

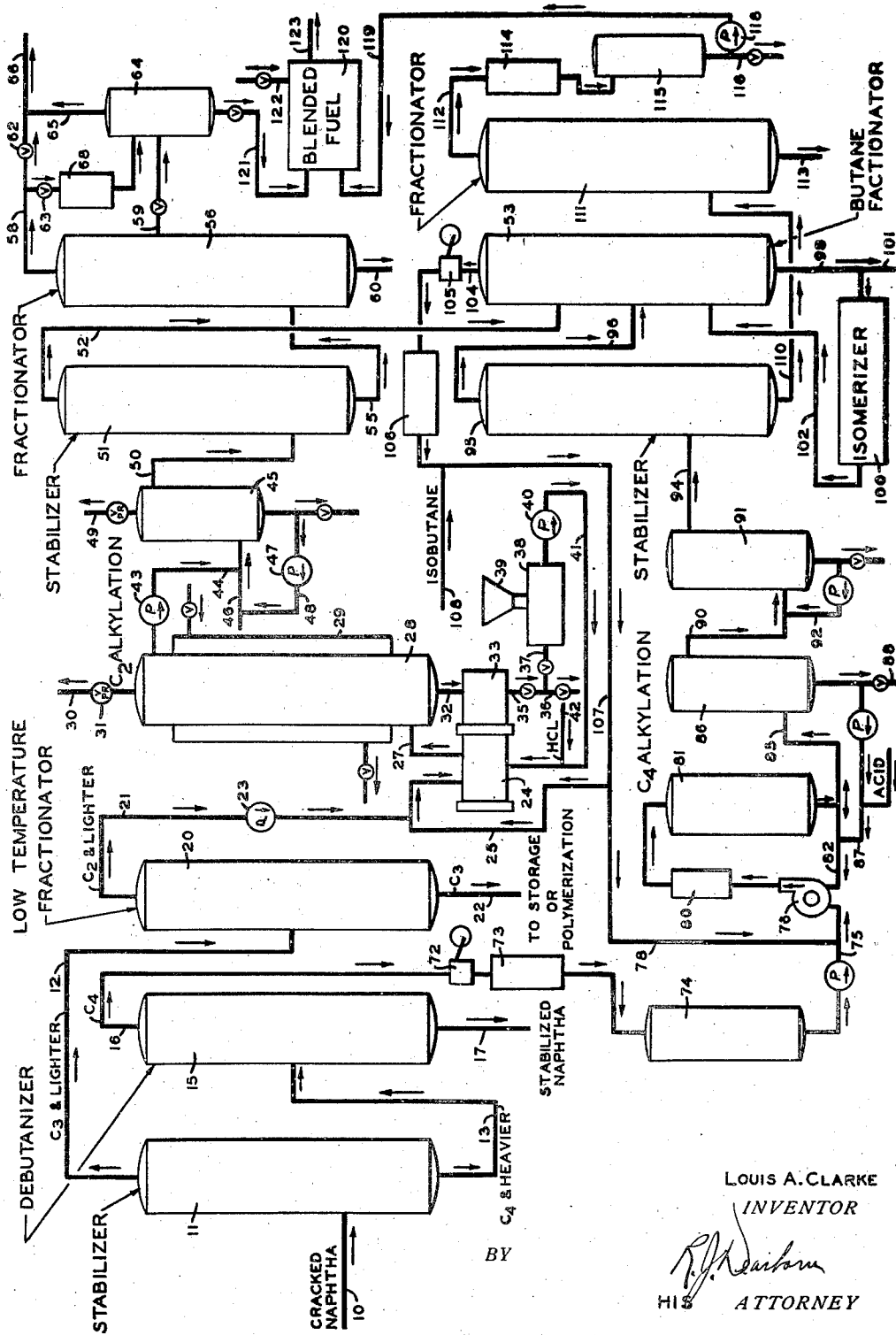
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ALKYLATION OF HYDROCARBONS

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ALKYLATION OF HYDROCARBONS

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This invention relates to the manufacture from normally gaseous hydrocarbons of high anti-knock saturated hydrocarbons suitable for use in the production of motor fuel and aviation gasoline. More particularly, the invention relates to the alkylation of isobutane with ethylene in the presence of an aluminum chloride catalyst for the production of 2,3-dimethyl butane or an alkylate of high anti-knock value containing a high proportion of 2,3-dimethyl butane.

This is a continuation-in-part of my copending applications, Serial No. 324,784, filed March 19, 1940, now Patent No. 2,394,368, and Serial No. 327,575, filed April 3, 1940.

United States Patent No. 2,174,883 has heretofore proposed the alkylation of isobutane with ethylene in the presence of aluminum chloride to produce motor fuel hydrocarbons. In accordance with this patent, solid aluminum chloride is suspended in liquefied isobutane, and precooled ethylene is introduced into the agitated suspension in a batch operation. The temperature of the reaction zone is maintained below 40° C. (104° F.); and a specific example lists a temperature of about 28° C. (82° F.). Less than 10% by weight of aluminum chloride based on the weight of the reacting hydrocarbons together with about 1% by weight of HCl is employed. This batch operation is carried out over a period of four hours, providing an average time of contact of 120 minutes. Under these conditions, a liquid product was obtained consisting of 25% hexane and approximately 20% each of octanes and decanes, with 80% of the product boiling below 150° C. (302° F.), of which the 150° C. end point fraction had a C. F. R. M. octane of 87. The patent also suggests a continuous type of operation wherein liquid isobutane, containing suspended therein the requisite amount of aluminum chloride, is pumped through a tubular treater at the entrance to which it receives the necessary addition of ethylene and hydrogen chloride.

I have discovered that by the use of different and critical conditions of operation, a substantially increased yield of a markedly different and superior type of alkylate consisting largely of the isohexane, 2,3-dimethyl butane, can be produced in continuous operation with greatly increased catalyst life. The process of the present invention can be employed to produce substantially pure 2,3-dimethyl butane in large yields, or can be utilized to produce alkylate containing the high content of 2,3-dimethyl butane and possessing superior qualities of boiling distribution range, higher octane and low volatility or R. V. P., which

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make it an excellent blending stock for motor fuel or aviation gasoline.

