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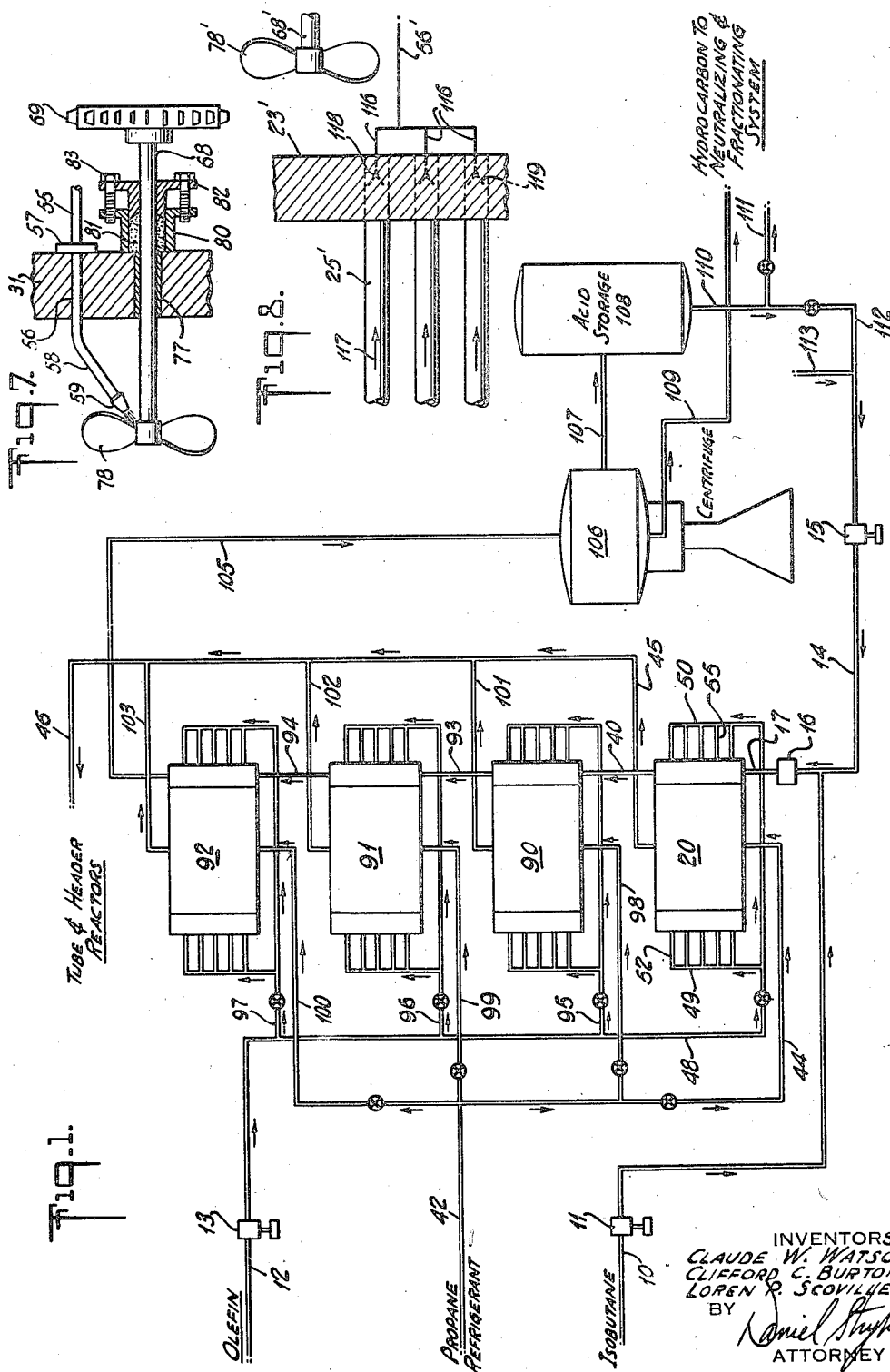
C. W. WATSON ET AL

