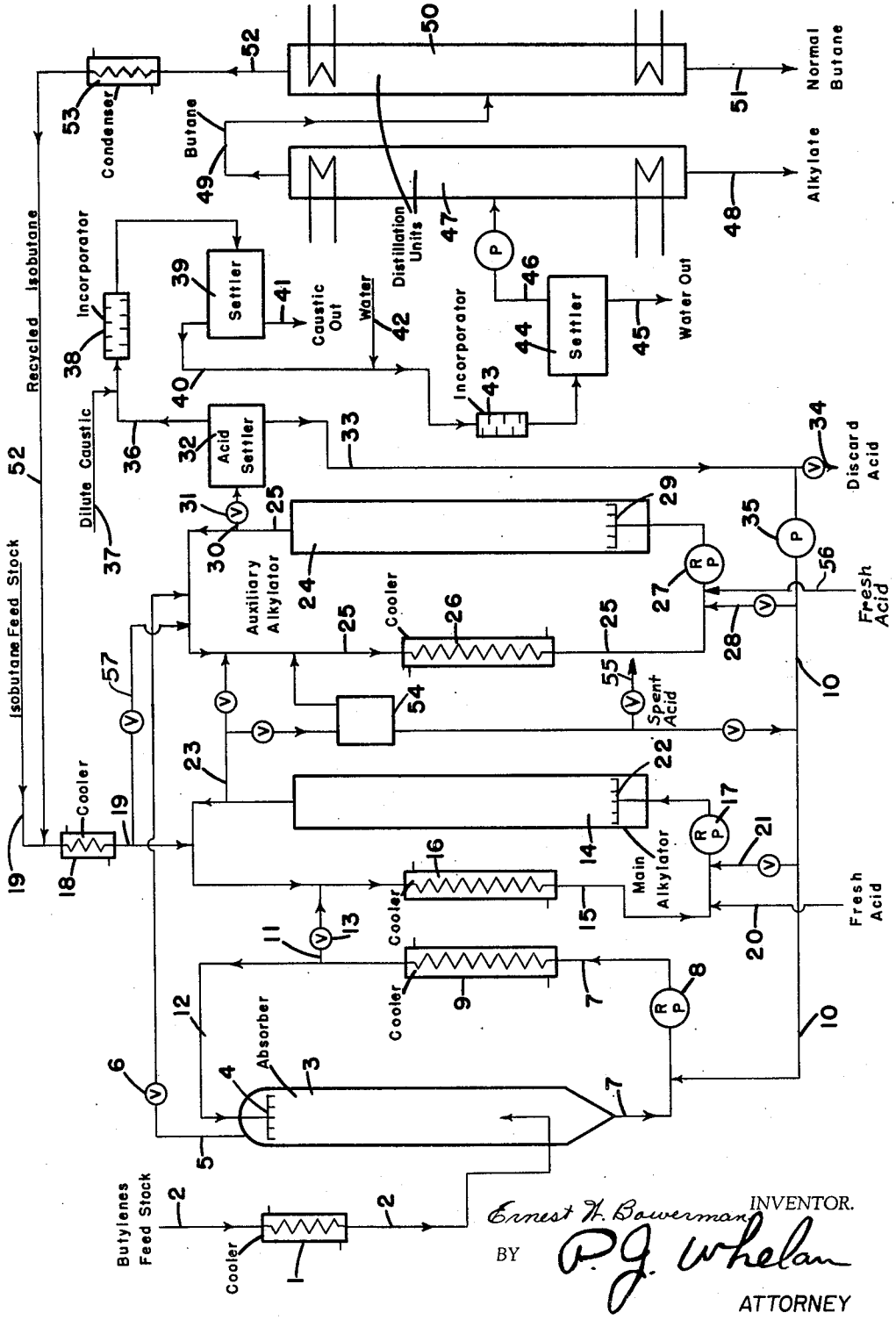
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ALKYLATION

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ALKYLATION

Ernest W. Bowerman, Baytown, Tex., assignor to Standard Oil Development Company, a corporation of Delaware

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The present invention is concerned with a process for the alkylation of isoparaffinic hydrocarbons with olefinic hydrocarbons. It is primarily concerned with an improvement on the two-stage alkylation process wherein olefinic hydrocarbons are selectively absorbed in sulfuric acid from admixture with paraffinic hydrocarbons in one stage and the acid absorbed olefinic hydrocarbons are reacted under alkylating conditions with isoparaffinic hydrocarbons in the second zone. The improvement involves the removal of olefins, polymer oils, alkyl sulfates and other corrosive or potentially corrosive acid reaction products from the unabsorbed paraffinic hydrocarbons discharged from the absorption stage and the conversion of these constituents into an additional quantity of good quality alkylate (a saturated, high-octane-number, hydrocarbon condensation product).

