Jan. 27, 1948. W. E. BRADLEY 2,435,028

ALKYLATION PROCESS

Filed July 12, 1938

Fig. 1.

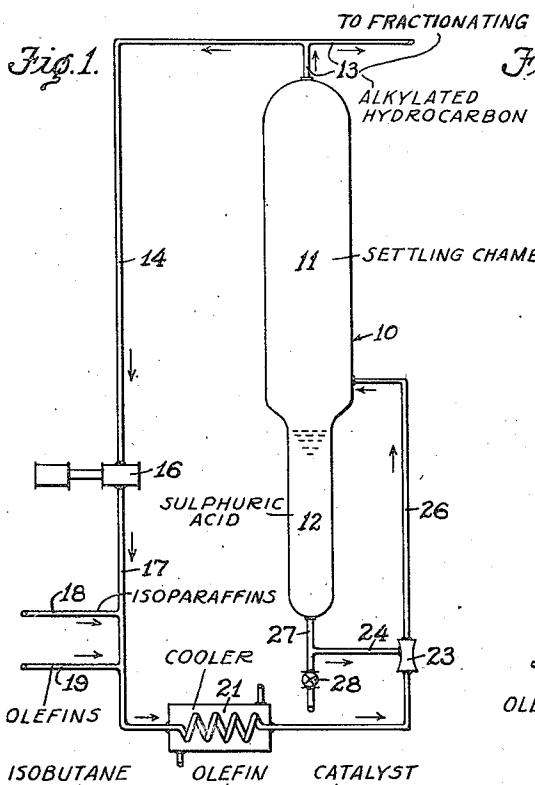


Fig. 2.

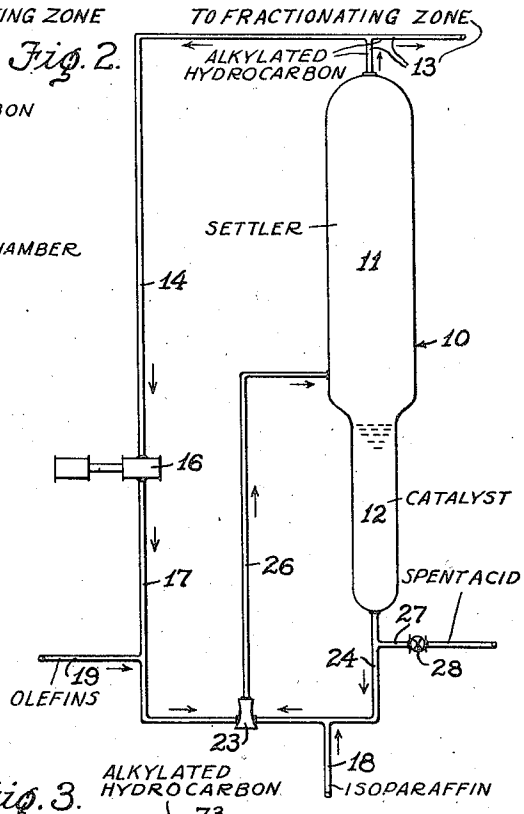
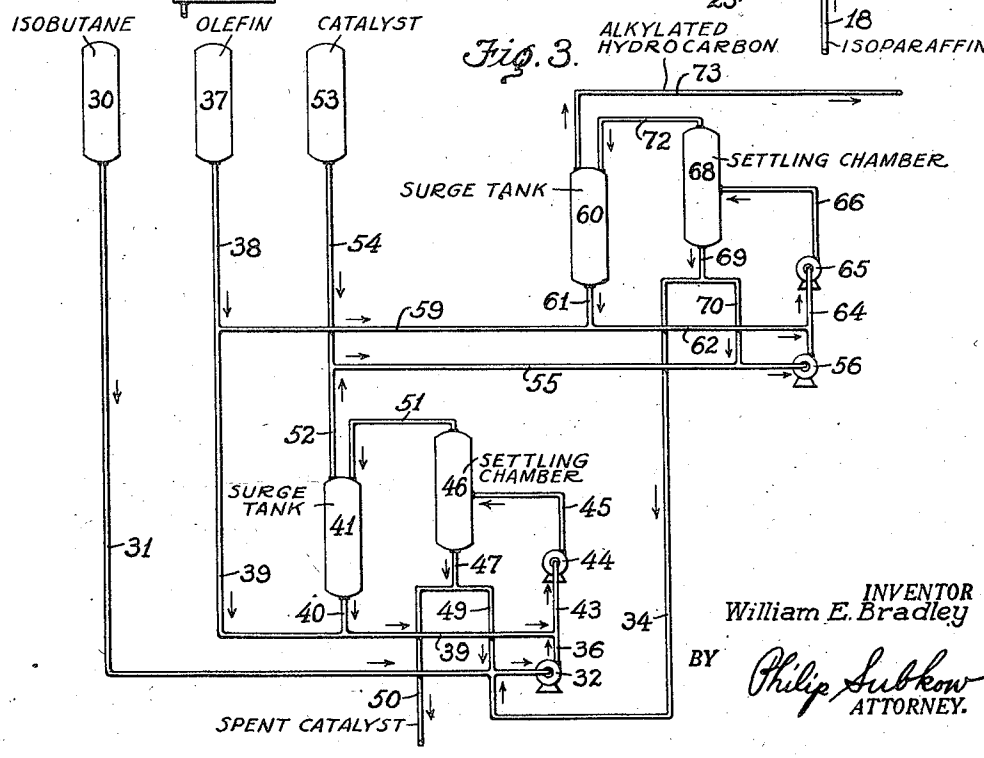


