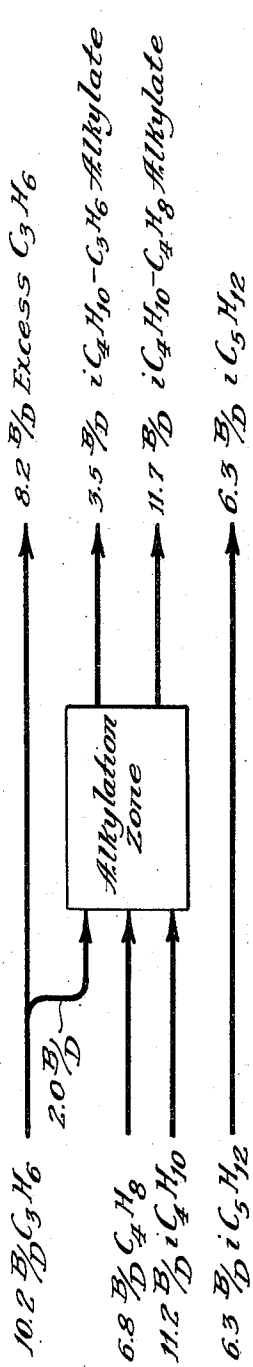
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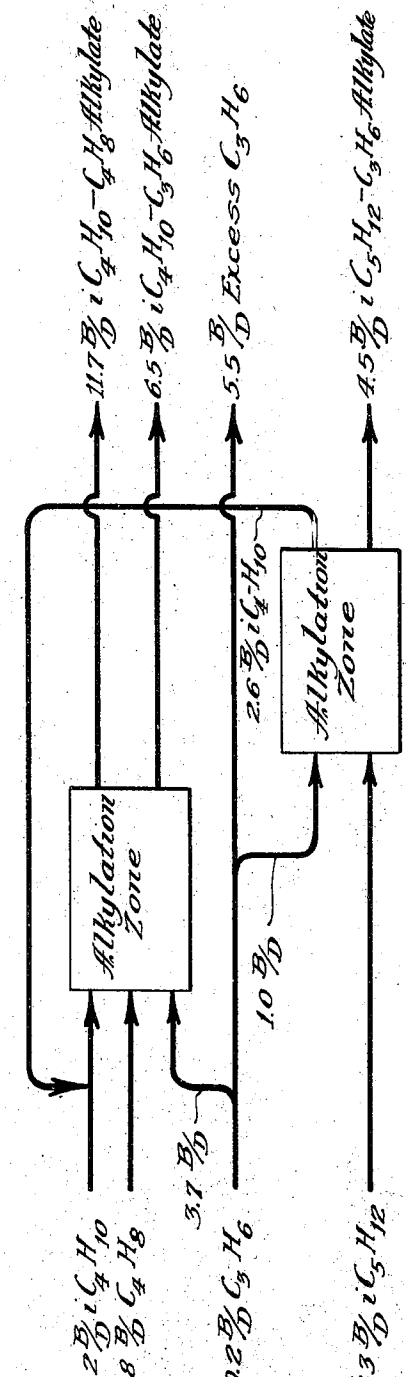
ALKYLATION OF ISOPARAFFINS

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Scheme I




Scheme II




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## ALKYLATION OF ISOPARAFFINS

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2 Claims. (Cl. 260—683.4)

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This invention relates to the production of saturated hydrocarbons by the catalytic alkylation of isoparaffins with olefins.

The production of relatively high molecular weight branched chain paraffins having valuable antiknock properties and therefore suitable for use in aviation fuels is of great importance in the petroleum industry. A convenient and widely used method for the synthesis of hydrocarbons of this type is the catalytic alkylation of lower boiling isoparaffins such as isobutane and isopentane with normally gaseous olefins such as propylene and butylenes. Among the various alkylation catalysts which may be employed are aluminum chloride and other metal halide catalysts, hydrogen fluoride, sulfuric acid, phosphoric acid, various halo sulfonic acids, etc. In commercial practice one of the most important alkylation reactions is the interaction of isobutane with butylenes to produce branched chain octanes. However, in most refineries the limiting factor in the isobutane-butylene alkylation process lies in the amount of isobutane which is available. In fact there is often such a deficiency of available isobutane that it is necessary to resort to special methods to produce isobutane, e. g., by the isomerization of normal butane.