One of the principal objects of the present invention is to provide a process for utilizing an available supply of refinery ethylene in the manufacture of a new type of alkylate of superior properties to that which has been heretofore produced from this C₂ olefin.

Another object of the invention is to provide a process for manufacturing 2,3-dimethyl butane in large quantities at reasonable cost from available supplies of ethylene.

Still another object of the invention is to provide an improved continuous process of this character which gives long catalyst life, and is readily carried out and controlled in commercial operation.

A further object of the invention resides in the production of a superior motor fuel or aviation gasoline of improved volatility and boiling range distribution by the blending of the herein described ethylene alkylate, or a fraction consisting largely of 2,3-dimethyl butane, with a conventional C₄ alkylate of high quality. Other objects and advantages of the invention will be apparent from the following description, the accompanying drawing and the appended claims.

In accordance with the present invention, isobutane is alkylated with ethylene in a continuous process wherein a much larger volume ratio of aluminum chloride catalyst to total hydrocarbons is maintained in the reaction zone than has heretofore been proposed, and wherein a much shorter time of contact between the reacting hydrocarbons and the catalyst than has heretofore been suggested, is employed. Thus, a volume ratio of catalyst to total hydrocarbons in the reaction zone in excess of about 0.06:1 is used to obtain the high proportion of isohexanes consisting essentially of 2,3-dimethylbutane by volume of the total liquid alkylate, and of at least 0.2:1, and preferably of the order of about 0.5:1 to 1:1 or higher, to obtain high yields of the desired alkylate on the basis of olefin charged and also greatly improved catalyst life. The time of contact is reduced to less than twenty minutes, and may be as short as about five minutes, and preferably ranges between ten and fifteen minutes. Further, a temperature range somewhat higher than that heretofore proposed has also been found critical in producing the advantageous results of the present invention. Thus temperatures within the range of 105–130° F. or somewhat higher, and preferably about 110–120° F., are employed.

Further, as distinguished from the prior practice in this art, where substantial amounts of a hydrogen chloride promoter of the order of 1% by weight or more based on the hydrocarbon charge have been specified, only very small amounts of HCl promoter less than about 0.2% by weight of the hydrocarbon charge in continuous operation are utilized. Preferably, the proportion of HCl on the basis of the hydrocarbon charge varies from about a trace to about 0.1% by weight. The hydrocarbon charge stocks may contain sufficient water to produce this small amount of HCl by reaction with the aluminum chloride; or small amounts of HCl, water, alkyl chloride or other material producing the minute amount of HCl promoter in the reaction zone can be added continuously or intermittently, such as with the hydrocarbon charge or with the recycled catalyst. Higher proportions of promoter have been found to cause degradation of the product and involve other disadvantages.

The hydrocarbon charge may comprise substantially only ethylene as the olefinic constituent thereof, although minor amounts of propylene may be included. Ordinarily, the propylene content of the charge is limited to not more than about 20% by weight based on the weight of the ethylene, and preferably is about 10% or less by weight of the ethylene content. Higher proportions of propylene result in substantial alteration of the composition of the product with a resultant lowering in octane number thereof and a reduction in catalyst life. The charge may comprise substantially pure hydrocarbons, namely, isobutane and ethylene, or ethylene containing a small proportion of propylene; but preferably refinery fractions are utilized to avoid the expense inherent in effecting separation of the pure compounds.

For example, a C₂ and lighter fraction containing ethylene, ethane, hydrogen and methane and with a small proportion of propylene as specified, can be satisfactorily employed under the conditions stated. The isobutane may be obtained from any suitable source, such as from refinery gas or from natural gas, and may be mixed with a small proportion of normal butane without deleterious results. For example, an isobutane-rich fraction containing about 90-95% isobutane and 10-15% normal butane as regularly produced in commercial debutanizing fractionating equipment is satisfactory. The hydrocarbon charge is continuously added to the agitated reaction zone so as to maintain the isobutane in substantial molar excess of at least about 3:1 and up to about 6:1 and higher with respect to the olefin or ethylene content. Sufficient pressure is utilized to maintain the isobutane in liquid phase. Under these conditions, the gaseous C₂ fraction is intimately mixed with the relatively large body of aluminum chloride catalyst and liquefied isobutane such that the ethylene is rapidly absorbed and reacted with the isobutane to produce the desired normally liquid alkylate. The reaction products pass continuously to a settling zone where a liquid hydrocarbon phase containing the excess isobutane and heavier separates from the catalyst phase, which latter may be continuously recycled, in whole or in part, with suitable fortification with fresh aluminum chloride as needed, to the reaction zone. The fixed and unreacted gases of the C₂ and lighter fraction are released from the settling zone and thus separated from the liquid product which is then

neutralized, stabilized and fractionated into the desired motor fuel fractions.

Under the conditions specified, a debutanized liquid alkylate is obtained which has a volume content in excess of about 70%, and generally about 80-85%, of isohexanes consisting almost entirely of 2,3-dimethyl butane. The remaining content of the alkylate is made up largely of octanes with only a few percent of pentanes and material higher boiling than octanes. Where propylene is present in the charge, a small proportion of heptanes are also produced. At least about 95-98% of the product boils below 311° F. and this fraction has a C. F. R. M. octane in excess of 90 and generally about 92-95.

The debutanized liquid product, being low in pentanes, has generally a lower front and volatility than debutanized C₄ alkylate produced by the conventional processes of catalytic alkylation of low-boiling isoparaffins with C₄ olefins in the presence of alkylating catalysts, such as strong sulfuric acid, HF, BF₃·H₂O complex, and the like. The C₂ alkylate also has a low R. V. P. but, at the same time, has a much lower boiling distribution range, due to the large content of 2,3-dimethyl butane which boils about 136° F., than the conventional C₄ alkylate. The hexane fraction consisting almost entirely of 2,3-dimethyl butane, or the alkylate boiling below about 311° F., constitutes a superior blending stock for the production of motor fuel or aviation gasoline. A highly satisfactory blend for aviation purposes is prepared by blending an aviation fraction of conventional C₄ alkylate with about 10-30% or more of the 2,3-dimethyl butane or the C₂ alkylate, the resulting blend having a C. F. R. M. octane of about 93-95 and which can be easily raised to 100 octane or higher by the addition of a relatively small amount of tetraethyl lead or other suitable anti-knock agent.

