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PROCESS FOR ISOMERIZING NORMAL PARAFFINS

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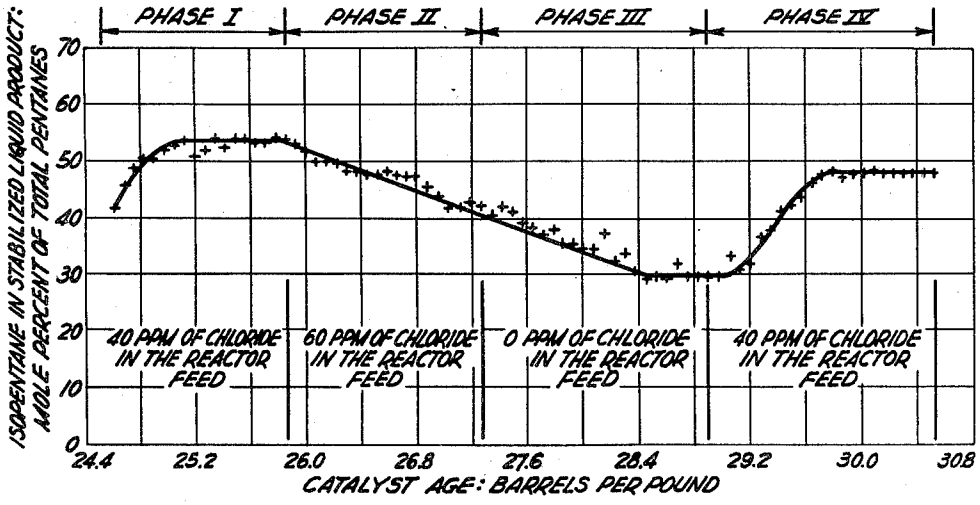


Fig. 1

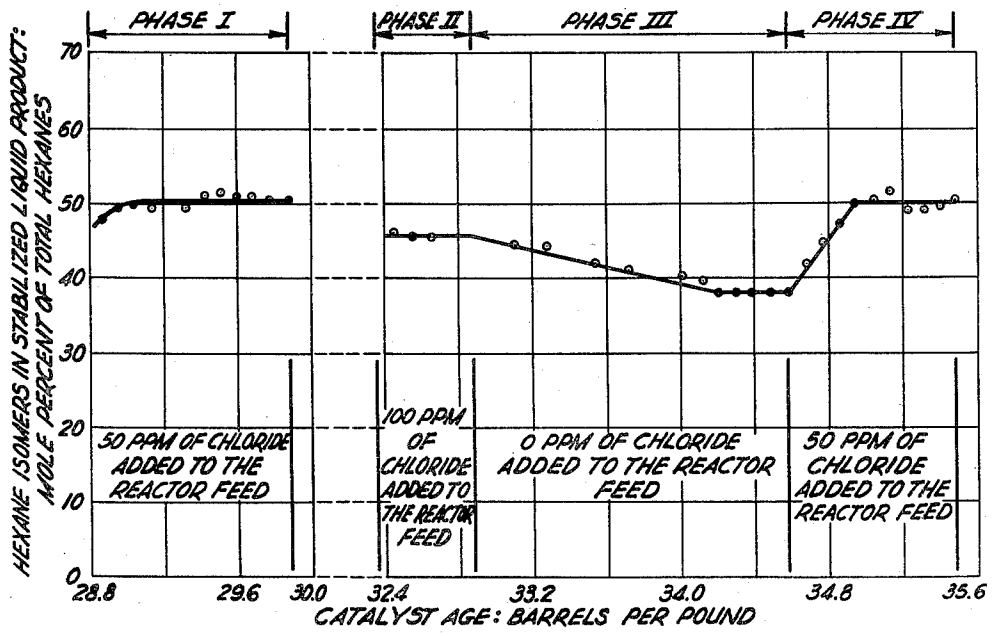


Fig. 2

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PROCESS FOR ISOMERIZING NORMAL PARAFFINS

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This invention relates to a process for hydroisomerizing light straight chain paraffins in the presence of a supported platinum catalyst while adding halogen to the reaction zone. More particularly, it relates to such a hydroisomerization process in which the activity of the catalyst is restored after a decline in activity owing to excessive halogen addition.