It is well known in the art that low boiling isoparaffins can be reacted with low boiling olefinic hydrocarbons in the presence of concentrated sulfuric acid to form an alkylate having a high octane number. Usually this reaction is carried out in a single-stage reaction system which is commonly called a single-stage process. In this type of operation it is common practice to blend the isoparaffinic feed stock (which is predominantly isoparaffin but may contain a small amount of normal paraffin) with the olefinic feed stock which comprises a mixture of olefins, isoparaffins and normal paraffins, and the blend is contacted with concentrated sulfuric acid under alkylating conditions. In this manner, the normal paraffin contained in the olefinic feed stock passes through the system as a diluent and it is finally segregated from the alkylate and the unreacted isoparaffin by distillation means. The objectionable feature to this type of process is the presence of normal paraffins in the reaction mixture which tends to lower the yield and octane number of the alkylate product boiling in the gasoline boiling range. In general, this tendency becomes greater as the concentration of normal paraffins increases. Since the olefinic feed stock is the principal source of the normal paraffins in the reaction mixture, it is evident that the normal paraffin content of this stock limits the extent to which the isoparaffin concentration can be built up in the reaction mixture while maintaining practical feed rates to the single-stage alkylation system.

Modifications of the single-stage system have been devised. These modifications employ the same basic principles used in the single-stage alkylation process; hence they have the same objectionable feature, the presence of relatively high concentrations of normal paraffins in the reaction mixture. One modification consists of employing a multiple of alkylation reactors in parallel hook-up. In this operation, the hydrocarbon feed stock streams are supplied with separate portions of the same going to the various reactors. Another modification of the single-stage process now in common use consists of a multiple of alkylation reactors and settling zones alternately spaced in series hook-up. In this setup, all of the isoparaffin feed stock is generally introduced into the first reactor of the series and it flows in consecutive order through all of the reactors and settling zones in the series. The olefinic feed stock, on the other hand, is divided into as many streams as there are reactors in the system so that a separate stream of the fresh olefinic feed stock may be introduced into each reactor. Although not absolutely essential, it is customary to employ and maintain separate bodies of acid catalyst for each reactor in the system. Each reactor, of course, is provided with means for controlling the reaction temperature as well as means for securing and maintaining intimate contact between the acid catalyst and the hydrocarbon reactants. The advantage of this modification is that it provides a means of maintaining a higher concentration of isoparaffins in the reaction mixture than can be secured with the same quantity of hydrocarbon reactants in a single reactor system.

The so-called "two-stage" process of alkylating isoparaffins with olefins has been devised to obviate the objectionable feature of introducing substantial quantities of normal paraffins into the reaction mixture, which is common to the single-stage process. The "two-stage" process consists first of absorbing the olefins from the olefinic feed stock in concentrated sulfuric acid and then of charging the acid extract to an alkylation reactor wherein it is contacted with an isoparaffin and additional acid of alkylation strength and under alkylation conditions to produce saturated, high-octane-number hydrocarbon condensation products, commonly known as alkylate. The virtue of the two-stage process lies in the fact that, by excluding from the alkylation stage the normal paraffins usually present in the olefinic charge stock, it is possible to obtain a much higher isoparaffin concentration in the hydrocarbon phase in the alkylation reactor than it is possible to obtain in the single-stage process with essentially the same auxiliary distillation

capacities. It has been demonstrated that the higher isoparaffin concentration, which prevails in the hydrocarbons in the reactor when the two-stage process is used, causes the octane number of the aviation gasoline fraction of the alkylate to be 1 or 2 octane numbers higher than that produced on a single-stage unit from the same feed stock and with the same operating conditions.