One object of the present invention is to produce greater quantities of isobutane alkylate from olefin-containing hydrocarbon fractions than have been produced by methods heretofore taught in the art. Another object of the invention is to utilize the maximum quantity of available olefins in the production of aviation gasoline from olefinic hydrocarbon fractions. A still further object of the invention is to produce the maximum amount of isobutane alkylate using readily available hydrocarbon fractions as charging stocks.

Broadly, the invention comprises alkylating isobutane with olefins, separately alkylating isopentane with propylene, and supplying isobutane produced in the isopentane alkylation step to said first named alkylation step.

In one specific embodiment the invention comprises producing substantially saturated gasoline boiling range hydrocarbons by alkylating isobutane with propylene and butylenes in the presence of a suitable alkylation catalyst, alkylating isopentane with propylene in a separate alkylation zone in the presence of hydrogen fluoride under alkylating conditions such that substantial amounts of isobutane are formed, and supplying isobutane from the said second alkylating step to the said first named alkylating step.

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The usual components of aviation gasoline are a low olefin content base stock, alkylate, and sufficient isopentane to meet the vapor pressure requirements of the final blend. An appropriate amount of tetra ethyl lead is, of course, added to the blend to obtain the desired antiknock value. The base stock often consists of substantially saturated straight run fractions, but in present day practice it has been found that base stocks having high aromatic contents are preferred. Base stocks containing appreciable quantities of aromatics and only small amounts of olefins are prepared by hydrocarbon conversion processes, particularly by the catalytic cracking of hydrocarbon oils followed by retreatment of the gasoline boiling range product to reduce the olefin content thereof. The gaseous hydrocarbons produced in hydrocarbon conversion processes such as catalytic cracking are excellent alkylation feed stocks since they contain large quantities of $C_3$ and $C_4$ olefins and also appreciable amounts of isobutane. In many catalytic cracking processes substantial amounts of isopentane are also produced.

As hereinbefore described the limiting factor in the alkylation process in many refineries is the supply of isobutane. The gaseous products from hydrocarbon conversion processes contain adequate supplies of olefinic reactants, but there is often insufficient isobutane to react with the available propylene and butylenes. Generally speaking, there is usually a sufficient amount of isobutane available to react with the butylenes present in the feed stock, but large amounts of propylene must often be discarded because of insufficient isobutane to react with it. By the process of the present invention the excess propylene is interacted with isopentane to produce a gasoline boiling range alkylate of satisfactory quality, but during the reaction substantial amounts of isobutane are also produced which may then be employed to react with further quantities of excess or marginal propylene.

It has been found that in the reaction of isopentane with propylene in the presence of a suit-

able alkylation catalyst and under suitable conditions substantial amounts of isobutane are produced as a side reaction. The extent to which isobutane is produced will depend upon many factors, particularly the catalyst and operating conditions employed. I have found that when hydrogen fluoride is employed for the alkylation of isopentane with propylene unusually large amounts of isobutane are formed especially at higher temperatures and higher molar ratios of isopentane to propylene.

Although the preferred catalyst for the interaction of isopentane with propylene is substantially anhydrous hydrogen fluoride, it is possible to employ catalysts containing as much as about 10% water. In fact, the commercially available "anhydrous" hydrogen fluoride generally contains up to about 2% by weight of water. Excessive dilution with water is undesirable since it tends to reduce the alkylating activity of the catalyst and introduces corrosion problems. It is also within the scope of my invention to employ hydrogen fluoride containing relatively minor amounts of various additives or promoters such as boron trifluoride.