The conversion of light straight chain paraffins to their branched chain isomers has great commercial advantage in the petroleum and chemical industries. It is important in petroleum refining, because the branched chain paraffins of the gasoline boiling range have higher octane ratings than their straight chain isomers. The branched chain isomers are also valuable as chemical intermediates. For example, isobutane is used in the alkylation process to produce branched heptanes and octanes, and isopentane is used in the production of isoprene.

A recently developed process for isomerizing low molecular weight normal paraffins is based on the discovery that the space-time-yield of branched chain isomers is remarkably high when the light normal paraffin is contacted with a platinum-alumina catalyst at an elevated temperature and pressure, at a high space velocity of above 5 liquid volumes of hydrocarbon per volume of catalyst per hour and a low concentration of hydrogen such that the mol fraction of hydrocarbon in the hydrocarbon-hydrogen feed mixture is above 0.5, and above 0.75 for superior space-time-yields, but below the hydrocarbon concentration of about 0.9 to 0.95 mol fraction which causes rapid deactivation of the catalyst. We use the term "space-time-yield of branched chain isomer" in its usual sense as meaning the volume of isoparaffin produced per hour per volume of catalyst. This is an important characteristic of the process commercially because it indicates the amount of the desired product that can be produced in a reactor of a given size in a particular period of time. The process is also characterized by high efficiency in terms of the ratio of isoparaffin yield to total yield of conversion product.

An improvement in the new hydroisomerization process comprises adding halogen to the reaction zone. For example, an alkyl chloride is added intermittently or continuously with the hydrocarbon feed or with the hydrogen or is otherwise introduced into the reaction zone during the catalytic contact. The result is that the yield of branched chain isomers is considerably increased in comparison with the yield obtained under similar conversion conditions in the absence of added halogen or the same yield is obtained under less severe reaction conditions.

The procedure of adding halogen to the hydroisomerization reaction zone is particularly advantageous in the new process of hydroisomerizing light straight chain paraffins with a high space velocity and low hydrogen concentration over a supported platinum catalyst, provided that the concentration of halogen in the reaction zone does not exceed a certain maximum, the exact value of which differs for different charge stocks, reaction conditions and catalysts. If this maximum halogen concentration is exceeded the addition of halogen not only does not produce an advantage but is deleterious in that the catalyst activity declines rapidly. Although an excessive concentration can be avoided by careful control of the rate of halogen addition, it is quite possible in plant operations that through inadvertence or miscalculation the rate of halogen addition will become too great or that by a cumulative effect the halogen concentration in the reaction zone will become excessive and the catalyst activity will decline. The present invention provides a method for restoring the catalyst activity without the necessity of oxidative regeneration of the catalyst or of shutting down the hydroisomerization process and replacing the deactivated catalyst.

The process of the invention in general comprises contacting with a platinum-alumina catalyst in a reaction zone a C_4 to C_6 aliphatic paraffin charge stock in admixture with hydrogen under hydroisomerization conditions, including a hydrogen concentration such that the mol fraction of hydrocarbon is greater than 0.5 but less than the mol fraction hydrocarbon corresponding to rapid catalyst aging, a charge liquid hourly space velocity of at least 5 volumes of hydrocarbon per volume of catalyst per hour, a temperature from 600 to 1000° F., and a pressure from 20 to 2000 p.s.i.g., while adding to the reaction zone in the vapor phase a material selected from the group consisting of halogens and halogen compounds that are volatile and decomposable under the process conditions and recovering from the reaction zone an effluent stream enriched in branched chain paraffins. This procedure is continued until the catalyst activity, as indicated by the degree of conversion of the feed stock declines rapidly. Thereafter, the introduction of halogen to the reaction zone is discontinued and a feed stock substantially free of halogen is charged until the rate of conversion reaches a substantially constant lower level. Thereafter, the introduction of halogen to the reaction zone is resumed.

In preferred embodiments of our process, after a decline in activity caused by excessive halogen concentration in the reaction zone, the feed stock substantially free of halogen is charged to the reaction zone until the rate of conversion reaches a substantially constant low level and for a throughput of at least one barrel of hydrocarbon per pound of catalyst. Thereafter, the introduction of halogen to the reaction zone is resumed at a rate no greater than the rate of addition of halogen during the previous period of halogen addition.