For commercial refinery practice, an unstabilized cracked naphtha resulting from either liquid or vapor phase cracking of hydrocarbon oil, can conveniently be utilized to supply the hydrocarbon charge stocks for producing the blended alkylate of the present invention. This naphtha may be stabilized to separate a C₃ and lighter fraction from a C₄ and heavier fraction, which latter is then debutanized to separate the desired C₄ olefinic fraction for conventional C₄ alkylation. The C₃ and lighter fraction may then be separated by low temperature fractionation into an overhead C₂ and lighter fraction containing not more than about 10-20% of propylene on the weight of the ethylene and a bottoms C₃ fraction. The C₂ and lighter fraction is then passed to the C₂ alkylation operation to produce the desirable 2,3-dimethyl butane, which latter is then blended in suitable proportion with the C₄ alkylate. The combination unit may utilize a common butane fractionator for separating the offgases from the stabilization of both the C₂ and C₄ alkylates, as well as isomerization products resulting from the isomerization of normal butane, to provide an isobutane-rich fraction which is recycled and split between the C₂ and C₄ alkylation operations. The various isobutane-normal butane fractions are preferably introduced into the common butane fractionator at different levels according to the isobutane content of the respective streams, thereby affording advantages in fractionation and in obtaining an overhead isobutane-rich fraction having a content of about 95% isobutane or higher. The required isobutane supply for the combination unit may be obtained in major part

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from the normal isobutane content of the cracking gases coupled with the isobutane produced by isomerization of normal butane content of the cracking gases, although additional isobutane can be supplied from a suitable extraneous source.

While under the critical operating conditions for C₂ alkylation, as specified above, solid aluminum chloride in particle or powdered form may be added directly to the liquefied isobutane of the hydrocarbon charge, as proposed in the prior art, this operation is not preferred since substantial advantages in yield and catalyst life are secured by use of the catalyst in different forms. The solid aluminum chloride, when added directly to the hydrocarbons in the reaction zone, provides a suspension which is rather difficult to pump, since it tends to pack when settling and transfer lines are apt to be fouled as a result. Further, the solid aluminum chloride under these conditions tends to pass into a gummy state forming plastic masses such that the fluidity of the catalyst suspension becomes low and it is further difficult to properly disperse the aluminum chloride throughout the reaction zone. Moreover, large amounts of the solid aluminum chloride are required to provide the necessary volume or weight ratios of catalyst to hydrocarbon in the reaction zone under these conditions, and the yield of alkylate per unit weight of catalyst consumed is greatly reduced.

One method of handling the aluminum chloride catalyst in continuous ethylene alkylation is that set forth and claimed in my mentioned copending application, Serial No. 324,784, wherein stationary beds of the solid aluminum chloride in divided or particle form are packed in one or more reaction zones through which the liquefied isobutane and gaseous ethylene are continuously passed, and the aluminum chloride beds are continuously flushed or washed with recycled alkylate to maintain them in active condition. As set forth in that application, a product is obtained from which can be distilled a fraction amounting to 85% by volume and boiling around 136° F., having an octane rating of 95 C. F. R. M. which is of course 2,3-dimethyl butane.

However, it is preferred to utilize the aluminum chloride catalyst in the form of a complex suspension as disclosed in my mentioned copending application, Serial No. 327,575. As set forth in that application, the alkylation catalyst comprises an active metallic halide, such as aluminum chloride, dispersed or suspended in an agitated fluid medium. The fluid medium comprises complex metallic halide-hydrocarbon compounds such as prepared by directly reacting aluminum chloride with paraffin or olefin hydrocarbons or suitable alkyl halides, such as propyl and butyl chlorides. Very satisfactory liquid complexes are obtained by heating aluminum chloride with kerosene or other higher boiling petroleum fraction, such as a higher boiling naphtha or gas oil. However, the preferred catalyst complex liquid is prepared by heating aluminum chloride with tertiary butyl chloride and separating the supernatant liquid product. Other aluminum chloride-hydrocarbon complexes can be employed such as the byproduct liquids resulting from conventional alkylation or isomerization operations with aluminum chloride.

To the body of preformed metallic halide-hydrocarbon complex liquid is added additional solid aluminum chloride to form the so-called complex suspension. This consists of the liquid complex containing suspended solid particles of the active

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aluminum chloride. When utilizing this complex suspension in continuous operation, it appears that mainly the active suspended particles of aluminum chloride are consumed, and the activity of the catalyst can be readily maintained by adding additional solid particles of aluminum chloride to the complex suspension, either continuously or intermittently. It has been found that by maintaining the proportion of liquid complex material to active suspended solid aluminum chloride relatively large, it is possible to maintain the catalyst in an active and effective form over a prolonged period of continuous operation with high economy in the use of aluminum chloride. A large body of the complex suspension relative to the total hydrocarbons maintained in the reaction zone can thereby be used and maintained in pumpable condition over long periods of operation, and at the same time effective contact between the suspended particles of active solid aluminum chloride and the reacting hydrocarbons are secured.

In the preparation of the aluminum chloride-hydrocarbon complex liquid, the proportions of the aluminum chloride and the hydrocarbon or alkyl chloride can be varied materially, since the aluminum chloride reacts with the oil to form a liquid complex and unreacted oil can later be separated from the liquid complex by stratification. An excess of the aluminum chloride on the basis of the oil may be used, and the complex liquid then separated from the excess aluminum chloride sludge. By way of example, one gallon of kerosene was heated to 220-240° F. in a mixer equipped with a stirring device, and 400 grams of aluminum chloride were introduced and reacted over a period of about eight hours. The reaction products were then allowed to stratify and any supernatant unreacted kerosene layer removed. Any unreacted aluminum chloride or solid sludge was then separated from the mobile liquid complex by decanting the latter therefrom.

The most effective complex liquid was prepared by reacting one part by weight of anhydrous aluminum chloride with about 2.5 parts of tertiary butyl chloride at about room temperature. This particular complex liquid, following separation from any unreacted aluminum chloride in the manner previously described, was found to possess greater fluidity and retained its fluidity over longer periods of use in the process.