2,474,924

ALKYLATION METHOD

Filed June 21, 1945

2 Sheets-Sheet 1



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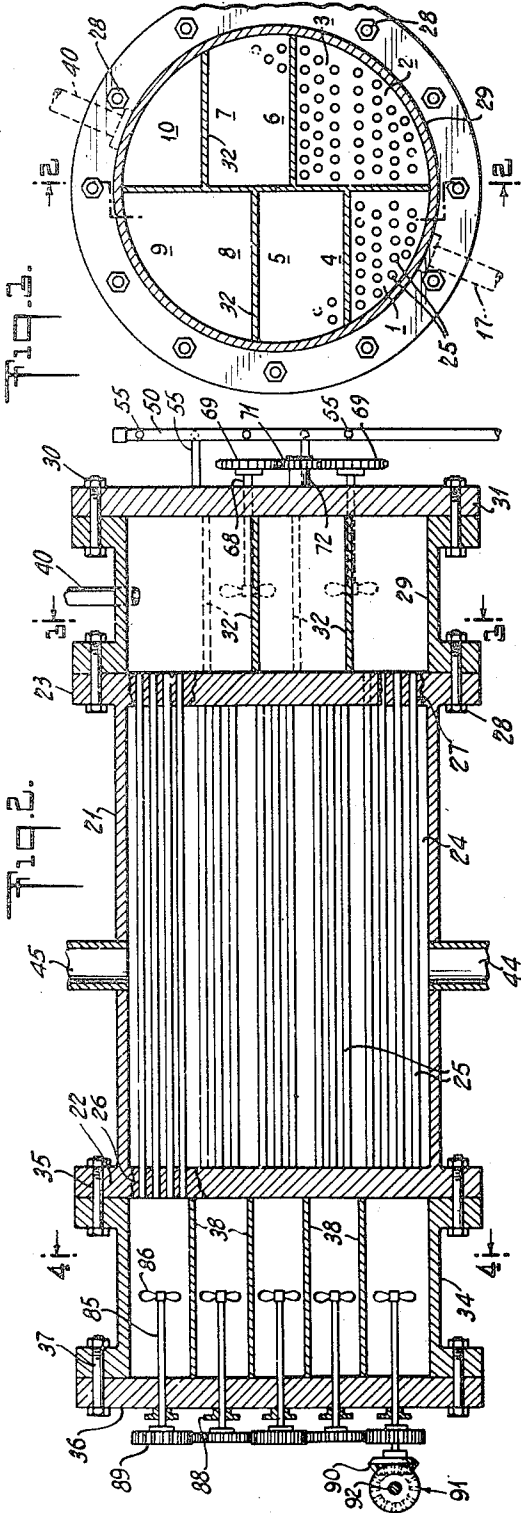
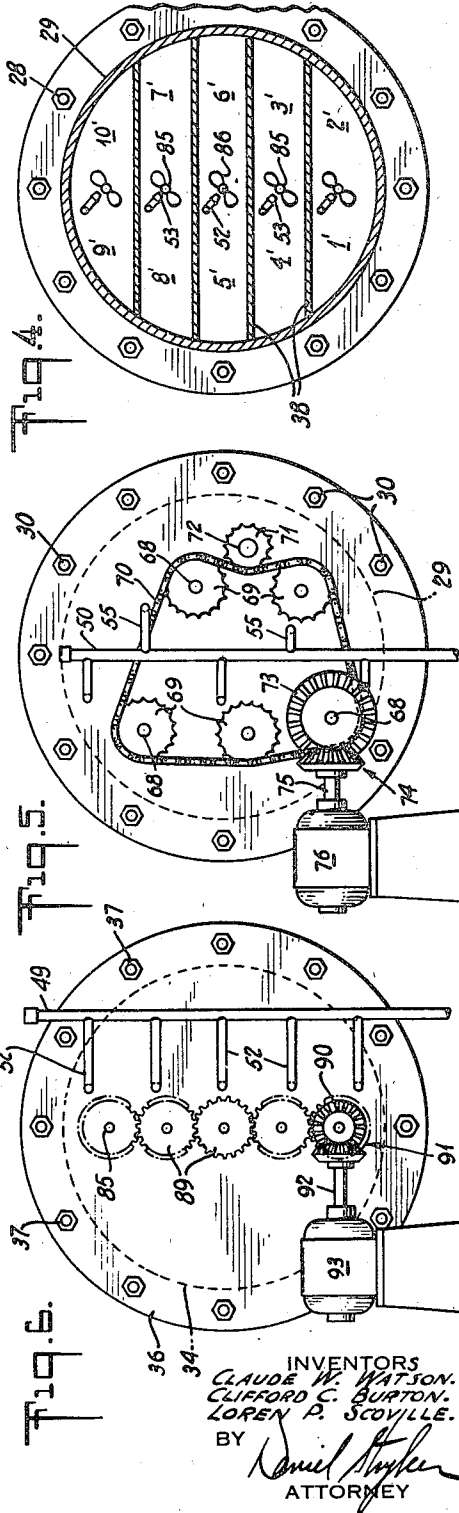
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2 Sheets-Sheet 2



## UNITED STATES PATENT OFFICE

2,474,924

## ALKYLATION METHOD

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2 Claims. (Cl. 260—683.4)

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This invention relates to the catalytic alkylation of a hydrocarbon or other organic compound having a replaceable hydrogen atom with a suitable alkylating agent, such as an olefin, for the production of gasoline hydrocarbons of high antiknock value suitable for aviation gasoline and motor fuel, or for the production of valuable alkylated organic products for other purposes. The invention is particularly applicable to the alkylation of a low-boiling isoparaffin, such as isobutane, with an olefin or other alkylating agent for the production of aviation gasoline of improved quality.

One of the principal objects of the invention is to provide an improved catalytic alkylation process capable of producing a superior alkylate containing higher proportions of highly branched paraffin hydrocarbons which give superior leaded octane ratings by both the AFD-1C and AFD-3C test methods, and smaller proportions of less highly branched hydrocarbons which have inferior octane ratings.

Another object of the invention is to carry out the alkylation reaction and separate the resulting alkylate from the catalyst with exceptionally short overall contact time, to thereby obtain an increased yield of primary alkylation products of improved quality and to prevent secondary or degradation reactions from altering the composition of the primary alkylate so obtained.

A further object of the invention is to carry out the alkylation reaction with extremely short or micro contact times, with unusually high catalyst to hydrocarbon ratios and with a set olefin or other alkylating agent space rate while still maintaining desired capacity.

An additional object of the invention is to provide an improved form of alkylation apparatus for carrying out the foregoing methods, and which is adaptable for catalytic alkylation generally.

Still another object of the invention is to provide improved alkylation apparatus of the tube and header heat exchanger type equipped for multipoint olefin or other alkylating agent injection, coupled with intensive agitation immediately adjacent the points of olefin addition, and with efficient refrigeration in the tube sections intermediate points of olefin addition, and which is capable of giving high capacity with the desired short contact time.

Other objects and advantages of the invention will be apparent from the following description when taken in conjunction with the accompanying drawing and appended claims.