Our process will be described in more detail by referring to the drawings of which:

Figure 1 is a plot of isopentane content of the liquid product against catalyst age during hydroisomerization of an n-pentane fraction while adding t-butyl chloride to the reactor feed; and

Figure 2 is a similar plot for the hydroisomerization of a refinery n-hexane fraction.

We have indicated that the hydrogen concentration in the feed to our process is maintained at a low level so as to favor high conversion of the straight chain paraffins to their branched chain isomers. Thus, as compared with reforming processes which treat naphthenic fractions principally to accomplish aromatization and hydrocracking and which normally employ hydrogen concentrations from 5,000 to 20,000 standard cubic feet of hydrogen per barrel of hydrocarbon (corresponding to about 0.15 to 0.04 mol fraction of hydrocarbon) our process uses hydrocarbon-hydrogen ratios from about 0.5 to 0.9 or 0.95 mol fraction of hydrocarbon in the charge.

The hydrogen employed in our process need not be pure hydrogen. A hydrogen stream which we have found produces excellent results consists essentially of about 80 to 90 mol percent hydrogen and 10 to 20 mol percent C_1 to C_4 hydrocarbons.

As we have also indicated, we obtain high space-time yields of branched chain paraffins by combining the use of a high space velocity with the use of low hydrogen concentrations and a platinum catalyst. By high velocity we means liquid hourly space velocities that are conventionally not considered practicable for satisfactory conversion in naphtha reforming processes, and more particularly, we means space velocities above 5 liquid volumes of hydrocarbon per volume of catalyst per hour. Preferably, our process uses space velocities above 8 vol./vol./hr. and we can use considerably higher space velocities, for example, as high as 25 vol./vol./hr. or higher and still obtain good conversions.

The catalyst for our process is composed of platinum supported on alumina. The platinum content of the catalyst is from 0.1 to 5.0 percent by weight and preferably is from 0.2 to 1.0 percent by weight. The catalyst preferably contains minor amounts, for example, from 0.1 to 10 percent by weight of chlorine and/or fluorine and/or other activating components. The catalyst can be in the form of irregular granules or of particles of uniform size and shape prepared by pilling, extrusion or other suitable methods. Particularly suitable catalyst compositions are described hereinafter in the working examples.

The high space-time yield of isoparaffin that characteristizes the hydroisomerization process carried out at high space velocity and low hydrogen concentration can be obtained at moderate reaction temperatures. Our process operates in the temperature range from 600° F. to 1000° F. The best yields, however, are obtained in the range from 650° F. to 900° F. The reaction temperature for any particular run will be selected according to the activity of the catalyst and the total conversion and conversion to isopentane desired. Normally, the temperature will be periodically raised in small increments, for instance, 5° F. to 25° F., as the catalyst activity gradually declines. The reaction pressure can range from 20 to 2000 pounds per square inch gauge (abbreviated hereinafter as p.s.i.g.), but best results are obtained at a pressure from 300 to 600 p.s.i.g.

We have indicated that the process of our invention applies to the type of hydroisomerization process in which a source of halogen is added in the vapor phase to the reaction zone. The halogen may be added as free halogen or as a halogen compound that vaporizes and decomposes under the reaction conditions to yield free halogen or hydrogen halide. We prefer chlorine compounds, for example, hydrogen chloride or an organic chlorine compound, preferably an alkyl chloride such as t-butyl chloride, propylene dichloride, etc. Although not necessarily equivalents, other halogens or halogen compounds can produce comparable effects in our process. Thus, alkyl bromides, fluorides and iodides can be used in lieu of the chlorides. A very small concentration of halogen in the reaction zone is used. Normally, a halogen concentration of 10 to 50 parts by weight of elemental halogen per million parts of hydrocarbon will produce the

desired activity. However, under certain conditions, e.g., low temperature, or with a catalyst of low activity, a higher concentration of halogen may be satisfactory. One suitable method of introducing the halogen is by adding to the liquid paraffinic feed a dilute solution of the halogen compound in a concentration sufficient to give the desired concentration of elemental halogen. Alternatively, a gaseous halogen compound can be added to the hydrogen stream or otherwise introduced into the reaction zone.