Fig. 3.



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Patented Jan. 27, 1948 2,435,028

UNITED STATES PATENT OFFICE

2,435,028

ALKYLATION PROCESS

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Application July 12, 1938, Serial No. 218,772

14 Claims. (Cl. 260—683.4)

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The present invention relates to the synthesis of hydrocarbons, and more particularly pertains to the manufacture of hydrocarbons having branched chain structures and which are especially suitable as automobile and aviation engine fuels or constituents thereof.

More specifically, the invention covers a process for reacting certain isoparaffinic hydrocarbons with olefins to produce branched chain paraffinic hydrocarbons boiling within the gasoline range, possessing high anti-detonating characteristics, and substantially free from products of polymerization boiling within such gasoline range. In one of its embodiments, the present invention includes a continuous process for the combining of isoparaffinic hydrocarbons of relatively low molecular weights with olefins, which may be normally gaseous or normally liquid, or both, to produce the above described branched chain paraffinic hydrocarbons.

Owing to the adoption of high compression ratio in automobile and aviation engines, an insistent demand has been made upon the petroleum refining and similar industries to furnish motor fuels which have high anti-knock values. Thus in the aviation industry many specifications require the gasoline to have a knock rating of about 100 iso-octane, as determined by the A. S. T. M. method, this gasoline to contain not more than 3 millimeters of tetraethyl lead per gallon. Also, in the case of aviation fuels, it has been considered advisable to limit the percentages of olefinic and aromatic bodies which may be present, consequently and indirectly requiring fuels consisting essentially of branched chain paraffins, it being known that the normal or straight chain paraffinic hydrocarbons boiling within the gasoline range have low octane ratings.

As a result of this requirement for gasolines of the branched chain type having high anti-knock values, it has been recently discovered that the relatively low molecular weight isoparaffins, such as isobutane and isopentane, may be chemically combined with olefins to produce the desired branched chain hydrocarbons boiling within the gasoline range and possessing the required high anti-detonating characteristics. Such reactions are termed "alkylation" in order to distinguish them from "polymerization" reactions, which consist in the combining of two or more olefinic molecules to form an olefin of proportionately higher molecular weight. It has also been previously discovered that such alkylation reactions between isoparaffins and olefins may be effected catalytically and at atmospheric or elevated pressures and at atmospheric or even subatmospheric temperatures. It has been further discovered that substances of the type of sulfuric acid, mixtures of sulfuric and phosphoric acids, chlorosulfonic acid and certain complexes of aluminum chloride and boron trifluoride may be effectively employed as the catalyst for such chemical combining of isoparaffins with olefins to produce the described branched chain paraffinic hydrocarbons boiling within the gasoline range and having high anti-detonating characteristics and being substantially free from products of polymerization boiling within the gasoline range.