Catalytic isoparaffin-olefin alkylation with

strong  $\text{H}_2\text{SO}_4$  and with  $\text{HF}$  has gone into wide commercial use for the production of aviation gasoline and motor fuel. In these commercial processes, contact times of the order of 20–60 minutes in the reaction zone, coupled with a substantial time of the order of 30–120 minutes for gravity settling, are conventional. A catalyst to hydrocarbon volume ratio in the reaction zone of around 1:1 and an olefin space rate averaging about 0.3 v./v./hr. are customarily used. These processes give a typical alkylate from isobutane-butylene alkylation in which the octane ( $\text{C}_8$ ) fraction contains mainly 2,2,4- and 2,3,4-trimethylpentanes together with an appreciable proportion of dimethylhexanes, the latter resulting in an appreciable lowering of both the clear and leaded octane values. While the 2,2,4- and 2,3,4-trimethylpentanes have fairly high clear octane values, the leaded octane values by the AFD-1C and AFD-3C test methods are not uniformly high. Thus, 2,2,4-trimethylpentane has a high 1C value but only a moderately good 3C value; and the 2,3,4-trimethylpentane has lower 1C and moderately high 3C values.

From tests on pure hydrocarbon compounds, it is known that certain highly branched paraffin hydrocarbons will give a combination of high 1C and 3C values. In the octane ( $\text{C}_8$ ) fraction, both 2,2,3- and 2,3,3-trimethylpentanes have this desirable property, with the former being somewhat superior to the latter. Among the heptanes, 2,2,3-trimethylbutane or triptane is outstanding. Likewise, among the nonanes, 2,2,3,3-tetramethylpentane is superior. While the desirable knock ratings of these pure hydrocarbons have been known, previous efforts to produce them in satisfactory yield by catalytic isoparaffin-olefin alkylation have been unsuccessful.

In accordance with the present invention, a radically new method involving the use of a completely different type of alkylation apparatus is employed to greatly reduce the overall contact time in the reaction and settling zones to less than five minutes and preferably less than 2–3 minutes. For example, the alkylation reaction or contact time in the reaction zone may be limited to a "micro" contact time, which expression is herein used to designate a fraction of a minute. Further, the reaction products discharged from the alkylation reaction zone are immediately subjected to positive separating action, as opposed to merely gravity separation, as by passing through a centrifuge, whereby the settling time may also be limited to not more than several minutes and preferably less than a minute. It

is to be understood that "contact time," as the expression is used herein, means the volume of hydrocarbon in the reactor divided by the volume of hydrocarbon charged per hour; thus, for a given velocity of once-through flow through the reactor, the contact time varies inversely with the acid to hydrocarbon volume ratio in the reaction zone.

Further, the alkylation reaction is carried out under conditions which are markedly distinguished from the prior practice in this art, and involve an optimum correlation of olefin feed distribution and mixing in a flowing stream of the isoparaffin and catalyst providing high isoparaffin concentration at the immediate points of olefin introduction, with high catalyst to hydrocarbon volume ratio, controlled olefin space rate in accordance with the mixing efficiency and the temperature, and refrigerative chilling of the reaction mix immediately adjacent the points of olefin addition. This is accomplished by passing the reactants or hydrocarbons in once-through flow through a pipe reactor of the refrigerated jacketed coil type or heat exchanger type, introducing the olefin by multipoint addition at a large number of points spaced throughout the length of the reaction zone, subjecting the flowing stream of reaction mix to intensive mixing or mechanical agitation immediately adjacent each point of olefin addition, controlling the olefin space rate so that the olefin is fed into the reaction mix in a quantity per unit of time less than that which results in undesired reactions such as hydropolymerization, this rate being a function of the mixing efficiency and the temperature, and refrigeratively chilling the flowing stream of reaction mix intermediate the spaced points of olefin addition. Further, as permitted by the improved mixing efficiency of the present invention, it is preferred to provide a catalyst to hydrocarbon volume ratio in the reaction zone considerably in excess of that previously used, so that the reaction mix contains about 75-95% catalyst by volume.

By a combination of the above-described conditions of the alkylation reaction with the overall short contact time of reaction and separation, a novel type of alkylate may be produced which is materially enriched in highly branched paraffin hydrocarbons which afford the desired high 1C and 3C ratings. It is postulated that the 2,2,3-trimethylpentane is a primary product of the alkylation of isobutane with butylene-1 and butylene-2; while 2,2,4-trimethylpentane is a primary alkylation product of isobutylene. Thus, it is theoretically possible to obtain nearly 100% of 2,2,3-trimethylpentane from a normal butylene charge stock substantially free from isobutylene; and to obtain about 70% 2,2,3-trimethylpentane to 30% 2,2,4-trimethylpentane from a total C<sub>4</sub> plant gas fraction. Moreover, it is postulated that prolonged contact of such primary alkylation products with H<sub>2</sub>SO<sub>4</sub> under alkylating conditions degrades those products, particularly the 2,2,3-trimethylpentane, into less desirable hydrocarbons. The extremely short overall contact time of the present invention inhibits such secondary or degradation reactions. It is further believed that the effective control of the alkylation reaction conditions as set forth above increases the selectivity of the reaction for the desired primary alkylation products, and materially reduces the yield of less highly branched paraffins, such as dimethylparaffins.

Conventional alkylation with long contact time

of the order of 20 minutes or more is capable of producing an alkylate containing as high as about 90% trimethylpentanes under optimum conditions with low olefin space rate and very high isoparaffin concentration in the reaction mix. Due to the method of olefin feed distribution previously used, and the comparatively lower mixing efficiencies of conventional alkylation reactors, the long time of contact was required to produce this quality of alkylate. However, this long time of contact apparently permitted initially formed primary alkylation products to isomerize or undergo degradation reactions, with the result that the alkylate obtained consisted mainly of the 2,2,4- and 2,3,4-trimethylpentanes and only small amounts of the more desirable 2,2,3- and 2,3,3-trimethylpentanes. In accordance with the method of the present invention, the greatly improved olefin feed distribution at a controlled temperature, coupled with effective agitation at the immediate zones of olefin introduction providing improved mixing efficiency, enable the alkylation reaction to be completed in a much shorter time, and prompt removal of the primary alkylation products from the acid inhibits the above-mentioned secondary degrading reactions.