Any of the above complex liquids themselves are comparatively ineffective in the present reaction of alkylating isobutane with ethylene, giving poor yields of a product which is generally lower in 2,3-dimethyl butane content, similar to that produced when solid aluminum chloride is added directly to the reacting hydrocarbons in the relatively small amounts previously employed. However, when a small proportion of solid aluminum chloride is added to and retained in suspension in the complex liquid, a superior catalyst for purposes of the present invention is obtained. The amount of solid aluminum chloride maintained in suspension in the complex can vary within wide limits, it being merely sufficient to have enough particles of suspended aluminum chloride thoroughly distributed throughout the large body of complex to provide effective contact between these particles and the reacting hydrocarbons. Generally, solid aluminum chloride in particle form is added to the complex liquid in the proportion of about 600 cc. of the complex liquid to 25-300 grams of aluminum chloride, and preferably about 600 cc. of complex liquid to 200 grams

of aluminum chloride, which is equivalent to about one part by weight of suspended solid aluminum chloride to four parts of the complex liquid.

In continuous operation with the complex suspension catalyst, very satisfactory results have been secured with a rotary type reactor of the character of a centrifugal pump having large clearances between the impeller and rotor housing. The hydrocarbon charge is continuously fed into the reaction zone within the rotor housing where it is intimately mixed with the large body of catalyst and hydrocarbons undergoing reaction. A stream of the reaction products is continuously discharged from the periphery of the rotor housing into a vertical water-jacketed settler, where the catalyst rapidly settles and separates from an upper hydrocarbon layer, and from which the lower catalyst suspension layer is returned by a short connecting line of large diameter to the feed inlet of the rotor housing.

However, various other types of conventional continuous mixers can be employed, such as a turbo-mixer having an interior mixing cone spaced from an exterior shell or casing with means for creating continuous recirculation of the contents through the cone and back through the annular channel between the cone and exterior shell. In this latter type of mixer, the hydrocarbon charge is generally fed into the recirculating stream opposite a constriction within the cone, and a stream of the reaction products is continuously withdrawn from an upper portion of the shell to the settler.

A portion of the catalyst may be continuously or intermittently withdrawn from the system and replaced with fresh catalyst. Particularly advantageous results have been secured by withdrawing a larger proportion of the catalyst from the recirculating body thereof than is to be discharged from the system, then discharging a minor proportion thereof, adding fresh solid aluminum chloride to the remaining major portion thereof, and returning the resultant revived complex suspension to the reaction zone.

In my mentioned copending application, Serial No. 324,784, the method of continuous operation with the fixed catalyst bed which is continuously flushed with recycle alkylate, as applied to the alkylation of low-boiling isoparaffins with olefins generically, is claimed. In my application Serial No. 515,649, filed December 27, 1943, as a continuation in part of my mentioned copending application, Serial No. 327,575, the method of continuous operation employing the activated complex type of catalyst, as applied to the alkylation of isobutane with ethylene, is claimed. In the present application, there is claimed the continuous alkylation of isobutane with ethylene in the presence of an aluminum chloride catalyst under the critical conditions set forth to produce 2,3-dimethyl butane or an alkylate consisting largely of 2,3-dimethyl butane, together with the combination of C₂ alkylation with C₄ alkylation to produce a blended aviation gasoline. In my application Serial No. 452,061, filed July 23, 1942, and Serial No. 484,765, filed April 27, 1943, the motor fuel comprising isobutane ethylene alkylate consisting mainly of 2,3-dimethylbutane, and motor fuel blends of this alkylate, are claimed.

In order to describe the invention further, reference will now be made to the accompanying drawing which is a flow diagram illustrating a preferred embodiment of a combination process for continuously producing C₂ and C₄ alkylates

and a blend thereof in a continuous manner from refinery cracking gases or an unstabilized cracked naphtha.

Referring to the drawing, an unstabilized cracked naphtha as obtained in conventional liquid phase or vapor phase cracking of hydrocarbon oil is supplied by line 10 to a stabilizer 11 from which an overhead fraction of C₂ and lighter is removed by line 12 and a bottoms of C₄ and heavier by line 13. The bottoms is fed into a debutanizer 15 from which an overhead C₄ stream is removed by line 16 and a bottoms streams of stabilized naphtha by line 17.

The overhead stream from line 12 is passed into a low temperature fractionator 20 which is operated under conditions to effect separation between an overhead C₂ and lighter fraction removed by line 21 and a bottom C₃ fraction removed by line 22 for further utilization as may be desired. Fractionator 20 is operated so that the C₂ and lighter fraction contains not more than about 10% by weight of propylene on the basis of the ethylene therein. It is of course obvious that the light fraction can be substantially denuded of all hydrocarbons heavier than C₂, although a minor proportion of propylene can be tolerated without deleterious results on the yield or quality of the product, and the small proportion of propylene serves to maintain the desired fluidity of the complex suspension catalyst over longer periods of operation.

A pump 23 forces the C₂ and lighter fraction into a continuous reactor 24 of a type heretofore described. A stream of liquefied isobutane is introduced by line 25 so as to mix with the C₂ and lighter fraction prior to contact of the latter with the complex suspension catalyst maintained in the reaction zone within the housing of rotor 24. The proportion of isobutane is regulated to provide the desired large molar excess on the basis of the olefin charged, as set forth above. A quantity of complex suspension catalyst is maintained within the circulating system, so that a volume ratio of catalyst to total hydrocarbons of the order previously stated is continuously maintained within the reaction zone.

Reaction products are continuously discharged by line 27 into the lower portion of a vertical settler 28 equipped with a water jacket 29, whereby the temperature of both the reaction and settling zone is maintained at about 105-130° F. or somewhat higher. In settler 28, stratification into a lower complex suspension catalyst layer, an upper liquid hydrocarbon layer, and a supernatant atmosphere of fixed and unreacted gases occurs. These gases comprising the unreacted ethane, methane and hydrogen are released from the upper portion of settler 28 by line 30 equipped with pressure release valve 31. Catalyst is continuously returned by the large diameter line 32 to the inlet 33 of rotor 24.