The alkylation of isoparaffins with olefins in the presence of a hydrogen fluoride catalyst is ordinarily conducted on a continuous scale by introducing the hydrocarbon charging stock and catalyst into a mechanically agitated reaction zone or any other zone suitable for effecting intimate contact between the hydrocarbons and catalyst. The hydrocarbon-catalyst mixture is maintained at the desired temperature and pressure for the required reaction time. It is desirable to maintain a substantial molar excess of isoparaffins over olefins in the hydrocarbon feed to the alkylation zone in order to promote alkylation as the principal reaction of the process. The reaction mixture is withdrawn and is introduced into a separation zone which ordinarily consists of a gravity settler. The lower catalyst layer is withdrawn and a major portion thereof may be recycled to the alkylation zone although another portion thereof may be withdrawn from the system and subjected to regeneration. Regenerated and/or fresh catalyst is supplied to the alkylation zone to maintain a relatively constant amount of catalyst within the reaction system. The upper hydrocarbon layer from the settler is subjected to fractionation for the recovery of gasoline boiling range products and for the separation of unconverted isoparaffins which are recycled to the alkylation zone.

The alkylation of isoparaffins with olefins in the presence of a hydrogen fluoride catalyst is carried out at a temperature of from about 0° F. to about 200° F. although the reaction temperature is preferably within the range of from about 50° F. to about 150° F. In the alkylation of isopentane with propylene it is preferred to employ temperatures in the upper portion of this range, namely, from about 75° F. to about 150° F. in order to favor the production of isobutane during the reaction. The pressure on the alkylation system is ordinarily just high enough to maintain the hydrocarbons and catalyst in substantially the liquid phase, e. g., from about 50 to about 500 pounds per square inch. The time factor in the alkylation process is conveniently expressed in terms of "space time" which is defined as the volume of catalyst within the contacting zone divided by the volume rate per minute of hydrocarbon reactants charged to the zone. Usually the space time will fall within the range of from about 5 to about 80 minutes although in certain cases it may be desirable to extend this range in either direction. It is preferable to maintain at all times a substantial molar excess of isoparaffins over olefins in the hydrocarbon feed to the alkylation zone, e. g., from about 3:1 to about 10:1 or higher. In order to promote the formation of isobutane during the alkylation of isopentane with propylene in the presence of hydrogen fluoride it is desirable to maintain a molar ratio of isopentane to propylene greater than 5:1, e. g., from about 5:1 to about 20:1. In general the volumetric ratio of hydrogen fluoride catalyst to hydrocarbon in the contacting zone should be about 1:1 although ratios of from about 0.5:1 to about 2.0:1 will give satisfactory results.

The invention can best be described by a typical illustration which, however, is not intended to limit the generally broad scope of the invention as defined in the claims.

Reference is now made to the drawing which illustrates schematically the advantages to be gained by the present invention. The charging stock comprises a $C_3$ to $C_5$ hydrocarbon fraction obtained from a typical high temperature catalytic cracking operation. In scheme I all of the available isobutane in the charge is alkylated with all of the available butylene and as much propylene as possible. The isobutane may be alkylated with butylenes and propylene jointly or in separate zones. In scheme II the process of the present invention is employed wherein all of the available isobutane in the charge is alkylated with all of the available butylene and part of the propylene and all of the available isopentane is alkylated with propylene. During the course of the isopentane-propylene reaction a substantial amount of isobutane is produced which is then utilized to react with marginal propylene to increase the overall production of alkylate. Here again the isobutane may be alkylated with the butylenes and propylene jointly or in separate steps as desired.

In scheme I the total isobutane comprising 11.2 barrels per day is interacted with 6.8 barrels per day of butylene and 2.0 barrels per day of propylene. The alkylation is carried out using a hydrogen fluoride catalyst at 100° F., 170 pounds per square inch, 30 minutes space time, and a molar ratio of isoparaffin to olefin in the charge of about 6:1. From this step there is a total production of 11.7 barrels per day of isobutane-butylene alkylate and 3.5 barrels per day of isobutane-propylene alkylate. The 6.3 barrels per day of available isopentane is not utilized, and 8.2 barrels per day of excess propylene is left over.