In connection with the two-stage alkylation process, it has been found that the operating conditions used for the absorption stage have a decided influence on the yield and quality of the alkylate which is subsequently produced with the extract, and on the acid replacement requirements for the entire process. It has been demonstrated that it is best to operate the absorption stage at low temperatures, for example 20 to 35° F., for absorbing butylenes; this keeps undesirable side reactions, such as polymerization, Ormandy-Craven type reactions, and oxidation reactions at a minimum. Likewise, it has been demonstrated that the retention time of the extract in the absorber should be low, and a downflow jet absorber that sprays acid down through a continuous rising hydrocarbon phase has been used to provide a condition which allows a short extract retention time. It has further been demonstrated that it is highly desirable to absorb the olefin in an extract rather than in pure sulfuric acid, and it has been shown that it is necessary to keep the molecular ratio of sulfuric acid to olefin in the extract phase at a definite maximum value. If acid to olefin ratios higher than this maximum value are allowed to exist in the extract phase, undesirable side reactions are accelerated.

The necessity of limiting the molecular ratio of acid to olefin in the extract phase at a maximum value introduces certain operating problems which must be circumvented if the maximum advantage of the two-stage alkylation process is to be realized. For example, in applying the two-stage process to normal butylenes alkylation, it is necessary to limit the sulfuric acid-to-butylene molecular ratio at a maximum value of 1:1. Such a ratio permits the formation of some dibutyl sulfates. These sulfates are more soluble in the liquid hydrocarbon phase than in the extract and as a consequence they are carried out of the absorber as solute in the residual hydrocarbon phase. Other constituents besides paraffins and some unabsorbed butylenes that are found to be present in the residual hydrocarbon in small concentrations are: polymers, hydropolymers, and sulfur dioxide. These materials must be removed from the residual hydrocarbon leaving the absorber before it can be used in other refinery operations or before it can be used for blending into gasoline stock. In addition, these hydrocarbon materials represent a sizable amount of potential alkylate which would be lost unless the materials are recovered and converted to alkylate in some manner.

One method proposed for removing side reaction products from the residual butane leaving the absorption stage is to distill the butane, removing the low boiling hydrocarbons as an overhead stream and removing a bottoms stream containing the polymers, hydropolymers, and alkyl sulfates. This bottoms stream is then charged to the alkylation stage along with the extract. The overhead stream is ready for use after caustic and water washing. The trouble with this procedure is that the alkyl sulfate present in the absorber residual hydrocarbon is partially decomposed at the temperature maintained in the still bottoms. The products of these decompositions are sulfuric acid, polymers, and sulfur dioxide and water. The sulfuric acid and the wet sulfur dioxide are both corrosive to steel equipment, and the fact that sulfuric acid is lost as sulfur dioxide and water causes the acid requirements for the over all two-stage alkylation process to be high.

Another method of handling the residual hydrocarbon stream leaving the absorber which is an improvement over the aforementioned procedure has been proposed. In this case the residual hydrocarbon phase leaving the absorber is charged to an evaporator wherein the low boiling hydrocarbons are removed as vapor, care being taken to prevent the temperature of the nonvolatile components from rising above 70° F. At this temperature the thermal decomposition of the alkyl sulfates is minimized. The nonvolatile stream from the evaporator is then recycled to the absorption stage. This practice of recycling tre evaporator bottoms back to the absorber represses the formation of neutral sulfuric acid esters because of the mass action effect on the equilibrium:

$$R_2SO_4 + H_2SO_4 \rightleftarrows 2RHSO_4$$

When using this method of handling the residual hydrocarbons leaving the absorption stage, it is necessary to condense the vaporized hydrocarbon stream, caustic wash and water wash it to remove sulfur dioxide before it can be used in the other refinery streams. Furthermore, a small amount of polymers are formed in the absorber stage even though the olefinic feed stock does not contain iso-olefins, for example, isobutylene, and these polymers would not be vaporized in the evaporator and as a result these high boiling constituents would need to be removed from the absorption system, otherwise a build-up of this type of material would occur.