In order to maintain the activity of the catalyst during long periods of continuous operation, a portion of the circulating catalyst body is withdrawn by valve controlled line 35 connecting with valve controlled discharge line 36 and valve controlled line 37. The major portion of the withdrawn catalyst preferably passes by line 37 into a mixer 38 equipped with suitable feed hopper 39 through which makeup solid aluminum chloride is supplied to the contents within mixer 38. The revived complex suspension is returned by pump 40 through line 41 to the reaction zone. A line 42 provides for the introduction of any re-

quired amount of HCl into the recycled catalyst stream passing to the reactor.

The unstabilized hydrocarbon liquid within settler 28 is continuously removed by pump 43 controlled by a constant leveling device and passed through line 44 into a neutralizer 45 wherein it is treated and neutralized by caustic soda solution supplied through line 46. The neutralized hydrocarbons separate into a supernatant layer from a lower caustic solution layer, which latter may be continuously recirculated by pump 47 and recycle line 48. Any remaining light gaseous hydrocarbons may be removed from the upper portion of neutralizer 45 by line 49 containing a suitable pressure release valve.

The neutralized hydrocarbons pass by line 50 into the stabilizer 51 wherein the alkylate is debutanized. The removed gases consisting essentially of the excess isobutane together with a minor proportion of normal butane are passed by line 52 to a common butane fractionator 53 to be hereinafter further described.

The stabilized C₂ alkylate passes from the lower portion of stabilizer 51 through line 55 to fractionator 56 where the alkylate is separated into the desired motor fuel fractions. Where the object is to produce substantially pure 2,3-dimethyl butane, the fractionator may be operated to take overhead by line 58 any C₆'s, and to remove by side stream 59 a close-cut hexane fraction having a boiling range of about 125-150° F., the remaining alkylate being discharged as bottoms by line 60 for use in motor fuel manufacture or other suitable purpose. In this case, valve 62 is open and valve 63 is closed. The side stream passes into an accumulator 64 from which vaporized hydrocarbons may be removed by overhead line 65 connecting with the gas discharge line 66 through which the gaseous products may be led to suitable condensers for recovery of the desirable pentane fraction. Inasmuch as this fraction contains a high proportion of isopentane, it may be led to a further fractionator where substantially pure isopentane may be recovered for blending stock.

If desired, fractionator 56 may be operated to take overhead a C₅-C₆ fraction; and in this case valve 62 is closed and valve 63 is opened so that the fraction passes through condenser 68 into accumulator 64, the side stream 59 being closed. Where the entire alkylate boiling within the aviation range is desired, fractionator 56 may be operated to take overhead a 311° F. end point fraction which passes through condenser 68 into accumulator 64, and only the small higher boiling bottoms is removed by line 60. While a single fractionator 56 has been shown, it is of course obvious that one or more fractionators may be employed in series, whereby any desired close-cut fraction such as substantially pure 2,3-dimethyl butane may be obtained.

The overhead C₄ olefinic fraction removed from debutanizer 15 by line 16 is forced by compressor 72 through cooler 73 into storage accumulator 74. From here, the liquefied C₄ fraction is passed through line 75 into mixer 76 of a conventional C₄ alkylation system. Isobutane for the C₄ alkylation is supplied by branch line 78 so as to provide the desired molar excess of isobutane to olefin in the reactor 76. It is to be understood that any conventional C₄ alkylation system which is capable of producing a high grade of C₄ alkylate, such as an aviation fraction having a C. F. R. M. octane of about 92-96 can be employed. Any of the conventional catalysts for this pur-

pose, such as strong sulfuric acid, HF, BF₃·H₂O complex, chlorosulfonic acid, etc., may be used. The system illustrated is the so-called pump and time tank arrangement of U. S. Patent No. 2,232,674, involving a centrifugal type of pump 76 forcing reaction products through a cooler 80 into a baffled time tank 81. Preferably, strong sulfuric acid is used with this system, and the reaction products are in the form of an acid-hydrocarbon emulsion, a substantial proportion of which is continuously recycled by line 82 to provide a high contact ratio of isoparaffin to olefin at the point of contact of the olefin with the catalyst, as is well understood. The conditions of temperature, acid to hydrocarbon ratio, time of contact and other factors for conventional C₄ alkylation are well understood and need not be further described. The conditions for sulfuric acid alkylation may be those set forth in U. S. Patents Nos. 2,260,943 and 2,211,747. The conditions for HF alkylation may be those described in U. S. Patent No. 2,267,730. The conditions for C₄ alkylation with BF₃·H₂O complex may be those set forth in copending application of Frank H. Bruner, Serial No. 271,746, now Patent No. 2,345,095. The conditions for chlorosulfonic acid alkylation may be those set forth in U. S. Patent No. 2,255,610. Inasmuch as no claims are presented herein to the C₄ alkylation per se, further description of this step is thought unnecessary.

A minor proportion of the recirculating emulsion is withdrawn by line 85 to settler 86, where acid is separated and recycled by line 87 or discharged by line 88. Unstabilized hydrocarbons flow by line 90 into caustic neutralizer 91 where they are neutralized by caustic soda solution recycled by line 92. The neutralized hydrocarbons pass by line 94 into stabilizer 95 where the C₄ alkylate is debutanized. An overhead gaseous fraction consisting of the excess isobutane and the normal butane included in the C₄ charge to the unit, a portion of which came from the refinery cracked gases and another portion from any makeup butane fraction from natural gas or other source, is passed by line 96 to the common butane fractionator 53, wherein these gases are fractionated together with the overhead gases from the stabilization of the C₂ alkylate supplied by line 52.

A bottoms fraction consisting essentially of normal butane is removed by line 98 and any portion thereof passed to a conventional isomerization unit 100, any excess being discharged by line 101. In the isomerization unit 100, the normal butane is converted to the extent of about 50-60% or more by volume into isobutane, such as by treatment in well known manner with conventional isomerization catalysts of the character of aluminum chloride, as disclosed in U. S. Patents Nos. 2,271,860, 2,208,362, 2,249,366 and 2,266,011. As the isomerization step per se forms no part of the present invention, further description thereof is thought unnecessary.