The rate of activation of the olefin for reaction with the isoparaffin, possible through the formation of an intermediate complex, is a function of the temperature, increasing rapidly rise in temperature. For example, butylene-2 will alkylate very slowly, if at all, at 0° F. with H<sub>2</sub>SO<sub>4</sub> catalyst; but in the range of 35-60° F., the rate of activation of this olefin increases many fold. Immediately at the time of activation of the olefin, it is necessary that isoparaffin be brought into contact with the activated olefin to produce the desired alkylate; otherwise, the activated olefin will undergo hydropolymerization or other undesired reactions with the acid and with itself. By distributing the olefin feed by multipoint addition, the likelihood of these undesired reactions taking place, with a given isoparaffin concentration in the reaction zone, is greatly reduced. But the required renewal of this isoparaffin concentration at the immediate zones of olefin addition and activation depends upon the mixing efficiency. Thus, the olefin space rate (volume of olefin added per volume of catalyst in the reaction zone per hour) is correlated with the temperature and the mixing efficiency, so that the olefin will be activated substantially as fast as introduced, and so that the isoparaffin renewal at the immediate zones of activation and reaction will be at least as fast as the olefin activation.

The actual olefin space rate may therefore vary widely within the range of about 0.05-0.5 v./v./hr. or somewhat higher, depending upon the reaction conditions. With a lower temperature where the rate of activation of the olefin is limiting, or with a lower mixing efficiency where the rate of renewal of the isoparaffin at the immediate zone of formation of activated olefin is limiting, a lower olefin space rate within the above range is employed. At somewhat higher temperatures, and with improved mixing efficiency, higher olefin space rates may be employed. While the temperature should thus be high enough to secure the desired rate of olefin activation for the particular olefin and catalyst employed, substantially higher temperatures are objectionable because the rate of olefin activation then increases rapidly beyond the mixing efficiencies attainable, and also because undesired oxidation reactions then

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occur with certain catalysts such as  $\text{H}_2\text{SO}_4$ . Consequently, it is important that localized temperature rises adjacent the immediate points of reaction be minimized, and this is effectively accomplished by refrigeration intermediate the large number of spaced points of olefin addition. The selection of the olefin space rate in accordance with the foregoing principles is best made by cut and try runs in accordance with the results attained; thus, for a given temperature and a given reactor, the olefin space rate is set somewhat below the point at which further increase results in evidence of hydropolymerization with appreciable reduction in catalyst life.

In the case where sulfuric acid is employed as the alkylation catalyst, the control of the olefin space rate is further correlated with the water content of the sulfuric acid in the reaction zone. Thus, lowering the water content of the sulfuric acid in the reaction zone has a similar effect to increasing the temperature in that the rate of activation of the olefin is increased; and, conversely, raising the water content of the system acid decreases the rate of activation of the olefin. It is preferred to operate in accordance with the present method with a water content of the system acid in the reaction zone less than 2% by weight, and better still less than 1% by weight, to secure the required high rate of olefin activation at temperatures low enough to avoid oxidation and other acid degrading reactions.

Novel alkylation apparatus has been devised to carry out the foregoing method. It is to be understood, however, that this apparatus is adaptable to catalytic alkylation generally and is not restricted to the short contact time or other improvements described above relating more particularly to isoparaffin-olefin alkylation. This apparatus comprises a continuous pipe reactor equipped with a multiplicity of olefin feed jets at spaced points along the length of the pipe reactor, coupled with mixing devices or mechanical agitators immediately adjacent each point of olefin addition, and a refrigerating jacket for the pipe reactor intermediate points of olefin addition. In its preferred embodiment, the pipe reactor is of the tube and header heat exchanger type having a tube bundle equipped with opposed baffled heads providing return bend compartments at opposite ends of the tubes, and forming a multi-pass flow path constituting the reaction zone. The olefin jets with associated mechanical agitators are mounted in the header compartments, and the intermediate tube bundle is equipped with the refrigerating jacket. The desired capacity of the apparatus is obtained by providing a large number of tubes per pass, whereby the flowing stream of reaction mix is sub-divided into a large number of parallel streams, each of small cross-section, in the tube section, and these streams are recombined as they emerge into each header compartment. A plurality of these pipe reactors or tube and header reactors are connected for series flow to provide the desired contact time and afford a large number of agitated points of olefin addition; and the reaction products discharging from the last reactor in series are led directly to a centrifuge where the rapid separation of catalyst from hydrocarbons takes place.

Referring to the drawing, which discloses preferred embodiments of alkylation apparatus constructed in accordance with the present invention,

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alkylation unit containing four series-connected reactors of the tube and header heat exchanger type, with a centrifugal separator;

Fig. 2 is a vertical sectional view through one of the tube and header heat exchanger reactors of Fig. 1, the section being taken on the plane of the line 2-2 of Fig. 3;

Fig. 3 is a vertical sectional view taken on the plane of the line 3-3 of Fig. 2;

Fig. 4 is a vertical sectional view taken on the plane of the line 4-4 of Fig. 2;

Fig. 5 is an end elevational view looking toward the right hand end of Fig. 2;

Fig. 6 is an end elevational view looking toward the left hand end of Fig. 2;

Fig. 7 is a partial vertical sectional view on an enlarged scale, illustrating the agitator shaft mounting and olefin jet connection; and

Fig. 8 is a partial vertical sectional view on an enlarged scale of a modified construction of multipoint olefin jet arrangement for each header compartment.