Our process is concerned with isomerizing the low octane number aliphatic paraffins having from 4 to 6 hydrocarbon atoms in the molecule to their isomers of higher octane rating. This involves isomerizing n-butane, n-pentane and low octane number hexanes to their branched chain isomers. By "low octane number hexanes" we mean n-hexane and the slightly branched hexanes; 2-methylpentane and 3-methylpentane. The hydroisomerization charge stocks for which the halogen addition technique is advantageous are low in naphthene and aromatics content. At least 90 volume percent of the hydrocarbon fraction consists of aliphatic paraffins. A small concentration of naphthenes or aromatics having boiling points close to those of the isomerizable straight chain paraffins can be tolerated but a large concentration of cyclic hydrocarbons is deleterious and makes it impossible to obtain the full benefits of the addition of halogen to the hydroisomerization. More specifically, large concentrations of cyclic hydrocarbons in the charge appear to cause catalyst deactivation and to inhibit isomerization of the normal paraffins.

The hydrocarbon charge stock for our process can be a substantially pure fraction of n-butane, n-pentane, n-hexane or a refinery fraction predominating in one or more of these n-paraffins. Most suitably, the charge stock is a refinery fraction that consists largely of one or more of the mentioned n-paraffins plus minor amounts of other hydrocarbons of similar boiling range that would normally be present in light straight run petroleum fractions or in n-butane, n-pentane, or n-hexane fractions recovered from the product of a conversion process such as catalytic reforming. For all of the possible charge stocks the essential feature is that the charge is at least 90 volume percent low octane number aliphatic paraffins of no more than 6 carbon atoms and thus has a low or negligible content of cyclic hydrocarbons.

We have observed that an excessive concentration of halogen in the reaction zone, instead of increasing catalyst activity, has the opposite effect. That is, it causes the catalyst activity to decline markedly. We have discovered, however, that the decline in activity is temporary and can be reversed by the procedure of our invention without the necessity of regenerating the catalyst and without shutting down the reactor. In accordance with the invention, when the catalyst activity rapidly declines, indicating "over haliding" or, in other words, an excessive concentration of halogen on the catalyst, we stop the addition of halogen and charge the hydrocarbon feed stock to the reaction zone free of halogen for a considerable throughput period. After a suitable period of charging the hydrocarbon feed free of chlorine or other halogen, for example, for a throughput of 1.0 to 2.0 barrels of hydrocarbon per pound of catalyst, we resume the addition of halogen to the reaction zone. We have discovered that the activity of the catalyst thereafter increases. This recovery of catalyst activity can be achieved to some extent after an even rather short period of charging of the halogen-free feed stock. However, much better results are obtained, that is, the activity of the catalyst is restored more nearly to its original high level, if the feed stock is charged free of halogen until the catalyst activity "lines out," or, in other words, reaches a constant low level. In typical operations of our process this has required charging of the halogen-free feed stock for a throughput of about 1.7 barrels of hydrocarbon per

pound of catalyst. After the catalyst has reached a "lined-out" low level of activity the addition of halogen is resumed, preferably at a known safe concentration, and within a reasonably short period of operation the activity of the catalyst returns substantially to the high level of activity observed before the decline caused by "over-haliding."

We do not wish to be bound by any theoretical explanation. However, we believe that the optimum halogen concentration in the reaction zone is a result of an equilibrium between the rate of introduction of halogen to the reaction zone with the feed and the rate of removal of halogen with the reactor effluent vapors. An equilibrium concentration remains in the reaction zone, either combined with the catalyst or dispersed in the reactant vapors. The most convenient way of introducing the halogen is by mixing a liquid halogen compound such as an alkyl chloride with the hydrocarbon feed stock prior to vaporization. Normally, a dilute stock solution of the halogen compound is prepared and added in the desired concentration to the hydrocarbon feed. The most convenient way to express the permissible halogen concentration for the reaction zone is in terms of the concentration of halogen in the hydrocarbon feed stock. As we have indicated, for most operations in accordance with the invention the suitable halogen concentration ranges from about 10 to 50 parts by weight per million parts of hydrocarbon. However, the maximum permissible contration or "safe" concentration which will increase catalyst activity without causing a rapid decline in activity will vary somewhat depending on the feed stock, the reaction conditions and the composition of the particular catalyst used.