The resulting isomerized products are returned by line 102 to the fractionator 53. Preferably, the points of introduction of lines 52, 96 and 102 into fractionator 53 are at different levels, depending upon the isobutane content of the materials handled by these various lines. The overhead gases from the stabilization of the C₂ alkylate being highest in isobutane content are introduced adjacent the upper end of the butane fractionator. The isomerization products of line 102,

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being generally lowest in isobutane content, are introduced below the mid-portion of the fractionator; and the offgases from the stabilization of the C₄ alkylate, which generally run in excess of 60% by volume of isobutane, are introduced at about a mid-point. With suitable reflux, as is well known, it is possible to take overhead by line 104 an isobutane-rich fraction consisting of about 95% or more of isobutane by volume. This fraction is compressed and liquefied by compressor 105 and cooler 106, and recycled by line 107 and split between lines 25 and 78 to supply the requirements of the C₂ and C₄ alkylation systems respectively. Any additional isobutane required for the combination processes may be introduced from an extraneous source by line 108.

The stabilized C₄ alkylate is removed as bottoms from stabilizer 95 by line 110 and introduced into fractionator 111 where an aviation fraction of about 311° F. end point may be taken overhead by line 112 and separated from a bottoms fraction which is removed by line 113. The aviation fraction passes through suitable condenser 114 into accumulator 115, from which any desired portion thereof may be discharged for use as motor fuel or aviation stock by the valve controlled line 116.

Any suitable proportion of the aviation fraction may be passed by pump 118 and line 119 into blending tank 120, to which is also supplied any desired proportion of blending stock from accumulator 64 by line 121. In this manner, the boiling range distribution of the C₄ alkylate can be desirably lowered without lowering the R. V. P. or the octane thereof. The 2,3-dimethyl butane or C₂ alkylate fraction consisting largely of 2,3-dimethyl butane thus constitutes a new source of

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gasoline specifications, thereby materially increasing the potential supply of this material. A suitable quantity of tetraethyl lead or other anti-knock agent can be added by line 122 to the blended fuel in tank 120, to provide an aviation gasoline of 100 octane or higher. It is to be understood that conventional base fuels, such as high anti-knock straightrun gasoline, can also be blended with this fuel when desired. The resultant blended fuel is discharged by line 123 to suitable tankage or for use.

While the C₄ alkylation step has been described above as applied specifically to the alkylation of low-boiling isoparaffins with C₄ olefins, it is to be understood that other olefinic charge stocks including C₅ olefins, olefin polymers such as diisobutylene, tri-isobutylene and cross-polymers of isobutylene and normal butylene and the like, and mixtures thereof, can be employed in this step, so long as a high-grade alkylate of broad boiling range having a C. F. R. M. octane above 90 is produced. The expressions "C₄ alkylation" and "C₄ alkylate" are employed in the description and claims for convenience in designating this step and the product produced thereby to include these various olefinic charge stocks as well as the C₄ olefins, which produce the high-grade alkylate of the character specified.

By way of example, the following runs are listed which have been carried out in accordance with the critical operating conditions set forth above. Each of these runs was carried out continuously in a rotary reactor of the character described with continuous recirculation of the complex suspension catalyst without revivification or the addition of fresh aluminum chloride, in order to obtain a measure of catalyst life:

	Run 1	Run 2	Run 3
Olefin.....	Ethylene.....	Ethylene.....	Ethylene.....
Isoparaffin.....	Isobutane.....	Isobutane.....	Isobutane.....
Catalyst.....	200 grams aluminum chloride.	600 cc. kerosene-aluminum chloride complex + 200 grams aluminum chloride.	600 cc. tertiary butyl chloride-aluminum chloride complex + 200 grams aluminum chloride.
Mol ratio, isobutane:ethylene.....	4.34.....	4.34.....	4.34.....
Temperature, ° F.....	105-110.....	110.....	110.....
Contact time in mins.....	18.....	11.....	11.....
Volume ratio, catalyst to hydrocarbons in reactor.....	About 0.06:1.....	About 0.8:1.....	About 0.8:1.....
Charge rate of hydrocarbons in pounds per hour.....	6.....	6.....	6.....
Total debutanized alkylate: Weight per cent yield basis of olefin.....	180.....	226.....	238.....
311° F. end point fraction:			
Volume per cent of alkylate.....	97.6.....	98.8.....	98.9.....
Bromine number.....	0.....	0.....	0.....
C. F. R. M. octane number.....	92.7.....	93.8.....	95.0.....
A. S. T. M. distillation of debutanized alkylate:			
I. B. P. ° F.....	110.....	132.....	129.....
10 per cent.....	130.....	137.....	136.....
20 per cent.....	139.....	140.....	138.....
30 per cent.....	144.....	141.....	140.....
40 per cent.....	148.....	142.....	142.....
50 per cent.....	152.....	144.....	144.....
60 per cent.....	157.....	146.....	146.....
70 per cent.....	164.....	149.....	148.....
80 per cent.....	182.....	159.....	155.....
90 per cent.....	225.....	197.....	181.....
95 per cent.....	245.....	232.....	232.....
E. P.....	264.....	273.....	260.....
Volume per cent hexane fraction of debutanized alkylate.....	73.5.....	85.0.....	85.1.....
Higher than hexanes, volume per cent.....	About 22.....	15.0.....	14.9.....
Total gallons 2,3-dimethyl butane per pound of free aluminum chloride.....	5.1.....	15.6.....	20.2.....

supply of blending stock for C₄ alkylate which is as good as, if not better than, isopentane for this purpose. As the 2,3-dimethyl butane is less volatile than isopentane, larger quantities of the former can be added to a given amount of C₄ alkylate, and the blended fuel still will meet aviation