For purposes of description, the invention is more particularly described in connection with the alkylation of isobutane with a suitable olefin, such as  $\text{C}_4$ ,  $\text{C}_3$ ,  $\text{C}_5$  or mixtures thereof, for the production of aviation alkylate. It will be understood that the invention is not so limited, and that the apparatus can be employed for catalytic alkylation generally, as more particularly described hereinafter.

Referring to Fig. 1, the isobutane feed is introduced through line 10 by pump 11; and the olefin feed is introduced through line 12 by pump 13. It will be understood that the isobutane includes fresh feed isobutane and also recycle isobutane separated from previously formed alkylate and returned to the system. It also will be understood that a portion of the recycle isobutane may be mixed with the olefin feed in line 12 to adjust the isobutane: olefin molar ratio to about 1:1 or somewhat higher.

The isobutane from line 10 meets a stream of recycle catalyst, such as strong  $\text{H}_2\text{SO}_4$ , passed through line 14 by recycle pump 15. The acid and isobutane in liquid phase then flow through a baffled mixer 16, and thence pass by pipe 17 into the inlet of the tube and header heat exchanger reactor indicated by the numeral 20.

The construction of this reactor is more particularly illustrated in Figs. 2-7 inclusive. As shown, a cylindrical shell 21 enclosed by end plates 22 and 23 forms a refrigerant chamber 24 surrounding a tube bundle consisting of a large number of tubes 25 of small cross-section. The end plates 22 and 23 are drilled as indicated at 26 and 27 respectively to receive the opposite ends of the tubes 25 with a snug fit. Bolted at 28 to the end plate 23 is a cylindrical channel member or insert 29. Bolted in turn to the outer end of the channel member 29 by bolts 30 is a header plate 31. The channel member 29 is provided with baffles 32 of a length to abut in sealing relation against end plate 23 and header plate 31, when the parts are properly assembled.

The construction of the baffles 32 carried by the channel member 29 is more particularly shown in Fig. 3. A central vertical baffle extends completely across the interior of the channel member. Branching from the central baffle and fastened to the interior of the channel are four horizontal baffles, two on each side of the central baffle and arranged in staggered relationship. Six compartments are thus formed within the members 23, 29 and 31. Compartment 1 (Fig. 3) is the

Fig. 1 is a diagrammatic elevational view of an

inlet compartment into which feed line 17 (indicated in dotted lines in Fig. 3) discharges. A portion of the tubes 25 communicate with said compartment 1 and lead the liquid mix fed to that compartment through the refrigerating chamber 24 to the opposite end of the reactor.

The left hand end of the reactor (Fig. 2) is likewise provided with a channel member 34 bolted at 35 to end plate 22; and a header plate 36 is bolted at 37 to the outer end of the channel member 34. Channel member 34 is in turn provided with four horizontal baffles 38, as shown more particularly in Fig. 4. The baffles 38 all are of a length adapted to sealingly engage the outer face of end plate 22 and the inner face of header plate 36 when the parts are assembled. Consequently, the left hand end (Fig. 2) of the reactor is divided into five compartments.

Flow through the reactor is as follows: The mixture of isobutane and acid introduced by inlet 17 into compartment 1 at the right hand end of the reactor passes by tubes 25 to the portion of the lowermost compartment at the left hand end of the reactor which is indicated by the numeral 1' in Fig. 4. An approximately equal number of tubes 25 in turn communicate with the right hand side (Fig. 4) of said lowermost compartment, which is indicated by the numeral 2'. The mixture then returns through said tubes to the lower part of the right hand compartment (Fig. 3) indicated by the numeral 2. Said compartment in turn communicates with another set of approximately equal number of tubes, as indicated by the numeral 3, through which the mixture returns to the left hand end of the reactor (Fig. 2) and to the right hand side of the next higher compartment indicated by 3' (Fig. 4). It will thus be evident that the numerals 1-10 (Fig. 3) and the numerals 1'-10' (Fig. 4) indicate ten passes through the reactor, the flow being from 1 to 1', 2' to 2, 3 to 3', 4' to 4, and so on for a total of ten passes until the reaction mix eventually reaches the discharge compartment 10 (Fig. 3), from where it is discharged by line 40.

Propane or other suitable refrigerant is supplied in liquid phase under pressure from a suitable storage reservoir by line 42, and then by branch line 44 to reactor 20. Branch line 44 discharges into the interior chamber 24 containing the tube bundle, so that substantially the entire length of the tubes 25 between the headers is effectively refrigerated. The expanded propane or other refrigerant discharges from chamber 24 by line 45 communicating with a line 46 which leads back to a suitable suction trap and thence to the compressors of the refrigerating unit in conventional manner.

The olefin feed supplied from line 12 by pump 13 passes through line 48 to manifolds 49 and 50 at the left and right hand ends respectively of the reactor (Fig. 1). Manifold 49 in turn supplies five branch lines 52 which extend through the header plate 36 and terminate in nozzles or jets 53 near the center (Fig. 4) of the header compartments. An olefin dispersion jet is thus provided for each of the five compartments at the left hand end of the reactor. Likewise, the manifold 50 (Fig. 5) at the right hand end of the reactor is provided with five branch lines 55 which extend through header plate 31 and terminate near the center of each of the compartments at this end, with the exception of the discharge compartment 10. This construction is more particularly illustrated in Fig. 7, wherein the branch pipe

55 passes through a drilled opening 56 in header plate 31. A sealing plate 57 which may be welded or otherwise secured, fastens the pipe in place and seals the same against leakage. The inner end of pipe 55 within the header compartment is bent downwardly as indicated at 58 and terminates in nozzle 59 at a position somewhat nearer the header plate 31 than to the end plate 23. It is thus seen that the olefin feed is dispersed at ten points which are spaced rather uniformly along the path of flow of the reaction mix through the reactor.