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In carrying out these catalytic alkylation processes, the reactions usually have been effected by commingling the olefins with a small excess of isoparaffins and subsequently contacting the mixture with the catalytic material. Although this method of operation resulted in the formation of "alkylate," i. e. products resulting from the interaction of isoparaffins with olefins, it has heretofore been impossible to prevent a certain amount amount of polymerization of the olefins which usually occurred simultaneously with the alkylation reaction since the catalysts for the alkylation reaction are likewise catalysts for the polymerization of olefins.

It is, therefore, the main object of the present invention to provide a process for the alkylation of isoparaffins with olefins to produce branched chain paraffinic hydrocarbons of the class described, these products of reaction being substantially free from products of polymerization of the olefins. It is a further object of the invention to provide a process for reacting isoparaffins with olefins in substantially the liquid phase, at ordinary or elevated pressures and at atmospheric or sub-atmospheric temperatures, in the presence of an alkylating catalyst under conditions whereby the products of reaction comprise branched chain paraffinic hydrocarbons boiling within the gasoline range and substantially free from products of polymerization.

It has now been discovered that the above and other objects may be attained by dissolving the olefins in an inert diluent in order to form a relatively dilute solution of the olefins thus introduced, and subsequently causing the alkylation of isoparaffins by the thus prediluted olefins. It has been further discovered that the reaction product formed by the chemical combination of olefins and isoparaffins, and therefore consisting essentially of branched chain hydrocarbons, may be employed as the above mentioned diluent for the olefins to be used in the alkylation reaction.

Although there is no desire to be limited by any theory of the case, one reason for the effectiveness of the alkylate as the diluent resides in the fact that the rate of alkylation of these branched chain hydrocarbons is so slow in comparison with the rate of alkylation of the low molecular weight isoparaffins, particularly if the latter are in excess, that the former reaction does not occur to any measurable extent.

It has been still further discovered that the above and other objects may be attained by providing a continuous or semi-continuous process in which at least a portion of the products of alkylation is continuously or otherwise withdrawn from the reaction zone and commingled with new quantities of the olefins or isoparaffins prior to the introduction of these hydrocarbons into the reaction zone. As will be brought out more fully hereinbelow, the portion of the alkylate used as the diluent may be commingled with new quantities of isoparaffins and olefins before the mixture is contacted with the catalyst. In the alternative, this alkylate fraction may first be commingled with the olefins (for purposes of their dilution) and the mixture thus produced may then be contacted and thoroughly mixed with the isoparaffins and the catalyst.

As previously stated, both polymerization and alkylation are competing reactions. In other words, catalysts employed in alkylation reactions also aid the polymerization of olefins. Therefore, the mere dilution of olefins in the complete absence of isoparaffins would not decrease the polymerization reaction when such diluted olefins are brought in contact with catalysts of the type of sulfuric acid, mixtures of sulfuric acid and phosphoric acid and chlorosulfonic acid, etc. It has been still further discovered that the alkylation of the relatively low molecular weight isoparaffinic hydrocarbons with normally gaseous or normally liquid olefins to produce high yields of branched chain hydrocarbons boiling within the gasoline boiling range and having high anti-detonating characteristics may be realized by recycling the products leaving the sphere of reaction and simultaneously introducing the isoparaffins in excess of the quantity theoretically necessary for the combining with the olefins being added. Such continuous dilution of the olefins with the products of alkylation and the simultaneous introduction of the excess quantities of isoparaffins into the sphere of reaction greatly decreases any possibility of polymerization of the olefins and simultaneously increases the chances of the olefins coming in contact with the isoparaffin molecules to be alkylated. Therefore, the products resulting from such procedure comprises alkylate which are substantially free from any products of polymerization, these alkylate having high anti-detonatting characteristics and boiling substantially within the gasoline range.