The kerosene-aluminum chloride complex and the tertiary butyl chloride-aluminum chloride complex of the above runs were prepared according to the specific examples given above. As will be noted from the table, run 1 employing a volume ratio of catalyst to hydrocarbons in the

reactor of about 0.06:1 at a temperature of 105–110° F. and a contact time of 18 minutes produced a total liquid or debutanized alkylate containing 73.5% by volume of hexanes, with 97.6% by volume of the total alkylate boiling below 311° F. From the A. S. T. M. distillation data on the debutanized alkylate, showing a very slow rate of temperature rise between the 20% point at 139° F. and the 60% point at 157° F., coupled with the high CFRM octane number of 92.7 for the 311° F. end point fraction of the alkylate, it is clearly evident that this hexane fraction consisted primarily of 2,3-dimethylbutane. However, at this low catalyst to hydrocarbon volume ratio in the reactor, a low yield of only 180% by weight based on the olefin charged was obtained; and a low catalyst life of only 5.1 gallons of 2,3-dimethylbutane per pound of free aluminum chloride was secured. In a run made under essentially similar conditions to run 1, except that the amount of solid aluminum chloride added to the reaction zone was approximately doubled, a yield of total debutanized alkylate of 189% by weight on the basis of the olefin charged was obtained, of which approximately 77% by volume boiled within the hexane fraction, and the 311° F. end point fraction had a C. F. R. M. octane of 90.0. The catalyst life was also low in this run, being less than half of the life of the complex suspension catalyst in runs 2 and 3 above. Where it is attempted to use a higher volume ratio of solid aluminum chloride distributed in the hydrocarbons in the reaction zone, difficulties of pumping due to the gummy character of the catalyst are encountered, with objectionably low catalyst life. The use of the complex suspension catalyst has been found to overcome these difficulties. The use of a low volume ratio of solid aluminum chloride suspended in the reacting hydrocarbons at conditions outside of the critical ranges set forth, such as at a temperature of about 100° F. and lower, gives still further reduction in yield of the hexane fraction. Batch operation with solid aluminum chloride mixed directly with the reacting hydrocarbons gave an inferior alkylate having a C. F. R. M. octane generally below 90, and a hexane fraction substantially below 70% by volume. Longer times of contact than about twenty minutes in continuous operation give rise to degradation reactions with loss of catalyst life, producing an inferior alkylate having a lower volume percentage of 2,3-dimethyl butane. A shorter contact time than about five minutes generally involves difficulties in settling and carry-over of catalyst, although the product is of fair quality.

A small proportion of propylene in the charge has been found to give an alkylate having a definite heptane content with a slightly lower hexane content and generally a slight rise in the pentane content. The octane number may also be reduced about 1–2 points. With proportions of propylene below about 10% on the weight of the ethylene, a good quality product was obtained with high catalyst life and the maintenance of improved fluidity of the recirculating catalyst. Runs made with slightly more than about 20% propylene on the weight of the ethylene, gave inferior alkylates having substantially less than 70% by volume of hexanes, and a catalyst life of only about half of that obtained with the lower propylene percentage.

It was thought that a small percentage of propylene in the charge might have a promoting

effect upon the alkylation of ethylene permitting the use of lower temperatures. However, this was found not to be the case. Runs made with about 10% propylene on the weight of the ethylene in the charge at 78–85° F. gave extremely poor yields of alkylate and low catalyst life. A temperature of at least about 105–110° F. was found to be critical in this case, as well as with a straight ethylene charge, in producing the desired high yields of good quality alkylate of the present invention with catalyst life on the order of 16.5 gallons of alkylate per pound of aluminum chloride and higher.

The effect of HCl concentration in the hydrocarbon charge above the critical range specified heretofore is particularly evident in a sharp reduction in lead susceptibility of the alkylate. Even a proportion as low as 0.13% HCl by weight on the hydrocarbon charge gave a substantial reduction in lead susceptibility of the alkylate, as is evident from the following clear and leaded octanes obtained on typical 311° F. end point fractions of alkylates prepared from isobutane-ethylene charges containing a small proportion of propylene in accordance with the present invention:

	Alkylate fraction prepared with 0.13% by weight of HCl in charge	Alkylate fraction prepared with merely trace of HCl in hydrocarbon charge
Clear octane No. C. F. R. M.	90.9	90.7
+0.5 cc. TEL/gallon....	91.7	95.8
+1.0 cc. TEL/gallon....	94.5	Iso-octane+0.03 cc. TEL/gallon.

A very small proportion of HCl varying from a trace to about 0.1% by weight on the hydrocarbon charge appears advantageous in continuous operation for the purpose of lowering the aluminum chloride requirement for equilibrium operation and the maintenance of satisfactory complex fluidity.

The following table sets forth tests which have been obtained on a typical ethylene-isobutane alkylate prepared in accordance with the present invention, a conventional C₄ alkylate and two blends thereof:

	100% C ₄ alkylate	100% ethylene-isobutane alkylate	90% C ₄ alkylate, 10% ethylene alkylate	80% C ₄ alkylate, 20% ethylene alkylate
Gravity °A. P. I.	70.9	80.7	71.7	72.7
ASTM distillation:				
I. B. P., °F.	111	110	105	103
10%.....	180	130	168	160
20%.....	199	135	188	177
30%.....	210	140	200	188
40%.....	217	142	210	199
50%.....	222	144	218	209
60%.....	225	146	222	218
70%.....	229	150	228	225
80%.....	234	155	233	231
90%.....	245	184	243	243
End point.....	310	257	310	302
R. V. P. pounds per square inch.....	5.4	10.1	6.3	6.0
Octane No. C. F. R. M.	92.3	94.5	92.9	93.1

Even though the above ethylene alkylate had not been stabilized to completely debutanize the same, as is evident from the high R. V. P., it is to be noted that the blends of this ethylene alkylate with the C₄ alkylate did not materially increase the R. V. P. of the latter. Moreover, the 50% point of the C₄ alkylate was substantially reduced by blending with the ethylene alkylate

while a slight increase in C. F. R. M. octane was realized.

It is of course obvious that the ethylene alkylate can be blended with other motor fuel fractions, such as aviation base fuels, motor fuels, and mixtures thereof with C₄ alkylate, to improve the front end volatility and octane thereof, without any substantial increase in the R. V. P. It is therefore evident that the present invention provides an efficient and economical process for producing a superior blending agent or alkylate from ethylene which has heretofore been thought less desirable than other normally gaseous olefins as an alkylating agent, due to the fact that ethylene reacts with difficulty in the presence of most alkylation catalysts, and alkylates of relatively poorer octane had been experimentally produced from this olefin with aluminum chloride under the conditions heretofore proposed.

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.