The example which follows illustrates the results obtainable by the process of our invention in the hydroisomerization of a refinery n-pentane fraction.

EXAMPLE 1

The single-pass hydroisomerization of a refinery n-pentane fraction was carried out in a series of phases over a fixed-bed platnium-alumina catalyst, the fresh catalyst containing 0.78 weight percent platinum, 0.3 weight percent chlorine and the balance substantially entirely alumina and having a density of 0.7113 gm./cc. The reaction conditions included a liquid hourly space velocity of 9.0 vol./vol./hr., hydrogen concentration corresponding to 0.75 hydrocarbon mol fraction, 400 p.s.i.g. pressure, 800° F. average temperature and with the addition of t-butyl chloride to the pentane fraction charge stock varying in concentration from 0 to 60 parts by weight of chloride (calculated as elemental chlorine) per million parts of hydrocarbon. The operating conditions, charge and product inspections and the yields for each phase are presented in detail in Table I. Figure 1 of the drawing plots the isopentane content of the stabilized liquid product against catalyst age in barrels of hydrocarbon charged per pound of catalyst.

It will be noted that the conversion data of Figure 1 and of Table I differ slightly. The data for Figure 1 are from analyses of small samples of stabilized liquid product taken at frequent intervals throughout the run and are calculated as isopentane content of the liquid product based on the total normal and isopentane content, i.e., mol percent isopentane based on total pentanes (but disregarding the small amount of cyclopentane). The isopentane yield data in Table I are from analyses of the product obtained toward the end of each phase. Specifically, the data for Table I were obtained by analysis of product collected during throughput intervals (bbl./lb./ of each phase as follows: Phase I, 25.3–25.8; Phase II, 26.7–27.1; Phase III, 28.3–28.8; and Phase IV, 29.8–30.4. Yield of isopentane is calculated as isopentane

content of the liquid product based on the total C_5 and heavier hydrocarbon content, including C_5 hydrocarbons collected in product gases. Therefore, the yield figures in Table I are slightly lower than in Figure 1, but both sets of figures demonstrate the variations in catalyst activity and conversion in the different phases of the run.

Table I

Phase No.	I	II	III	IV
Normal Pentane Charge:				
Composition, Percent by Volume—				
Isopentane	5.1	5.4	3.9	5.0
n-Pentane	89.9	88.8	90.1	87.3
Cyclopentane	0.3	0.5	0.4	0.3
Pentenes	1.2	1.0	2.2	2.2
Hexane Isomers	3.5	4.3	3.4	5.2
Chloride, p.p.m.	40	60	0	40
Gas Charge:				
Composition, Percent by Mol—				
Hydrogen	80.2	80.7	80.1	80.6
Methane	18.7	18.2	18.2	18.0
Ethane and Heavier	1.1	1.1	1.7	1.4
Operating Conditions:				
Average Reactor Temp., °F.	801	801	800	800
Reactor Pressure, p.s.i.g.	400	400	400	400
Space Velocity, vol./vol./hr.	9.1	9.1	9.2	9.1
Hydrogen in Gas Charge, s.c.f./bbl. of Liq. Chg.	405	398	373	371
Hydrogen-Hydrocarbon in Reactor Chg., Mol Fraction—				
Hydrogen	0.24	0.24	0.23	0.23
Hydrocarbon	0.76	0.76	0.77	0.77
Composite Product Yields, Percent by Vol. of Liq. Chg. (Corr. to 100—Wt. Bal.):				
Debutanized Liquid Product (Corr. for Pentanes in Gas)	100.0	100.1	100.1	100.0
Isopentane	51.8	43.5	28.9	46.8
n-Pentane	45.5	52.9	67.7	51.0
Cyclopentane	0.4	0.6	0.6	0.3
Pentenes	0.6	0.7	0.8	0.5
Hexane Isomers	1.7	2.4	2.1	1.4
C_4 and Lighter Gas	4.4	4.2	4.0	4.3
Total Hydrocarbons	104.4	104.3	104.1	104.3
Chloride, p.p.m.	10	15	4	9
Conversion, Percent of n-Pentane in Reactor Feed Converted to Other Products	49.3	40.4	24.9	41.5
Hydrogen Consumption, s.c.f./bbl. of Liquid Charge	13	−8	−19	−11