I have now discovered a more simple means for handling the residual liquid hydrocarbon phase which leaves the absorption stage of the two-stage alkylation process. In accordance with my invention the residual hydrocarbon leaving the absorber is contacted with sulfuric acid of alkylating strength in the presence of an isoparaffin and under alkylation conditions. This treatment causes the alkyl sulfates, any unabsorbed olefins, and olefin polymers to react with the isoparaffin to produce alkylate. This alkylate is about equal in quality to that produced in the single-stage alkylation process and it is only slightly inferior to the alkylate produced in the regular alkylation stage of the two-stage alkylation process. This new alkylation operation may be carried out in a separate and independent system from that of the two-stage process; however, it is preferable to have the two systems integrated so that the hydrocarbon product stream (comprising alkylate and unreacted isobutane) from the alkylation stage of the two-stage system becomes the principal source of isobutane for the auxiliary alkylation system.

The process of this invention may be more clearly understood by reference to the attached drawing which is a diagrammatic flow plan of a preferred embodiment of this invention. For purpose of description it is assumed that the olefin feed stock is a normal refinery butane fraction from which all isobutylene has been removed, and which is comprised of normal butyl-

enes, isobutane and normal butane. It is also assumed that the isobutane feed stock is comprised primarily of isobutane but that it does contain some normal butane. The catalyst is assumed to be sulfuric acid of alkylation strength, preferably between 90 and 98 per cent strength by titratable acidity.

In this embodiment, liquefied butylene feed stock is precooled to a temperature in the range between about 20° F. and 35° F. by means of cooler 1 in line 2 before being introduced into absorber 3 at a point near its bottom. Absorber 3 is preferably a closed vertical tower equipped with a conical bottom and provided with a downwardly directed spray header 4 located at a point near the top of the tower and through which acid-butylene extract is introduced into the absorber. As the butylene feed stock flows upwardly through absorber 3, a large portion of the butylenes contained in the feed stock is absorbed by the downwardly flowing acid-butylene extract introduced through spray header 4. The hydrocarbons in the butylene feed stock which are not absorbed by the acid in absorber 3 are withdrawn from the absorber by means of line 5 in which is located control valve 6. The acid-butylene extract is withdrawn from absorber 3 by means of line 7 which is equipped with pump 8 and cooler 9. Make-up acid, preferably of alkylation acid catalyst composition, is introduced into the stream of acid-butylene extract ahead of pump 8 by means of line 10 and the mixture is passed through cooler 9 wherein sufficient refrigeration is supplied to control the temperature in the absorber within the range between about 20° F. and 35° F. The stream leaving cooler 9 is divided with one portion being diverted to the main alkylation system through line 11, and the other portion being recycled to the absorber 3 by means of line 12 which communicates with spray header 4. The quantities of butylene feed stock, make-up acid, and recycled acid-butylene extract which are fed into absorber 3 are adjusted so that the molecular ratio of acid to butylene in the acid phase does not exceed 1:1. It is preferable to control the acid-butylene extract recycle rate so as to allow complete coalescence of extract in the bottom of the absorber. The absorber system is operated at a pressure sufficiently high to maintain the hydrocarbons in the liquid phase and the pressure in the system is preferably greater than the pressure maintained in the alkylation system which will be described in a subsequent part of this specification. The absorber system is designed so that the extract is not retained in the system more than 20 to 40 minutes.