The invention may, therefore, be stated to reside broadly in a process of interacting relatively low molecular weight isoparaffins with normally liquid or normally gaseous olefins or with both types of olefins to produce branched chain paraffinic hydrocarbons boiling within the gasoline range possessing high anti-detonating characteristics and substantially free from products of polymerization or olefins within the gasoline boiling range, the process comprising pre-dilution of the olefins with the products of alkylation and with excess quantities of isoparaffins and the subsequent commingling of said mixture with the alkylation catalyst. The invention further resides in the process of reacting isoparaffins with olefins to produce motor fuel fractions which comprises continuously withdrawing a portion of the products of alkylation with olefins being introduced into the sphere of reaction, continuously introducing isoparaffins in excess of the quantity theoretically necessary for the combining of the olefins introduced and contacting said mixture at optimum temperatures and pressures with the alkylating catalyst.

In its most specific embodiment, the invention resides in a continuous process of alkylating low molecular weight isoparaffins with the above described olefins. This process comprising the steps of pre-diluting the olefins with the products which have previously passed through the alkylation reaction zone, and bringing this mixture in intimate contact with isoparaffins and the alkylating catalyst, the isoparaffins being employed in quantities in excess of those theoretically necessary for the combining with the introduced olefins.

More specifically stated, the process includes the steps of continuously commingling excess quantities of isoparaffins with olefins and a portion of the alkylate fraction removed from the sphere of reaction, commingling said mixture with the alkylating catalyst, introducing the hydrocarbon-catalyst mixture into a settling zone thereby effecting at least a partial separation between the catalyst and the hydrocarbons, withdrawing the catalyst for further commingling with new quantities of hydrocarbons to be treated, simultaneously withdrawing the products of reaction from said settling chamber and employing a portion of said products for commingling with and dilution of new quantities of olefins introduced into the reaction zone. The invention also includes the maintenance of optimum pressures and temperatures, these conditions of operation varying with the hydrocarbon treated, the catalyst employed, etc.

As an alternative, the process includes the separate dilution of the olefins with the alkylate withdrawn from the settling chamber and the commingling of this mixture with another mixture comprising the catalyst and isoparaffins to be alkylated, these isoparaffins, as stated before, being employed in quantities in excess of those theoretically necessary for chemical combination with the olefins introduced.

For a better understanding of the various phases of the present invention, reference is made to the accompanying drawings in which:

Figure 1 is a diagrammatic elevational view of an embodiment in which the recycled portion of the alkylate is commingled with the hydrocarbons to be treated prior to the contact of this mixture with the alkylating catalyst; and

Figure 2 shows in diagrammatic elevation a modified sketch of an apparatus in which the recycled alkylate are continuously commingled with fresh quantities of olefins, followed by the commingling of this mixture with another mixture containing the catalyst and the isoparaffins to be alkylated.

Referring now to the drawing, and particularly to Figure 1 thereof, there is shown a reaction chamber 10 which consists of two superimposed sections 11 and 12. The upper section 11 may be termed the settling chamber, while the lower section 12, which is shown to have a relatively smaller diameter, is the acid or catalyst cham-

ber. The upper end of chamber 11 is provided with a discharge pipe 13, a branch line 14 extending from this pipe 13 to a pump 16. The discharge end of the pump opens into a line 17 which is provided with inlet lines 18 and 19 for the introduction of fresh quantities of isoparaffinic and olefinic hydrocarbons, respectively. Line 17 may also be provided with a cooler 21, the purpose of which will be discussed more fully hereinbelow. A mixer or similar commingling device 23 is attached to the discharge end of line 17, line 24 leading from the lower end of catalyst chamber 12 also opening into this mixer 23. A pipe 26 communicates the discharge end of mixer 23 with the lower portion of settling chamber 11. For purposes of discharging the contents of reaction chamber 10 as well as for the purpose of adding fresh quantities of catalyst, pipe 24 may be provided with a branch line 27 equipped with a valve 28.