Each of the header compartments containing an olefin jet is also equipped with a mechanical agitator to subject the reaction mix to intensive agitation immediately adjacent each point of olefin entry. As shown, header plate 31 provides bearings for a series of five shafts 68 (Figs. 2 and 5). Each of said shafts carries on the exterior of the header plate a sprocket wheel 69. The five sprocket wheels are interconnected by sprocket chain 70, which is tightened by the usual idler sprocket 71 mounted on idler shaft 72. The lowermost sprocket shaft 68 extends outwardly beyond the sprocket wheel 69, and this extension carries a bevel gear 73 meshing with bevel gear 74 on driving shaft 75 of motor 76.

As shown more particularly in Fig. 7, header plate 31 carries a bearing sleeve 77 within which shaft 68 is rotatively mounted. The shaft extends inwardly within the header compartment to about midway between header plate 31 and end plate 23. Mounted on the inner extremity of the shaft are suitable agitating blades 78 which are adapted to violently churn or agitate the reaction mix in each compartment. On the exterior of header plate 31, the shaft passes through a suitable stuffing box having an outer casing 80 within which is compressed packing 81 by the sliding plunger 82 actuated by screws 83.

The left hand header of the reactor is likewise equipped with five shafts 85 (Figs. 2 and 6) mounted within header plate 36, each shaft carrying within its compartment agitating blades 86 associated with an olefin jet 53 similar to the arrangement in Fig. 7. In this case, however, the shafts 85 are in vertical alignment so that the agitators 86 are positioned centrally of the header compartments (Fig. 4). Each shaft 85 passes through a suitable stuffing box 88 to the exterior and has mounted thereon a gear 89. As shown, the five gears 89 are interconnected in line, so that rotation of the bottom shaft 85 through the bevel gear 90 meshing with bevel gear 91 on shaft 92 of driving motor 93 drives all the agitators 86.

In the specific embodiment shown, the reactor comprises a tube and header having ten passes, with 22 tubes per pass, and ten points of olefin entry in the header compartments or zones of intense mechanical agitation. The flowing stream entering the first compartment 1 receives dispersed olefin in the immediate zone of agitation provided by agitator 78. Then the stream is divided into a large number of small parallel streams flowing through the tubes 25 where it is subjected to efficient refrigerative cooling to immediately remove the heat of reaction. Upon emerging into header compartment 1'-2', where the small streams are recombined, a further charge of olefin is dispersed into the recombined streams in the immediate zone of agitation provided by agitator 86. The reaction mix is then alternately subdivided into the small parallel

streams and recombined in the header compartments, where further charges of olefin are introduced while the mixture is subjected to mechanical agitation. While ten passes are shown in the reactor, it will be understood that any convenient number can be provided. Moreover, desired capacity of the reactor is obtained by the number of tubes per pass, and the volume of the header compartments, which of course can be varied substantially from that shown. The tubes 25 are ordinarily constructed of about 1/2" to 2" in diameter, with a 3/4" tube being preferred, to provide adequate heat exchange surface. As shown, the reactor is of the short tube exchanger type, wherein the tubes are generally about 3-4 feet or somewhat more in length. The short length permits the tubes to be carried in rigid heads, thereby providing an economical construction. However, the use of longer tubes with a floating header to provide for expansion and contraction is included within the scope of the present invention.

The volume of each header compartment may be roughly equivalent to the total volume of the tubes in a single pass, although this can be varied. In fact, the time of contact in a given reactor of this type can readily be varied by altering the width of the channel members 29 and 34, with corresponding alteration in the length of the baffles 32 and 38, to thereby increase or decrease the size of the header compartments. It is preferred to provide the reactor with "blown-up" heads, which signifies compartments of increased size over those ordinarily provided in a conventional heat exchanger. This affords additional room for mounting of the agitators and the olefin jets and also affords control of the time of contact or flow through the reactor.

It will be appreciated that the present reactor does not depend upon turbulent flow to provide agitation. In fact, for economy in power consumption, it is ordinarily preferred to operate the reactor with an emulsion velocity below the range of turbulent flow. For this purpose, an emulsion velocity through the 3/4 inch tubes of less than about five feet per second is employed, such as an emulsion velocity of about two-four feet per second which is within the range of viscous flow. Moreover, positive mechanical agitation in the header compartments appears to give more effective results, possibly due to the more efficient action of the agitator blades in resaturating the acid with isobutane. It is postulated that the alkylation reaction takes place between the isobutane in solution in the acid and the activated olefin. Consequently, the effective dispersion of the olefin by jetting from a small-sized nozzle or orifice of the order of 1/16-1/4 inch in diameter, and preferably about 1/8 inch, with an effective pressure drop of about 5-50 pounds per square inch and preferably about 25-35 pounds per square inch, coupled with the renewal of the surface at the interface and the resaturation of the acid with isobutane following each point of olefin addition and reaction, provide high selectivity in the alkylation reaction with corresponding improvement in quality of the resulting alkylate. Furthermore, local overheating is prevented, due to the fact that the reaction mix is subjected to very efficient refrigeration immediately following each point of olefin addition, by being subdivided into small parallel streams which afford very large heat exchange surface. Even with a low olefin space rate, high capacity of the unit is maintained by

the rapidity of once-through flow through the reactor, and by the high acid-to-hydrocarbon ratio in the reaction mix.