The main alkylation reaction system, comprising alkylation reactor 14 and reaction-mixture-recycle line 15 which is equipped with cooler 16, and a recycle pump 17, is filled with alkylation reaction mixture comprising isobutane, acid-butylene extract, alkylation acid catalyst and alkylate product. This reaction mixture is continuously circulated in the alkylation reaction system and it is maintained under conditions of temperature, pressure, catalyst strength and proportion of reactants which are known to be favorable for promoting the alkylation of isobutane with acid-absorbed-butylene extract and which do not constitute a part of this invention. However, for purpose of clarification it is enumerated that the reaction mixture should contain at least 40 volume per cent acid catalyst and the hydrocarbon phase should contain at least 50 volume per cent of isobutane, preferably above 60 volume per cent. The reaction mixture should be maintained at a temperature in the range between about 30° F. and 50° F. and under a pressure lower than that maintained in the absorption system but still sufficiently high to maintain the hydrocarbon reactants in the liquid phase. The main alkylation reactor should be of sufficient size to provide for a butylene feed rate of from 0.1 to 0.2 volume per hour per volume of acid catalyst in the main alkylation system. The acid-butylene extract diverted from the absorption system by means of line 11 is introduced into the main alkylation reaction system preferably at a point in reaction-mixture-recycle line 15 ahead of cooler 16 and recycle pump 17. Isobutane feed stock precooled to a temperature in the range between 30° F. and 50° F. by means of cooler 18 in line 19 is also introduced into recycle line 15 preferably at a point ahead of cooler 16 while fresh make-up sulfuric acid of alkylating strength, preferably of 95 to 98 per cent titratable acidity, is introduced into line 15 at a point between cooler 16 and recycle pump 17 by means of line 20. Alkylation catalyst separated from reaction mixture diverted from the system and segregated for product recovery is recycled to the system by means of valve controlled line 21 which is in communication with line 15 ahead of pump 17. The hydrocarbon reactants, fresh acid and recycled acid catalyst introduced into line 15 are intimately mixed with one another and with the circulating reaction mixture as they pass through pump 17 and jet header 22 located in the bottom of reactor 14 and in communication with line 15. A portion of the reaction mixture discharged from reactor 14 through recycle line 15 is diverted through valve controlled line 23 to an auxiliary alkylation system which is described hereinafter.

In a conventional two-stage alkylation process such as the one which has just been described the usual procedure is to pass the reaction mixture withdrawn from the main alkylation system, such as by means of line 23, directly to an acid separator, such as separator 32, wherein the acid catalyst is separated from the hydrocarbons and the latter is segregated for the recovery of alkylation product. In accordance with my invention, this stream of hydrocarbons segregated for alkylate product recovery may be introduced into an auxiliary alkylation reactor wherein it is contacted under alkylation conditions and in the presence of sulfuric acid catalyst with the hydrocarbon stream withdrawn from absorber 3 by means of line 5 to effect alkylation of the unreacted isobutane present in the stream of hydrocarbons segregated for alkylate product recovery with the butylenes, butylene polymer oil and the alkyl sulfates present in the hydrocarbon stream withdrawn from absorber 3. It is generally desirable to pass the reaction mixture to an acid separator, such as indicated by numeral 54, to separate an acid phase from a hydrocarbon phase and pass the hydrocarbon phase into line 25 and withdraw the acid phase to line 10. It is sometimes desirable to withdraw from the system a portion of the acid separated in vessel 54 by outlet 55 and to add an equivalent amount of fresh acid to auxiliary alkylator vessel 24 by inlet 56. It will be understood that this is an optional operation and that if desired the mixture may be passed directly from unit 14 into line 25, bypassing the separating stage. However, in accordance with a preferred embodiment of my invention, the reaction mixture (comprising acid catalyst and hydrocarbon)

flowing through line 23 is introduced directly into an auxiliary alkylation reaction system which comprises alkylation reactor 24 and alkylation-reaction-mixture recycle line 25 which contains cooler 26 and recycle pump 27. Line 23 preferably communicates with line 25 at a point ahead of cooler 26. This stream of reaction mixture diverted from the main alkylation reaction system becomes the principal source of acid catalyst and isobutane for the auxiliary alkylation reaction system. Similarly, the stream of non-acid-absorbed hydrocarbons withdrawn from absorber 3 and introduced through line 5 into recycle line 25 ahead of cooler 26 becomes the source of "olefins" for the auxiliary alkylation reaction system. As previously stated, this stream of hydrocarbons contains a small amount of unreacted butylenes, some butylene polymers and some butyl sulfate, all of which I have found react readily with isobutane under favorable alkylation conditions to produce good quality alkylate. Where desirable, additional alkylation acid catalyst may be introduced into the auxiliary alkylation system by means of valve controlled line 28 which communicates with line 25 ahead of pump 27. Intimate contact between the hydrocarbon reactants and the acid catalyst is effected as the mixture passes through recycle pump 27 and jet header 29, located in the bottom of reactor 24, and in communication with recycle line 25. Part of the reaction mixture leaving the auxiliary reactor 24 through line 25 is diverted to acid settler 32 by means of line 30 which contains control valve 31. The balance of the reaction mixture is recycled through cooler 26, pump 27 and jet header 29 for purpose of removing heat of reaction to control the temperature in the reactor and providing mixing. The volume ratio of reaction mixture recycled to the total incoming hydrocarbon feed oils should be in the order of 20:1 to 40:1. The conditions of temperature and acid strength employed in this auxiliary alkylation system are substantially the same as those employed in the main alkylation system. The pressure should be sufficiently high to maintain liquid phase but should not be as high as the pressure maintained in the main alkylation system for purpose of promoting flow of reaction mixture from the main alkylation system to the auxiliary alkylation system. Because of the normal butane contained in the stream of hydrocarbons introduced from absorber 3, the concentration of isobutane in the hydrocarbon phase of the reaction mixture will be somewhat lower in the auxiliary reactor than in the main reactor; but in the interest of obtaining a reasonable yield of good quality alkylate, this isobutane concentration should not be allowed to become less than 30 mol per cent. If necessary for the maintenance of a suitable isobutane concentration in vessel 24, fresh isobutane feed stock which has been introduced by inlet 19 and passed through cooler 18 may be withdrawn through branch 57 and added to the stream circulating through line 25.