The operation of the above described structure is as follows, it being assumed that sulfuric acid is employed as the alkylating catalyst and that an isoparaffin fraction predominating in isobutane is to be alkylated. Before initiating the alkylation, reaction chamber 12 is filled with the sulfuric acid catalyst, which is preferably of a concentration between about 96 and 100% sulfuric acid. The space above the acid is then filled with alkylate from a previous run or, preferably, with the isoparaffin fraction to be alkylated. Thereafter, pump 16 is caused to operate and simultaneously fresh quantities of isoparaffins and olefins are introduced into the system through lines 18 and 19, respectively. The mixture passes through cooler 21 wherein it is brought to the optimum temperature which in this case is in the neighborhood of 40° F. to 70° F., it being understood that specific temperature limitations presented herein are given only as an illustration and not for the purpose of limiting the invention. The isoparaffin-olefin mixture is thus conveyed through mixer 23 wherein it is caused to be thoroughly and intimately commingled with the acid withdrawn from chamber 12 through line 24. The hydrocarbon-acid mixture is then conveyed through line 26 to settling chamber 11 in which the separation of the acid from the hydrocarbon first occurs, the acid dropping down into chamber 12 while the hydrocarbon phase passes upwardly in chamber 11. The alkylation reaction occurs in mixer 23, line 26 and in the reaction chamber 10. Since the reaction chamber is completely filled with the hydrocarbon-acid mixture, and since both the isoparaffins and the olefins are maintained in a liquid phase in the system, the hydrocarbon phase passes continuously out of reaction chamber 10 into line 13. The rate of this discharge is proportional to the rate of introduction of fresh quantities of isoparaffins and olefins through lines 18 and 19, respectively. A portion of the hydrocarbon phase, equivalent to the olefin and isoparaffin added through lines 18 and 19, is withdrawn from the system through line 13, the balance being recycled through line 14, pump 16 and line 17 for further commingling with new quantities of isoparaffins and olefins.

It is thus seen that the operations according to the invention described above permit a constant dilution of the olefins introduced, this dilution being caused by the commingling of the olefins with the products of reaction continuously removed from settling chamber 11 through lines 13 and 14. Although it is possible to introduce the isoparaffins through line 18 in quantities only sufficient to react with the olefins continuously introduced through line 19, it is preferable to employ a relatively large excess of isoparaffins thus further aiding in preventing the polymerization of the olefins. Obviously, the constant presence of isoparaffins (which in the instant case comprises a fraction predominating in isobutane) causes a presence of such isoparaffins in the hydrocarbons removed through line 13. Therefore, the fraction thus withdrawn out of the system through line 13 comprises alkylate and unreacted isoparaffins. The latter may be easily separated from the alkylate as by fractionation and may be returned into the system through line 18.

Although the alkylation reaction between the isoparaffins of the type of isobutane, isopentane and isohexane and the normally gaseous or normally liquid olefins is not sufficiently exothermic to cause any marked temperature rise in the system, nevertheless, the operations of the above system cause a gradual heating of the hydrocarbons being treated. This heating may be either due to the mechanical energy introduced into the pumps or may be caused by heat evolved by the oxidation of some of the hydrocarbons by the sulfuric acid. Obviously, this heating may be due to other causes which are unknown at the present time. Whatever may be the cause of such heating, the alkylation of the above isoparaffins by the olefins in the liquid phase and in the presence of the sulfuric acid catalyst should preferably be realized at relatively low temperatures of the order of 40° F. to 70° F. It is for this purpose that line 17 is provided with cooler 21.

