in the above described isomerization reaction may be subjected to further refining or processing as desired. For example, the isomerized hydrocarbons or any portion thereof may be passed to an alkylation reaction. Thus, when pentane is isomerized to produce isopentane the overhead from the fractionator 10 comprising isopentane and promoter may be passed directly to an alkylation unit for the production of safety fuel. The alkylation operation may involve reaction of isopentane with an olefin such as triisobutylene in the presence of an aluminum chloride catalyst. On the other hand, it is contemplated that the entire reaction product from the isomerization operation may be passed directly to an alkylation reaction depending upon the type of final product desired.

The feed to the isomerization reaction may comprise normal paraffin hydrocarbons or a mixture of normal and isoparaffin hydrocarbons, including pentanes, hexanes, heptanes and the like.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. In a process for isomerizing normal pentane, the steps comprising passing normal pentane to a reaction zone containing an aluminum halide isomerization catalyst maintained in the presence of hydrogen chloride at a temperature in the range 160 to 200° F. such that normal pentane is converted in relatively large amount to isopentane, effecting contact between normal pentane and the catalyst in the presence of added cyclohexane amounting to about 10 to 25% by weight of the normal pentane undergoing treatment and sufficient to substantially inhibit cracking of the pentane during contact with the catalyst, and withdrawing from the reaction zone a hydrocarbon mixture comprising isopentane.

2. A continuous method for isomerizing normal paraffin hydrocarbons which are normally free from naphthene hydrocarbons comprising maintaining an isomerization reaction zone containing an aluminum halide isomerization catalyst under isomerizing conditions at an elevated temperature not in excess of about 300° F. such

that the isomerization reaction is normally accompanied by substantial hydrocarbon cracking, continuously passing to said reaction zone feed hydrocarbons consisting essentially of normal paraffins, effecting contact between said normal paraffins and the catalyst in the presence of an amount of added naphthene hydrocarbon relatively small compared to the paraffin hydrocarbons undergoing conversion in the reaction zone, introducing the added naphthene hydrocarbon to the reaction zone in an amount sufficient to inhibit substantially said hydrocarbon cracking but insufficient to prevent isomerization of said normal paraffin hydrocarbons to a substantial extent, effecting substantial isomerization of normal paraffins during passage through the reaction zone, and continuously withdrawing from the reaction zone isomerized paraffin hydrocarbons.

3. The method according to claim 2 in which the added naphthene hydrocarbon is present in the reaction zone to the extent of about 10 to 25% by weight of the reactant hydrocarbon within the reaction zone.

4. The method according to claim 2 in which the added naphthene hydrocarbon is one having from about 3 to 20 carbon atoms per molecule.

5. The method according to claim 2 in which the added naphthene hydrocarbon is cyclohexane.

6. A continuous method for isomerizing normal paraffin hydrocarbons which are normally free from naphthene hydrocarbons comprising maintaining an isomerization reaction zone containing aluminum halide isomerization catalyst under isomerizing conditions at an elevated temperature not in excess of about 300° F. such that the isomerization reaction is normally accompanied by substantial hydrocarbon cracking, continuously passing to said reaction zone a hydrocarbon consisting essentially of normal paraffins, effecting contact between said paraffin hydrocarbons and the catalyst in the presence of an added relatively small amount of naphthene hydrocarbon of substantially different boiling temperature range than the paraffins undergoing conversion, introducing the added naphthene hydrocarbon to the reaction in an amount sufficient to inhibit substantially said hydrocarbon cracking but insufficient to prevent isomerization of said normal paraffin hydrocarbons to a substantial extent, effecting substantial isomerization of the normal paraffins during passage through the reaction zone, continuously withdrawing a stream of hydrocarbon reaction mixture from the reaction zone, subjecting the withdrawn hydrocarbons to fractionation to separate therefrom a fraction comprising isomerized hydrocarbons and a fraction comprising said naphthene hydrocarbons, and continuously recycling said naphthene hydrocarbon fraction to the reaction zone.

7. A process for isomerizing hydrocarbons which comprises passing a natural gasoline fraction boiling in the range about 137 to 156° F. to a reaction zone containing aluminum chloride

maintained in the presence of hydrogen chloride at a temperature of about 200 to 210° F., effecting contact between said gasoline fraction and the aluminum chloride in the presence of added cyclohexane amounting to about 10% by weight of said gasoline fraction such that cracking of the gasoline fraction is substantially inhibited and such that the new product comprises a substantial amount of 2,2-dimethylbutane, and withdrawing from the reaction zone a hydrocarbon mixture comprising isomerized hydrocarbons including said 2,2-dimethylbutane.

8. In the process for the isomerization of an isomerizable normal paraffin having from 5 to 6 carbon atoms with an aluminum halide catalyst at an elevated temperature below about 266° F. at which degradation would normally take place, the improvement which comprises recycling through the isomerizing zone a mixture of inter-isomerizable pentamethylene and hexamethylene cycloparaffin hydrocarbons in an amount sufficient to inhibit substantially said degradation, whereby selective isomerization of the normal paraffin hydrocarbon is effected.

9. In the process for the isomerization of an isomerizable normal paraffin hydrocarbon having from 5 to 6 carbon atoms with an aluminum halide catalyst at an elevated temperature below about 266° F. at which degradation would normally take place, the improvement which comprises adding to the hydrocarbon to be isomerized a cycloparaffin hydrocarbon chosen from the group consisting of cyclopentane, cyclohexane, and their methylated derivatives, in an amount sufficient to inhibit substantially said degradation, whereby isomerization of the normal paraffin hydrocarbon is effected without substantial degradation.

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#### REFERENCES CITED

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

#### UNITED STATES PATENTS

| Number    | Name                | Date          |
|-----------|---------------------|---------------|
| 2,220,092 | Evering et al. .... | Nov. 5, 1940  |
| 2,249,337 | Visser et al. ....  | July 15, 1941 |
| 2,250,410 | van Peski .....     | July 22, 1941 |
| 2,280,710 | Lynch .....         | Apr. 21, 1942 |
| 2,288,866 | Hoog .....          | July 7, 1942  |
| 2,299,716 | van Peski .....     | Oct. 20, 1942 |
| 2,300,249 | Evering et al. .... | Oct. 27, 1942 |
| 2,303,083 | Kuhl .....          | Nov. 24, 1942 |
| 2,308,792 | Thomas .....        | Jan. 19, 1943 |
| 2,313,054 | de Simo et al. .... | Mar. 9, 1943  |

#### OTHER REFERENCES

Ind. & Eng. Chemistry, July 1932, pages 814 to 818.  
Nat. Pet. News, Feb. 12, 1936, page 36.