The stream of reaction mixture diverted from the auxiliary alkylation reaction system by means of line 30 and passed to acid separator 32 is settled and separated in this separator into an acid phase and a hydrocarbon phase. The acid phase is withdrawn from separator 32 by means of line 33, a portion of it being discarded through line 34 and the balance being recycled to the absorption and alkylation systems by means of line 10 and pump 35, which is located in line 10. Line 10 is connected with the main alkylation reactor system by means of line 21 and with the auxiliary alkylation system by means of line 28.

The hydrocarbon phase separated in acid separator 32 is withdrawn by means of line 36, is admixed with dilute caustic, introduced by means of line 37, and the mixture is passed through incorporator 38 before being introduced into caustic separator 39. In caustic separator 39, the caustic is settled and separated from the hydrocarbons, the hydrocarbons being discharged through line 40 and the caustic being discharged through line 41. As the hydrocarbons flow through line 40 they are admixed with water introduced by means of line 42 and the mixture passes through an incorporator 43 before being introduced into water separator 44 for separation into a water phase and a hydrocarbon phase. The water phase is withdrawn through line 45.

The hydrocarbon phase is withdrawn from water separator 44 by means of line 46 and it is introduced into distillation unit 47 where it is separated into a butane fraction and an alkylate fraction. The alkylate fraction is withdrawn as a residual material through line 48 and it may be further processed in any manner desired. The butane fraction is removed as an overhead produce through line 49 and it is introduced into distillation unit 50 wherein it is split into an isobutane fraction and a normal butane fraction. The normal butane fraction is withdrawn from the distillation unit, as a residuum, through line 51. The isobutane is withdrawn from distillation unit 50 by means of line 52 and, after being condensed in condenser 53, it is introduced into the isobutane-feed-stock charge line 19. In this manner, the recovered isobutane is recycled to the main alkylation reaction system along with the isobutane feed stock.

The process of this invention will be further illustrated in the following example which is not to be construed as limiting the invention in any manner.

Example

In this experiment an apparatus and a continuous operation of the type hereinbefore described was employed. The butylene charge stock consisted of 20 mol per cent normal butylenes, 12 mol per cent isobutane and 68 mol per cent normal butane. On the basis of each 100 mols of the butylene charge stock introduced into the acid absorption system, this feed stock was contacted with 1480 lbs. of sulfuric acid alkylation catalyst of 91 per cent titratable acidity in the presence of recycled acid-butylene extract. This quantity of alkylation catalyst was sufficient to furnish about 1.0 mol of H_2SO_4, based on titratable acidity, for each mol of butylenes absorbed. With a hydrocarbon contact time of about 40 minutes in the absorption zone, the acid phase absorbed 13.8 mols of butylenes, leaving dissolved in the hydrocarbon phase 3.0 mols of unreacted butylenes, 2.8 mols of butylenes in the form of dibutyl sulfate and 0.4 mol of butylenes in the form of polymer oil. The absorption operation was carried out at a temperature of 25° F. under a pressure of 100 pounds per square inch gauge, using an extract retention time in the absorber of about 40 minutes.