The assembly shown in Figure 2 is somewhat similar to that described hereinabove. Thus, reaction chamber 10 consists of the superimposed settling chamber 11 and acid chamber 12, the acid being withdrawn from the bottom through line 24 while the products of reaction leave at the top through line 13. As in the previous case, a portion of the hydrocarbon phase thus withdrawn is recycled through pump 16 and through lines 14 and 17. The main difference resides in the fact that only the olefins are commingled with the alkylate fraction thus circulated, this olefin fraction being introduced through line 19. The fresh quantities of isoparaffins (which, as described, may be employed in quantities in excess of those theoretically necessary to combine with the olefins) are commingled with the acid catalyst, this mixture being then conveyed to mixer 23 wherein it is intimately commingled with the olefin-alkylate mixture coming through line 17. The mass thus produced then passes through line 26 into the reaction chamber 10 wherein it separates as described in connection with the operations of the process shown in Figure 1. Thus, the main difference between the two process and assemblies resides in the fact that whereas in the first process both the isoparaffins and olefins are commingled with the alkylate fraction before coming in contact with the catalyst, in the second process the isoparaffins are activated by the catalyst before the diluted olefins are introduced into the mixture.

Figure 3 shows a diagrammatic flow sheet of a multi-stage alkylation system according to the process of the present invention. In this case the isoparaffinic fraction, such as isobutane, is stored in tank 30, the isobutane being preferably maintained under pressure and in a liquid state. This liquefied fraction is continuously fed through line 31 into a mixing device 32, such as a centrifugal

mixing pump. The catalyst, such as sulfuric acid, is introduced into line 31 through line 34. This catalyst is withdrawn from the next succeeding reaction stage, as will be more fully explained hereinbelow. The commingled isoparaffin-catalyst mixture then passes continuously through line 36 into which the olefinic fraction is fed from tank 37 through lines 38 and 39. This olefinic fraction is diluted with the product of alkylation introduced through line 40 into line 39 from the surge back 41. The mixture of the diluted olefins and isoparaffins and catalyst is then conveyed continuously through line 43 into a mixer 44 wherein it is actively commingled. The mass is then passed through line 45 into a settling chamber 46 wherein the hydrocarbon first separates as the supernatant layer, the catalyst settling in the bottom being withdrawn through line 47. If desired a portion of this catalyst may be returned via 49 to be commingled with fresh quantities of isoparaffinic fraction conveyed through line 31 into mixer 32. The residual spent catalyst may be withdrawn from the system through line 50. The hydrocarbon phase from chamber 46 passes through line 51 into the aforementioned surge tank 41. As stated, a fraction of this alkylated hydrocarbon is continuously withdrawn through line 40 for the purpose of diluting the olefins passing through line 39 into the reaction zone. The remaining fraction which contains the branched chain alkylated hydrocarbons, the unreacted isoparaffins and the paraffinic hydrocarbons, which will be contained in the isoparaffinic and olefinic fractions thus treated, is removed from this first reaction stage through line 52 to be conveyed through the second reaction stage. This hydrocarbon fraction is commingled with optimum quantities of fresh catalyst withdrawn from tank 53 through line 54, the mixture passing through line 55 and through the mixer 56, similar to the above described mixing device 32. Simultaneously and coincidentally a portion of the olefinic fraction is withdrawn from line 38 through line 59 and diluted with the alkylate fraction contained in surge tank 60, this alkylate fraction being withdrawn from said tank 60 through line 61. The thus diluted olefins then pass through line 62 into line 64 wherein it meets the isoparaffin-catalyst mixture from mixer 56. The mass then passes through a second mixing device 65 for the purpose of additional and intimate commingling. As in the first stage the mixture thus produced is then conveyed through line 66 into settling chamber 68. The catalyst settling to the bottom of this chamber is withdrawn through line 69. If desired, a portion of this catalyst may be recycled by conveying it through line 70 into line 55. The remainder of the partially spent catalyst passing through line 34 for the alkylation of new quantities of isoparaffins conveyed into the system through line 31. The alkylate fraction is removed from the top of settler 68 through line 72. This hydrocarbon fraction is then conveyed into the above described surge tank 60 from which a portion of the alkylate fraction may be withdrawn from the system through line 73 for purposes of further treatment if found necessary.