I claim:

1. The method of manufacturing a motor fuel of high anti-knock value and relatively low-boiling range but of unusually low volatility for that boiling range, which comprises alkylating isobutane with essentially ethylene and not more than 20% by weight of propylene based on the ethylene as the olefinic constituent in the presence of a relatively large body of aluminum chloride catalyst providing a volume ratio of catalyst to hydrocarbons in the reactor in excess of 0.06:1 at a temperature of about 105–130° F., under sufficient pressure to maintain isobutane in the liquid phase and a contact time of about 5–20 minutes to thereby produce a total normally liquid alkylate boiling almost entirely below 311° F. and containing at least 70% by volume of isohexanes consisting essentially of 2,3-dimethyl butane, the balance being mainly octanes and heptanes with only a few percent of pentanes, whereby the said ethylene alkylate has a relatively low-boiling distribution range but at the same time a low volatility and R. V. P. and a C. F. R. M. octane in excess of 90, separately alkylating isobutane with C₄ olefins substantially free from propylene in the presence of an effective alkylation catalyst other than a metallic halide capable of producing a broad boiling range alkylate within the aviation gasoline boiling range of high octane content and a substantially higher boiling distribution range than said ethylene alkylate, separating a debutanized broad boiling range fraction boiling within the aviation gasoline range and having a C. F. R. M. octane of at least 90 from said C₄ alkylate, and blending a fraction of said ethylene alkylate containing the C₅–C₆ content thereof with the said aviation fraction of the C₄ alkylate in a proportion to add about 10–30% by volume of 2,3-dimethylbutane to materially lower the 50% boiling point of said aviation fraction of C₄ alkylate without materially raising the R. V. P. thereof, and at the same time improving the antiknock characteristics of said C₄ alkylate.

2. The method according to claim 1 wherein unstabilized cracked naphtha is fractionated to separate a C₃ and lighter fraction from a C₄ and heavier fraction, the said C₃ and lighter fraction is subjected to low temperature frac-

tionation to separate a C₂ and lighter fraction containing a small proportion of propylene which is less than 10% by weight on the weight of the ethylene content thereof, the said C₄ and heavier fraction is stabilized to separate a C₄ fraction, and the said C₂ and lighter fraction and the said C₄ fraction are supplied respectively to the said ethylene and C₄ alkylation operations.

3. The method in the manufacture of aviation gasoline which comprises alkylating isobutane with a C₂ cracked gas fraction containing ethylene and not more than 10% by weight of propylene on the basis of the ethylene in the presence of an aluminum chloride catalyst under alkylating conditions including a substantial molar excess of isobutane to ethylene, a volume ratio of catalyst to hydrocarbons in the reaction zone in excess of 0.06:1, a temperature of 105 to about 130° F., sufficient pressure to maintain isobutane in liquid phase, a proportion of added promoter sufficient to provide HCl in the reaction zone in an amount less than 0.2% by weight of the hydrocarbon charge, and a contact time of about 5–20 minutes to produce a total C₂ alkylate containing a major proportion by volume of 2,3-dimethylbutane, alkylating isobutane with a C₄ cracked gas fraction containing butylenes in the presence of an effective alkylation catalyst other than a metallic halide to produce a C₄ alkylate containing a high proportion of octanes, separating gases lighter than C₄ from the C₂ alkylate, debutanizing the resultant C₂ alkylate and the C₄ alkylate, blending debutanized C₂ alkylate with debutanized C₄ alkylate, combining offgases from the debutanization of the C₂ alkylate with offgases from the debutanization of the C₄ alkylate and fractionating the combined offgases to separate an isobutane-rich fraction from a normal butane fraction, and recycling and splitting the isobutane-rich fraction between the C₂ and C₄ alkylation operations.

4. The method according to claim 3, wherein at least a portion of the normal butane fraction is isomerized to form isobutane, and isomerization products are returned to the combined offgas fractionating step.

5. The method according to claim 3, wherein the normal butane fraction is isomerized to form isobutane, isomerization products are returned to the combined offgas fractionating step, and the points of entry of the isomerization products, the C₄ alkylate offgases and the C₂ alkylate offgases into the common fractionator are at progressively higher levels in accordance with the isobutane content of the respective streams.

6. In the continuous alkylation of isobutane with ethylene in the presence of an aluminum chloride alkylation catalyst, wherein isobutane and ethylene are continuously fed into an alkylation reaction zone containing an aluminum chloride catalyst, reaction products are continuously discharged from said zone and a stabilized hydrocarbon alkylate recovered from said products, the improvement which comprises maintaining the molar ratio of isobutane to olefin in excess of about 3:1, providing an olefin feed containing ethylene as the essential olefinic component with not more than about 20% by weight based on the ethylene of other olefins including propylene, providing sufficient pressure to maintain the isobutane in liquid phase, maintaining the temperature of the reaction zone within the range of 105° F. to about 130° F., maintaining the catalyst to hydrocarbon volume ratio in the reaction zone in excess of about 0.06:1, adding to the reaction

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zone a small amount of material selected from the group consisting of HCl, water and alkyl chlorides which provides HCl promoter in the reaction zone in an amount equivalent to not substantially more than about 0.2% by weight of HCl on the basis of the hydrocarbon charge, and providing a contact time within the reaction zone of less than 20 minutes but not less than about 5 minutes, whereby an overall normally liquid alkylate is produced containing a major proportion by volume of hexanes consisting primarily of 2,3-dimethylbutane.

7. The method according to claim 6, wherein the catalyst to hydrocarbon volume ratio in the reaction zone is in excess of 0.2:1, whereby improved catalyst life and yield of alkylate are obtained.

8. The method according to claim 6, wherein the HCl on the basis of the hydrocarbon charge

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is not more than about 0.1% by weight, whereby the alkylate has improved lead susceptibility.

9. The method according to claim 6, wherein the olefin feed is a refinery fraction containing propylene in addition to ethylene as the only olefinic constituents, the proportion of propylene in said fraction being not more than about 10% by weight of the ethylene contained therein, whereby improved catalyst life and higher yields of the isohexanes are obtained.

10. The method according to claim 6, wherein the overall normally liquid alkylate is fractionated to separate material higher boiling than C₆ hydrocarbons, whereby an alkylate fraction is obtained containing not more than a few per cent of material other than hexanes, said hexanes consisting primarily of 2,3-dimethylbutane.

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