The acid extract containing the 13.8 mols of absorbed butylenes (derived from the 100 mols of butylene feed stock charged to the absorber) was withdrawn from the absorption system and introduced into the main alkylation system along with an isobutane feed stock containing 71.6 mols of isobutane and 10.9 mols of normal bu-

tane. These streams were introduced into the circulating stream of alkylation reaction mixture which was withdrawn from the top of the main reactor and recycled to the bottom of that reactor. There were also introduced into this stream of circulating alkylation reaction mixture 1,060 pounds of 97.0 per cent strength sulfuric acid and a sufficient quantity of alkylation acid catalyst of 91 per cent titratable acidity (which was withdrawn from the acid settler following the auxiliary alkylation reactor and which was recycled to this main alkylation system) to maintain in the main alkylation reactor a volume ratio of acid phase to hydrocarbon phase of about 1:1. This alkylation operation was carried out at a temperature of 35° F. under a pressure of about 70 pounds per square inch gauge, with the volume ratio of recycled alkylation reaction mixture to the isobutane feed stock being in the order of 20:1. Under these conditions of operation, 13.1 mols of butylenes out of the 13.8 mols of butylenes charged in the form of acid extract were converted to alkylate having an average molecular weight of 114.

The stream of reaction mixture withdrawn from the main alkylation system and introduced into the auxiliary alkylation system was comprised of about equal volumes of acid phase and hydrocarbon phase. The hydrocarbon phase contained 58.5 mols of isobutane, 10.9 mols of normal butane and 13.1 mols of alkylate. This stream of reaction mixture was introduced into the emulsion recycle line of the auxiliary reactor along with the residual butane stream withdrawn from the absorption system. In addition, a sufficient quantity of alkylation acid catalyst was withdrawn from the acid settler and recycled to the emulsion recycle line of the auxiliary alkylation reaction system to maintain about 1:1 volume ratio of acid phase to hydrocarbon phase in the auxiliary reactor. The residual butane withdrawn from the absorption system contained 12 mols of isobutane, 68 mols of normal butane, 3 mols of unreacted butylenes, 2.8 mols of butylenes in the form of dibutyl sulfate and 0.4 mol of butylenes in the form of polymer oil. In this auxiliary reactor, the alkylation reaction was carried out at a temperature of 35° F. under a pressure of 40 pounds per square inch gauge. The emulsion recycle ratio employed in this system was about 20 volumes of reaction mixture per volume of hydrocarbons introduced into the system. The reaction mixture discharged from this auxiliary alkylation system was passed to an acid settler wherein the hydrocarbon phase was separated from the acid phase. As previously stated, the major portion of the acid phase was recycled to the absorber, the main alkylation reactor and the auxiliary alkylation reactor; however, a quantity of this acid equivalent to the make-up acid introduced into the main alkylation reactor was discarded. This discarded acid contained a carbonaceous diluent material equivalent to 1 mol of butylenes.

Distillation of the hydrocarbon phase leaving the acid separator showed it to contain 64.6 mols of isobutane, 78.9 mols of normal butane, and 19 mols of alkylate. This alkylate was found to have a bromine number of 0, showing it to be free of unsaturates. Prolonged treatment of the alkylate with either a hot acidic or a hot basic aqueous solution failed to give any hydrolytic products, indicating that all the alkyl sulfates and other side reaction products had been removed from the hydrocarbon mixture. This alkylate was found to contain 92.9 volume per cent of material boiling below 320° F. which had an A. S. T. M. octane number of 94.8; whereas, an alkylate prepared from a single-stage process made under conditions comparable to those employed on the auxiliary alkylation reactor contained only 89.6 volume per cent of material boiling below 320° F. which had an octane number of only 93.7. In a separate operation wherein the hydrocarbon product leaving the main alkylation reactor was segregated, it was found that the alkylate formed in this main alkylation reactor was of exceptionally high quality containing 94.5 volume per cent of material boiling below 320° F. and having an octane number of 95.3.

It is obvious to those skilled in the art that many modifications of this invention may be employed without departing from the spirit and scope of the invention. For example, with modifications obvious to those skilled in the art, the process of this invention may be adapted for use in the alkylation of isobutane with pentylenes or propylene or in the alkylation of isopentane with butylenes or propylene.