It is thus seen that the multi-stage system described hereinabove is of the type shown in Figure 2. That is, a system in which the olefins are diluted with alkylate and then commingled with the isoparaffin-catalyst mixture. It is, however, obvious that it is possible to modify this system so that the isoparaffins and olefins are diluted with the alkylate fraction before they come in contact with the catalyst. In other words, the process shown in Figure 1 and described hereinabove, may be similarly employed for multi-stage alkylation.

The term "isoparaffins" or "isoparaffinic hydrocarbons" as employed in the present specification and claims relates to the lower members of the series, and particularly to isobutane, isopentane and isohexane. It has been discovered that the rates of alkylation of these isoparaffinic hydrocarbons maintaining other conditions equal are not the same. Thus, the rate alkylate formation when isopentane is used is considerably slower than the alkylation rate of isobutane, while the rate of alkylation of isohexane is even still lower. As to the terms "olefins" and "olefinic hydrocarbons," they relate herein to both the normally gaseous olefins and the normally liquid olefins. It is to be understood that although some catalysts may not cause the alkylation of isoparaffins with ethylenes, the process described and claimed herein includes the use of catalysts and of conditions of operation which favor alkylation with this olefin. It is also to be noted that it is not desirable to employ very high boiling olefins since the alkylation reactions become unfavorable when such olefins are used. Thus, it is preferable, although not absolutely essential, to employ olefinic fractions having not more than about 12 carbon atoms per molecule.

It is to be understood that the reference to isoparaffinic and olefinic hydrocarbons includes the use of these hydrocarbons individually or in mixtures with other hydrocarbons of the same class, as well as mixtures thereof with other hydrocarbons. Therefore, the reference to olefinic hydrocarbons includes hydrocarbon fractions, such as hydrocarbon gases derived from cracking operations and which contain the reactive olefins.

Although the invention is described herein in connection with two preferred embodiments, it is obvious that a number of modifications and rearrangements may be made without departing from the scope of the invention. For example, in some cases and under some circumstances, it may be desirable to eliminate the recirculation of the catalyst. In such a case, the catalyst may be continuously withdrawn from chamber 12 through line 27, and new catalyst introduced into mixer 23 through line 24. Or it may be advantageous to introduce and commingle the catalyst with the hydrocarbons immediately before the introduction of the mixture into the reaction chamber 10. Also, gravity separation of the acid and hydrocarbon phases in chamber 10 may not be found to be sufficiently rapid, in which case, it may be desirable to employ separators, such as centrifugal separators, in conjunction with or in lieu of chambers 11 and 12.

Although the above description was made in connection with the alkylation of the isoparaffins with olefins in the presence of a sulfuric acid catalyst, it is obvious that the process is not limited to a particular catalyst and that other catalysts which favor alkylation of isoparaffins may be employed. Thus, the catalyst may consist of a mixture of sulfuric and phosphoric acids, or may comprise chlorosulfonic acid or certain complexes of aluminum chloride or boron trifluoride. Again, the catalyst may consist of the above acids in combination with certain metallic salts, such as phosphates, sulfates, chlorides, nitrates, and acetates of metals of the type of cadmium, zinc, sil-

ver, mercury, copper, barium, etc. Similarly, it may be advisable to employ certain agents which will remove any water present or formed in situ, it being understood that the presence of water is undesirable, particularly when the acid catalysts are employed.

It is to be understood that the process is not limited to the chemical union of olefins and isoparaffins, but includes the alkylation of other hydrocarbons, such as aromatics. Also, the invention covers the cracking alkylation of aromatics and isoparaffins, this reaction including the step of reacting olefinic molecules with isoparaffinic or aromatic molecules to produce branched chain molecules having a molecular weight less than that which would be obtained if the reaction were of the simple addition type.

Although the invention has been described in connection with the description of certain preferred embodiments, it is to be understood that there is no intention to be limited thereby, the invention being co-extensive with the scope of the appended claims.