While in the specific form shown in Figs. 2-7, the olefin feed pipe 56 for each compartment terminates in a single jet 59, it will be understood that the pipe 56 can be provided with a plurality of branches extending to different locations throughout said compartment, such as a so-called Christmas tree construction, with each branch provided with an olefin feed jet. In this manner, the olefin may be dispersed by multipoint addition throughout the volume of each compartment, in addition to the multipoint addition at spaced points or compartments along the path of flow through the alkylation apparatus as previously described.

In Fig. 8 there is disclosed a modification of this general type adapted for multipoint addition adjacent each compartment of the tube and header heat exchanger reactor. Similar elements to those previously described in Figs. 2-7 are indicated by similar primed reference numerals. Thus, the end plate at the right hand end of the tube bundle is indicated by 23' supporting the tubes 25'. It will be understood that this construction is particularly adapted to a tube and header heat exchanger reactor having about 3-20 tubes per pass. The olefin feed pipe 56', which passes through the outer header plate (not shown), is connected within the header compartment to a plurality of branch pipes indicated at 116. Each branch pipe extends into the end of a tube 25' discharging into that compartment, the direction of flow through said tubes being indicated by the arrows 117. It is thus apparent that the branch pipes 116 extend into the ends of the one set of tubes which discharge into that compartment, but not into the other set of tubes which receive liquid flowing out of that compartment. Each pipe 116 terminates in a suitable mixing nozzle 118 discharging counter to the direction of flow through the tube. Preferably, the nozzles 118 are constructed to disperse the olefin feed in the form of conical jets 119, so that the olefin is substantially evenly distributed throughout the cross-section of the tube 25'. In the preferred construction, as many branch pipes 116 having dispersing nozzles 118 are provided for each compartment as there are tubes discharging into that compartment. However, it will be obvious that only certain of the tubes 25' feeding into any compartment need be provided with olefin dispersing jets, since the small streams are immediately discharged into and combined within the compartment where further mixing takes place.

Due to the effective mixing and agitating action of the jets 118 introduced with substantial pressure drop counter to the flow of reaction mix through the small diameter tubes, it is possible to dispense with the mechanical agitators in the header compartments, particularly where some form of orifice or baffle mixing action is provided in each compartment. However, it is preferred to also provide a mechanical agitator indicated at 78' with its shaft 68' within each compartment. The agitator is preferably mounted centrally and between the inlet and outlet tubes in the manner previously described.

As shown more particularly in Fig. 1, the reaction mix discharging by line 40 from reactor 20 is immediately passed to the inlet of a second reactor 90 which may be identical in construction with reactor 20. Two additional reactors 91

and 92, also of the same construction, are connected for series flow by the lines 93 and 94. Olefin feed to the reactors 90, 91 and 92 is supplied by the valve-controlled branch lines 95, 96 and 97 respectively, which supply manifolds at opposite ends of each reactor as previously described. This provides a total of forty points of olefin addition in once-through flow through the reaction zone. Propane refrigeration for reactors 90, 91 and 92 is furnished by the valve-controlled branch lines 98, 99 and 100 respectively, with the expanded refrigerant being discharged to the return line 46 by lines 101, 102 and 103 respectively. While four tube and header heat exchanger reactors are thus shown connected in series, it will be understood that any desired number can be employed to provide the required contact time and number of points of olefin injection. Moreover, it is obvious that a single reactor with sufficient passes can be employed for this purpose, although it is generally more economical to construct the individual reactors of a uniform smaller size and connect a number in series as shown.

While a reactor of the tube and header heat exchanger type is preferred, it is to be understood that any suitable pipe reactor of the heat exchange type, such as a concentric pipe reactor with enlarged return bends to provide for the mounting of the mechanical agitators and olefin injectors, can be employed. Moreover, while mechanical stirrers or agitating blades located at the immediate zones of olefin introduction are preferred, it is to be understood that other forms of intensive mixing at said zones of olefin feed, such as the use of mixing nozzles and orifice plates in the header compartments or return bends with substantial pressure drop, the use of fins, pins or other protuberances within the pipe coil to give a shearing effect on a flowing emulsion stream etc., are not excluded from the scope of the present invention.

The reaction products discharging from the last reactor 92 pass by line 105 to centrifuge 106, where the acid is immediately separated and discharged by line 107 to acid storage tank 108. The hydrocarbon phase, removed from the center zone of the centrifuge, discharges by line 109 and passes to conventional neutralizing and fractionating equipment. Acid from storage tank 108 is withdrawn by line 110. A minor proportion of the acid may be discharged to recovery by valve-controlled line 111, and the balance passed by valve-controlled line 112 together with makeup acid from line 113 to the recycle pump 15 which returns the recycle acid to the alkylation unit.

Conventional conditions for sulfuric acid alkylation, other than the conditions specified above, may be used. These include an isoparaffin to olefin feed ratio of about 3:1 to 8:1 or higher, an acid titratable acidity in the reaction zone of about 85 to 96%, that is, about 89-96% for  $C_4$  and about 85-92% for  $C_5$ , with makeup acid of about 98-100% strength, a temperature of about 20-100° F. and preferably about 35-60° F., and sufficient pressure to maintain the hydrocarbon reactants in the liquid phase. Moreover, while the short contact time and higher acid-to-hydrocarbon ratio are preferred to obtain the superior quality of alkylate, it will of course be obvious that the reactor of the present invention can be employed under conventional conditions with contact times of about 20-30 minutes or more and acid-to-hydrocarbon ratios of as low as about 0.8:1 up to the high ratio specified above. Moreover, while the present invention enables the iso-

paraffin concentration in the hydrocarbon phase of the reacted mix to be reduced to about 40-50% with substantial economy, higher isoparaffin concentrations of around 60-70% and higher by volume can of course be employed.