During Phase I of Example 1 the chloride dosage was 40 parts per million and as shown in Figure 1 conversion corresponded to about 53.3 mol percent isopentane in the liquid product (based on total normal and isopentane). The chloride was increased to 60 parts per million in Phase II. The activity decreased rapidly, evidently as a result of "over-chloriding" of the catalyst. After the conversion had dropped to about 41 percent as shown in Figure 1, the addition of chloride was stopped and in Phase III the n-pentane fraction was charged to the reactor free of chloride. The conversion decreased further until it lined out at a value of about 30 percent isopentane, as shown in Figure 1. Thereafter, in Phase IV t-butyl chloride was again added to the pentane charge at a rate of 40 parts per million (calculated as elemental chlorine) and the conversion increased to about 47.5 percent. The results as plotted in Figure 1 and as listed in Table I show that removal of chloride from the feed for a substantial period followed by resumption of chloride addition restores the catalyst activity in operations in which the catalyst has become "over chlorided." The procedure extended the life of the catalyst for at least 6 to 8 barrels per pound after the activity had dropped to a low level, despite rather unfavorable reaction conditions used in some periods immediately following the resumption of chloride addition.

Example 2 which follows illustrates the results obtainable by the process of our invention in the hydroisomeri-

zation of a normal hexane fraction, the inspection data for which are given in the following table:

Table II

INSPECTION OF n-HEXANE FRACTION

Composition, percent by vol.:	
2,3-dimethylbutane, 2-methylpentane	1.7
3-methylpentane	7.1
n-Hexane	85.7
Methylcyclopentane	2.9
Cyclohexane	—
Benzene	2.6
Heptane isomers	—
Total	100.0
Octane number:	
Motor, clear	32
Motor, +3 cc. TEL	68
Research, clear	36
Research, +3 cc. TEL	68
Sulfur, percent	0.002

EXAMPLE 2

The hydroisomerization of the n-hexane fraction was carried out in a series of phases over a fixed bed of platinum-alumina catalyst particles which when freshly prepared had a surface area of 398 sq. m./g. and contained 0.59 wt. percent platinum, 0.4 wt. percent chlorine, 0.10 wt. percent sulfur, 0.24 wt. percent SiO_2 and the balance substantially entirely alumina. The reaction conditions included: average reactor temperature of 800° F., reactor pressure of 400 p.s.i.g., liquid hourly space velocity of 6.0 vol./vol./hr. and a hydrogen concentration corresponding to a mol fraction hydrocarbon in the reactor charge of 0.51. In certain phases of the operation, chlorine in the form of t-butyl chloride was continuously added with the n-hexane fraction in different concentrations. In one phase, the chlorine concentration was 50 p.p.m. of hydrocarbon and in another phase, in which the catalyst became "over-chlorided," the chlorine concentration was 100 p.p.m. When the catalyst activity had declined owing to "over-chloriding" the n-hexane fraction was charged free of added halogen for a throughput of about 1.6 barrels of hydrocarbon per pound of catalyst following which the addition of chloride at a rate of 50 p.p.m. of hydrocarbon was resumed. The catalyst activity was largely restored. The catalyst activity was largely restored. Figure 2 of the drawing plots the results of Example 2 in terms of the concentration of hexane isomers in the stabilized liquid product (as mol percent of total hexanes) against the catalyst age in barrels per pound for the different phases of the example.

The catalyst of Example 2 had been used for hexane hydroisomerization for a total throughput of about 29 barrels of hydrocarbon per pound of catalyst before the operation pertinent to Example 2 was begun. Therefore, the plot of catalyst age in Figure 2 begins at a value of about 29 barrels per pound. As Figure 2 shows, the conversion (measured as hexane isomer: percent of total hexanes) was 50.5 percent during Phase I with 50 p.p.m. of chloride added to the reactor feed. In Phase II shortly thereafter the rate of chloride addition was increased to 100 p.p.m. and the conversion decreased to 45.5 percent. Thereafter, in Phase III, no chloride was added to the feed and the conversion further decreased to about 38 percent. Then in Phase IV chloride was again added at a rate of 50 p.p.m. and the conversion increased to 50 percent, thus indicating that the catalyst returned substantially to the activity that it had before "over-chloriding."