I claim:

1. In a process for the alkylation of an isoparaffin with an olefin in the presence of an alkylation catalyst, wherein the isoparaffin and the olefin are continuously fed to the alkylation system and contacted therein with the catalyst under alkylating conditions to produce alkylation reaction products, and the reaction products are settled to separate a catalyst phase from an alkylate phase containing a high proportion of isoparaffin, the improvement which comprises prediluting the olefin feed to the alkylation system with separated alkylate containing a high proportion of isoparaffin prior to contacting the said olefin with the catalyst and precontacting the isoparaffin feed with alkylation catalyst prior to contacting the prediluted olefin with the resulting isoparaffin-catalyst mixture.

2. A process according to claim 1 in which the isoparaffin is isobutane.

3. A process according to claim 1 in which the catalyst is sulfuric acid.

4. A process according to claim 1 in which the isoparaffin comprises isobutane, the olefin comprises butylenes and the catalyst comprises sulfuric acid.

5. In a process for the alkylation of an isoparaffin with an olefin, wherein the isoparaffin and an alkylation catalyst are passed serially through a multiple stage reaction system, each stage comprising a mixing zone and a cooperating settling zone, and wherein the olefin is introduced in portions into a plurality of said stages to react with the isoparaffin in the presence of the catalyst in the mixing zones to produce alkylation reaction products which separate in the cooperating settling zones into catalyst layers and alkylate layers containing a high proportion of isoparaffins, the improvement which comprises introducing at least one of said portions of olefin into a portion of an alkylate layer from one of the settling zones of said plurality of stages to predilute the olefin with alkyate containing a high proportion of isoparaffins prior to bringing the olefin into contact with catalyst.

6. A process according to claim 5 in which the isoparaffin is isobutane.

7. A process according to claim 5 in which the catalyst is sulfuric acid.

8. A process according to claim 5 in which the isoparaffin comprises isobutane, the olefin comprises butylenes and the catalyst comprises sulfuric acid.

9. A process according to claim 5 in which a portion of the catalyst layer separated in the settling zone of each stage is recirculated to the mixing zone of the same stage.

10. In a process for the alkylation of an isoparaffin with an olefin, wherein the isoparaffin and an alkylation catalyst are passed serially through a multiple stage reaction system, each stage comprising a mixing zone and a cooperating settling zone, and wherein the olefin is introduced in portions into a plurality of said stages to react with the isoparaffin in the presence of the catalyst in the mixing zones to produce alkylation reaction products which separate in the cooperating settling zones into catalyst layers and alkylate layers containing a high proportion of isoparaffins, the improvement which comprises introducing the olefin into a portion of the alkylate layer removed from the settling zone of each of said plurality of stages to predilute the olefin with alkylate containing a high proportion of isoparaffins prior to bringing the olefin into contact with catalyst in the mixing zone of the same stage.

11. A process according to claim 10 in which the isoparaffin is isobutane.

12. A process according to claim 10 in which the catalyst is strong sulfuric acid of alkylating strength.

13. A process according to claim 10, in which the flow of catalyst and isoparaffins through said multiple stage reaction system is countercurrent.

14. A process according to claim 10, in which another portion of the alkylate layer from one of the settling zones is contacted with catalyst from the next succeeding zone prior to contacting the prediluted olefin being fed to the next succeeding stage with the resulting alkyate-catalyst mixture.

WILLIAM E. BRADLEY.

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Certificate of Correction

Patent No. 2,435,028. January 27, 1948.

WILLIAM E. BRADLEY

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Column 2, line 23, strike out the word "amount" second occurrence; column 3, line 60, for "anti-detonatting" read *anti-detonating*; column 4, line 5, after the word "alkylation" insert *from the reaction zone, commingling said products of alkylation*; column 5, line 69, for "permit" read *permits*; column 7, line 11, for "surge back 41" read *surge tank 41*; column 8, line 13, after the word "rate" insert *of*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 20th day of April, A. D. 1948.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.