In scheme II on the other hand the same quantities of original isobutane and butylene are charged to the isobutane alkylation step and in addition 6.3 barrels per day of available isopentane are reacted with 1.0 barrel per day of propylene in a separate alkylation step using a hydrogen fluoride catalyst at 100° F., 220 pounds per square inch, 35 minutes space time, and a molar ratio of isopentane to propylene of about 7.2:1. In this step there is a production of 2.6 barrels per day of isobutane along with 4.5 barrels per day of isopentane-propylene alkylate. The 2.6 barrels per day of isobutane are supplied to the first alkylation step wherein they may then be reacted with an additional 1.7 barrels per day of marginal propylene which was not consumed in scheme I. The net production in scheme II consists of 11.7 barrels per day of isobutane-butylene alkylate, 6.5 barrels per day

of isobutane-propylene alkylate, and 4.5 barrels per day of isopentane-propylene alkylate.

The advantages of the invention are illustrated in the following comparison of the two schemes:

| Type of Alkylate | Productions in Barrels per Day | |
|---|---|---|
| | Scheme I | Scheme II |
| Butylene-Isobutane | 11.7 | 11.7 |
| Propylene-Isobutane | 3.5 | 6.5 |
| Propylene-Isopentane | | 4.5 |

It can thus be seen that the production of isobutane-propylene alkylate is increased by approximately 86% in scheme II, and in addition a considerable quantity of isopentane-propylene alkylate is produced. By operating the isopentane-propylene alkylation step under conditions conducive to the formation of isobutane, it is thus possible to produce isobutane-propylene alkylate at the expense of the less desirable isopentane-propylene alkylate. Although the isopentane-propylene alkylate is satisfactory for incorporation in aviation fuels, its antiknock value is relatively lower than that of other alkylates and its chief function, therefore, is in the nature of a base stock. The A. S. T. M. octane number of the aviation gasoline boiling range fraction of an isobutane-propylene alkylate prepared using a hydrogen fluoride catalyst is of the order of 91 whereas the A. S. T. M. octane number of isopentane-propylene alkylate prepared using a hydrogen fluoride catalyst is of the order of 74.

It will be seen that my invention provides one method of solving an important problem which arises during the commercial operation of the alkylation process. It enables the refiner to utilize marginal propylene for the production of a satisfactory isopentane-propylene alkylate while at the same time producing extra quantities of isobutane which can be reacted with more marginal propylene to increase the total aviation gasoline production from a given hydrocarbon charging stock.



I claim as my invention:

1. An alkylation process which comprises reacting isobutane with an olefin under alkylating conditions, separately alkylating isopentane with propylene in the presence of hydrogen fluoride at a temperature of from about 75° F. to about 150° F. while maintaining a molar ratio of isopentane to propylene of from about 5:1 to about 20:1, whereby to produce a substantial amount of isobutane concurrently with the alkylated isopentane, and supplying the isobutane thus produced to the first-mentioned alkylating step.

2. A process for the production of hydrocarbons boiling in the gasoline range which comprises alkylating isobutane with propylene and butylene, separately alkylating isopentane with propylene in the presence of hydrogen fluoride at a temperature of from about 75° F. to about 150° F. while maintaining a molar ratio of isopentane to propylene of from about 5:1 to about 20:1, whereby to produce a substantial amount of isobutane concurrently with the alkylated isopentane, and supplying the isobutane thus produced to the first-mentioned alkylating step.

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## Disclaimer

2,436,483.—*Robert J. Newman,* Riverside, Ill. ALKYLATION OF ISOPARAFFINS. Patent dated Feb. 24, 1948. Disclaimer filed May 19, 1950, by the assignee, *Universal Oil Products Company.*

Hereby enters this disclaimer to claim 1 of said patent.

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