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**PROCESS FOR PRODUCING HIGHLY BLANCHED PARAFFIN HYDROCARBONS  
FROM NAPHTHENIC HYDROCARBONS**

It is known that straight chain paraffinic hydrocarbons, preferably those with 4 to 6 carbon atoms, can be isomerized to branched paraffinic hydrocarbons under elevated pressure in the presence of hydrogen by means of aluminum halides as catalyst. In this manner n-butane may be converted into i-butane, or n-pentane into i-pentane, for example. It has also been proposed to use substantial amounts of gaseous paraffinic hydrocarbons, in addition, preferably propane or butane, in the above processes.

The straight chain initial product required may be obtained, for example, by fractionation from paraffin base petroleum oils or from hydrocarbon mixtures that have been produced by catalytic hydrogenation of carbon monoxide at ordinary or slightly increased pressure. These two raw materials consist exclusively of aliphatic hydrocarbons.

Many hydrocarbon oils, such as fractions of naphthenic base petroleum oils or coal tar oils, or high pressure hydrogenation products of lignite or coal, etc. are mixtures of paraffinic hydrocarbons with more or less significant quantities of naphthenic constituents. Thus, for example, n-hexane obtained from such products contains comparatively large amounts of methylcyclopentane, or n-heptane may contain a considerable proportion of methylcyclohexane, etc. A fractionation of such mixtures into paraffinic and naphthenic constituents by rectification is not directly possible because the boiling points of the two types of hydrocarbons having the same number of carbon atoms differ very little, mostly only 2-3° from each other.

Naphthenic hydrocarbons, in contrast to paraffinic hydrocarbons, have heretofore not been possible to use for producing highly branched paraffinic hydrocarbons, that is, such having several tertiary or one quaternary carbon atoms; in fact, they are troublesome in conversions in the presence of aluminum chloride by the known processes when admixed with paraffinic hydrocarbons because they are inclined to form liquid addition compounds with  $AlCl_3$  and consequently give rise to a high consumption of catalyst. Heretofore, naphthenic hydrocarbons have only been possible to use for the production of branched paraffinic hydrocarbons by treating them with hydrogen at temperatures in excess of  $400^\circ C$  and under pressures of 200 atm., and more, in the presence of highly active hydrogenation catalysts. In this process, however, a large quantity of the initial product is cracked to low boiling and gaseous hydrocarbons. In the reaction products of this process comparatively small quantities of branched paraffinic hydrocarbons are encountered and, moreover, they consist pre dominantly of hydrocarbons with only one tertiary carbon atom, while hydrocarbons with several tertiary or one quaternary carbon atoms are practically not formed. The properties of aviation fuels, as required at present, depend on the presence of highly branched hydrocarbons.

It has now been found that highly branched paraffinic hydrocarbons can also be produced without formation of gas from naphthenic hydrocarbons or from hydrocarbon mixtures containing substantial amounts thereof when they are treated at temperatures below  $150^\circ C$ , preferably between 50 and  $100^\circ$ , in the presence of hydrogen under a pressure in excess of 10 atm., preferably between 30 and 200 atm., using aluminum halide as catalyst. The naphthenes in that case may be individual products or mixtures of several products. In contrast to the prior method of operation at higher temperatures there is hardly any cracking to compounds having a lower number of carbon atoms, and paraffinic hydrocarbons are almost exclusively produced which have the same number of carbon atoms as the initial naphthenic material.

The resulting paraffinic hydrocarbons consist to a large extent of hydrocarbons with several tertiary or one quaternary carbon atom that is, of such which possess particularly favorable automotive properties. Addition of propane is not necessary in this case.

The consumption of catalyst is low, although cycloparaffins, as stated above, are inclined to form liquid addition compounds with the aluminum halide, resulting in a rapid decline of the activity of the catalyst under the previously adopted conditions. The consumption of catalyst can be still more reduced by adding metals or metallic oxides or halides of metals of the 6th or 8th group, those of the second column of the first group of the periodic system, or halides of arsenic or antimony. Such additions repress the tendency of the aluminum halides to form liquid addition compounds and the catalyst can be recovered in a practically unchanged form after the conversion. The preparation of such a catalyst is preferably accomplished by mixing the two constituents in a finely ground state. To increase the activity it is of advantage to heat or to fuse this mixture close to the point of sublimation of the aluminum halides.

The catalyst can be arranged in lump form in the reaction chamber or be introduced in a finely divided form as a suspension into the reaction chamber together with the hydrocarbons to be converted, in liquid or vapor phase. It is preferable to use the catalyst in an amount of at least 10% by wt., referred to the reaction product contained in the reaction chamber. A substantial increase in the activity of the catalyst is obtained by an addition of hydrogen chloride. It is of advantage to use an amount of at least 10% by wt. of HCl, referred to the reaction product contained in the reaction chamber. On the other hand, traces of moisture must be very carefully avoided inasmuch as they cause a reduction in the conversion and increase the consumption of catalyst.

### Example

400 parts by wt. of cyclohexane are mixed with 60 parts by wt. of aluminum chloride and 30 parts by wt. of liquid dry hydrogen chloride and heated in the presence of hydrogen in an iron autoclave during 6 hrs., with agitation, to 100°C under a pressure of 150 atm. The resulting product contains 1% of iso-butane, 20% of 2,2-dimethylbutane (neohexane), 6% of 2,3-dimethylbutane and 18% of 2- and 3-methylpentane together with a small quantity of n-hexane. The remainder consists of unconverted cyclohexane and small quantities of methylcyclopentane. The catalyst can be recovered in an unchanged condition.

### Claim

Process for producing highly branched paraffinic hydrocarbons from naphthenic hydrocarbons or from hydrocarbon mixtures containing substantial amounts of naphthenic hydrocarbons, characterized in that these initial materials are treated with aluminum halide as catalyst at temperatures below 130°C, preferably at 50-100°, in the presence of hydrogen and, preferably, hydrogen chloride under a pressure in excess of 10 atm., preferably between 30 and 200 atm.