The present invention is applicable to the alkylation of any low-boiling isoparaffin with any normally gaseous or normally liquid olefin. Thus, the isoparaffin may be isobutane, isopentane or isohexane. The olefin may be ethylene, propylene, butylenes, pentylenes, hexylenes, other higher boiling monomeric olefins or certain selected fractions of cracked naphthas, olefin polymers such as di-isobutylene, tri-isobutylene, cross polymers of isobutylene and normal butylenes, and various mixed or non-selective polymers. In place of olefins as the alkylating agent, various alkyl esters, such as the sulfates, chlorides, fluorides, etc., may be used. Moreover, various aliphatic alcohols and ethers, such as tertiary butyl alcohol, isopropyl alcohol, butyl ether, etc. may be employed as the alkylating agent, particularly with catalysts which have tolerance for water liberated in the reaction. The expression "alkylating agent" is used herein throughout the description and claims to denote any of the above compounds which react with an isoparaffin or other organic compound having a replaceable hydrogen atom in this alkylation reaction to produce alkylated hydrocarbons. In place of the pure hydrocarbons or other alkylating agents, it is of course to be understood that various refinery fractions, such as a  $C_4$ ,  $C_3-C_4$ ,  $C_4-C_5$ ,  $C_5$ , etc. may be employed.

The present invention is applicable to the use of any of the well-known alkylation catalysts, such as sulfuric acid, hydrofluoric acid, aluminum chloride-hydrocarbon complex,  $BF_3 \cdot nH_2O$ , chlorosulfonic acid, fluorsulfonic acid and the like. The various conditions for the reactions employing these catalysts are well known; and conventional conditions coupled with the features of the present invention as set forth above may be used.

While the reactor of the present invention is particularly suitable for use in the short or micro contact time, alkylation of isobutane with  $C_3$ ,  $C_4$ , or  $C_5$  mono-olefins or their corresponding esters to produce a superior quality of isoparaffin alkylate as described above, it is to be understood that the reactor is applicable to the alkylation of any organic compound having a readily replaceable hydrogen atom with a suitable alkylating agent. For example, the method and apparatus described herein can be employed for the alkylation of a normal paraffin with an olefin or other alkylating agent, employing a catalyst effective for this normal paraffin alkylation, such as  $HF-BF_3$ , aluminum chloride with hydrogen chloride, and the like. Likewise, the invention is applicable to the alkylation of aromatics and hydroxyaromatics, such as benzene, toluene, xylene, phenol, cresol, etc., with an alkylating agent such as an olefin, an alcohol, an alkyl halide, etc. The expression "organic compound having a replaceable hydrogen atom" is used for convenience throughout the description and claims to designate the various materials described above which can be alkylated with the mentioned alkylating agents in the presence of suitable alkylation catalysts as described.

The following example of the present invention is listed for purposes of illustration. The alkylation reaction system comprises four reactors of the tube and header heat exchanger type connected in series, with the reaction products from

the last reactor discharging to a centrifuge in the manner disclosed in Fig. 1. Each reactor is of the short tube type having  $\frac{3}{4}$  inch diameter tubes four feet in length. A total of 864 tubes are included in the tube bundle which is mounted within a casing 36 inches in diameter. The headers are constructed to provide ten tube passes with roughly about 86 tubes per pass. Utilizing a flow velocity through the reactor system of 3.36 feet per second with a pressure drop of 90 pounds per square inch, a contact time for flow through the reactor system of about 15 seconds is provided with normal size heat exchanger heads. The above figures apply to a 500 barrel per day alkylation unit. Utilizing 40 olefin injection points equipped with mechanical agitation, as illustrated in Figs. 1-7, with an emulsion temperature of 50° F., a propane temperature of about 32° F. is required to remove the heat of reaction and the sensible heat, as well as the mechanical heat at this extremely short or micro contact time. As propane temperatures considerably below this can be economically provided, it is apparent that the contact time can be still further reduced, or the olefin space rate increased above the 0.05 v./v./hr. for which the unit was designed. By equipping each of the four series-connected reactors with blown-up heads, affording twice the volume in the header at each end of the reactor over the standard size, a total contact time in the reactor of approximately one minute results. The overall contact time in the reaction and separating zones in the former case is slightly more than one minute; while the overall contact time with the blown-up heads is slightly less than two minutes.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. The method in the alkylation of an alkylatable organic compound having a replaceable hydrogen atom with an alkylating agent in the presence of a liquid alkylation catalyst, which comprises introducing a mixture of said alkylatable organic compound in liquid phase and the liquid alkylation catalyst in a flowing stream to the inlet of a combined reaction and chilling zone, dividing the flowing stream into a substantial number of parallel streams, each of small cross-section and having a velocity within the

range of viscous flow but below the range of turbulent flow, recombining the said parallel streams while maintaining the continuous flow thereof, reversing the direction of flow of the recombined stream, repeating the division into small parallel streams and the recombination thereof with reversal of direction of flow a substantial number of times during once-through continuous flow through the combined reaction and chilling zone, introducing alkylating agent by multipoint addition into the reaction mix at the spaced regions of recombination of the small parallel streams by at least ten feed jets, each having a diameter of not more than  $\frac{1}{4}$ ", subjecting the reaction mix to mechanical agitation at each spaced region of recombination and immediately adjacent each point of alkylating agent addition, and refrigeratively chilling the parallel small streams between the spaced points of alkylating agent addition.

2. The method according to claim 1, wherein the organic compound is a low-boiling isoparaffin, the alkylating agent is an olefin, the alkylation catalyst is a mineral acid, the flowing stream comprises about 75-95% by volume of the acid catalyst, the olefin is added at a space rate of less than about 0.5 v./v./hr., each of said parallel streams has a diameter not greater than 2" and the contact time for flow through the combined reaction and chilling zone is less than two minutes.

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