The examples above show the advantages of adding halogen to the hydroisomerization feed when operating under conditions of high space velocity and low hydrogen concentration in that high conversion is obtained when a proper amount of halogen is introduced to the reactor. The results also show the damaging effect of excessive halogen addition. They further show that the applicants have developed a valuable method for restoring the activity of the catalyst after loss of activity due to over-haliding. The activity is restored by the applicants' method without taking the reactor off stream and without resorting to oxidative regeneration.

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 the hydroisomerization process which comprises contacting with a platinum-alumina catalyst a hydrocarbon fraction reactor feed comprising at least 90 volume percent of at least one aliphatic paraffin having from 4 to 6 carbon atoms in admixture with hydrogen in a concentration corresponding to a mol fraction of hydrocarbon greater than 0.5 but less than the mol fraction hydrocarbon corresponding to rapid catalyst aging, at a charge liquid hourly space velocity of at least 5 volumes of hydrocarbon per volume of catalyst per hour, a temperature from 600 to 1000° F. and a pressure from 300 to 600 p.s.i.g., while adding to the reactor feed an alkyl halide that vaporizes under the process conditions, and recovering from the reaction zone an effluent stream enriched in branched chain paraffins, the improvement which comprises restoring the catalyst activity following a rapid decline in the branched chain paraffin content of the product by charging said hydrocarbon fraction to the reaction zone substantially free of halogen until the catalyst activity reaches a substantially constant level, and thereafter resuming the addition of said alkyl halide to the hydrocarbon feed in a concentration from 10 to 50 parts of halogen per million parts of hydrocarbon.

2. In the hydroisomerization process which comprises contacting with a platinum-alumina catalyst a hydrocarbon fraction reactor feed comprising at least 90 volume percent of at least one aliphatic paraffin having from 4 to 6 carbon atoms in admixture with hydrogen in a concentration corresponding to a mol fraction of hydrocarbon greater than 0.5 but less than the mol fraction hydrocarbon corresponding to rapid catalyst aging, at a charge liquid hourly space velocity of at least 5 volumes of hydrocarbon per volume of catalyst per hour, a temperature from 650° to 900° F. and a pressure from 300 to 600 p.s.i.g., while adding to the reactor feed an alkyl chloride that vaporizes under the process conditions, and recovering from the reaction zone an effluent stream enriched in branched chain paraffin, the improvement which comprises restoring the catalyst activity following a rapid decline in the branched chain paraffin content of the product by charging said hydrocarbon fraction to the reaction zone substantially free of halogen until the catalyst activity reaches a substantially constant level and for a throughput of at least one barrel of hydrocarbon per pound of catalyst, and thereafter resuming the addition of said alkyl chloride to the hydrocarbon feed in a concentration not greater than the concentration added to the reactor feed before said rapid decline in the branched chain paraffin content of the product.

3. In the hydroisomerization process which comprises contacting with a platinum-alumina catalyst consisting essentially of platinum supported on alumina and containing a minor amount of chlorine a hydrocarbon feed comprising at least 90 volume percent of an aliphatic paraffin selected from the group consisting of pentanes and hexanes in admixture with hydrogen in a concentration corresponding to a mol fraction of hydrocarbon greater than 0.5 but less than the mol fraction of hydrocarbon corresponding to rapid catalyst deactivation, at a charge liquid-hourly space velocity of at least 5 volumes of hydrocarbon per volume of catalyst per hour, a tem-

perature from 600° to 900° F. and a pressure from 300 to 600 p.s.i.g., while adding to the reactor feed an alkyl chloride that vaporizes under the process conditions, and recovering from the reaction zone an effluent stream enriched in branched chain paraffins, the improvement which comprises restoring the catalyst activity following a rapid decline in the branched chain paraffin content of the product by charging the reactor feed to the reaction zone substantially free of halogen until the catalyst activity reaches a substantially constant level and for a throughput of at least one barrel of hydrocarbon per pound of catalyst, and thereafter resuming the addition of

said alkyl chloride to the feed in a concentration not greater than the concentration added to the feed before said rapid decline in the branched chain paraffin content of the product.

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