I claim:

1. In a two-stage alkylation process consisting of an absorption zone, wherein a mixed feed stock containing olefins and paraffins is contacted with sulfuric acid to form an extract phase containing the bulk of the olefins and a raffinate phase containing paraffins, some unabsorbed olefins, some olefin polymer oil and some alkyl sulfates, and a main alkylation zone, wherein the said extract is reacted with an isoparaffin under alkylation conditions, the improvement which comprises withdrawing reaction mixture from the main alkylation zone and passing it to an acid settler wherein the mixture is settled and separated into an acid phase and a hydrocarbon phase, withdrawing the hydrocarbon phase from said acid settler and passing it to an auxiliary alkylation zone, separately withdrawing the acid phase from the said acid settler, discarding from the system a portion of the said withdrawn acid and recycling the balance of the said withdrawn acid to and distributing it between the absorption zone and the main alkylation zone, introducing fresh make-up acid into the main alkylation zone in an amount equivalent to the acid discarded from the system, withdrawing raffinate from the said absorption zone and passing it to said auxiliary alkylation zone wherein it is contacted under alkylating conditions and in the presence of sulfuric acid alkylation catalyst with the hydrocarbon phase introduced therein from the said acid settler to effect alkylation of unreacted isoparaffin present in the hydrocarbon phase with olefins, olefin polymer oil and alkyl sulfates present in the raffinate, withdrawing reaction mixture from said auxiliary alkylation zone and passing it to an acid separator wherein the mixture is settled and separated into an auxiliary acid phase and a hydrocarbon phase, withdrawing the hydrocarbon phase from said acid separator, separately withdrawing the auxiliary acid from the said acid separator, discarding a portion of the auxiliary acid withdrawn from said acid separator and recycling the balance of that acid to the auxiliary alkylation zone, and introducing into the auxiliary alkylation zone make-up acid equivalent in amount to the auxiliary acid discarded.

2. In a two-stage alkylation process consisting of an absorption zone, wherein a mixed feed stock containing olefins and paraffins is contacted with

sulfuric acid to form an extract phase containing the bulk of the olefins and a raffinate phase containing the paraffins, some unabsorbed olefins, some olefin polymer oil, and some alkyl sulfates, and a main alkylation zone, wherein the said extract is reacted with an isoparaffin under alkylation conditions, the improvement which comprises withdrawing raffinate from the absorption zone and passing it to an auxiliary alkylation zone, withdrawing reaction mixture from the main alkylation zone and passing it to said auxiliary alkylation zone wherein it is reacted with the raffinate under conditions of alkylation and in the presence of sulfuric acid catalyst to effect alkylation of unreacted isoparaffin present in the reaction mixture with olefins, olefin polymer oil and alkyl sulfates present in the raffinate, withdrawing reaction mixture from said auxiliary alkylation zone and passing it to an acid settler wherein the mixture is settled and separated into an acid phase and a hydrocarbon phase, withdrawing the hydrocarbon phase from said acid settler, separately withdrawing the acid phase from the acid settler, discarding from the system a portion of the withdrawn acid and recycling the balance of the acid to and distributing it between the absorption zone, the main alkylation zone and the auxiliary alkylation zone, and introducing fresh make-up acid into the main alkylation zone in an amount equivalent to the acid discarded from the system.

3. In a two-stage alkylation process comprising an absorption zone where a mixed feed stock containing olefins and paraffins is contacted with sulfuric acid to form an extract phase and a raffinate phase and a first alkylation zone wherein the said extract is reacted with an isoparaffin under alkylating conditions, the improvement comprising withdrawing the raffinate from the absorption zone and passing it to a second alkylation zone, withdrawing the alkylation mixture from the first alkylation zone and passing it to the second alkylation zone where it is allowed to react with the raffinate under alkylation conditions, removing reaction mixture from said second alkylation zone, and separating a hydrocarbon phase therefrom.

4. In a two-stage alkylation process comprising an absorption zone where a mixed feed stock containing olefins and paraffins is contacted with sulfuric acid to form an extract phase and a raffinate phase and a first alkylation zone wherein the said extract is reacted with isoparaffin under alkylating conditions, the improvement comprising withdrawing the raffinate from the absorption zone and passing it to a second alkylation zone, withdrawing from the first alkylation zone fluid which has taken part in the alkylation reaction and passing at least a portion thereof to the second alkylation zone, where it is allowed to react with the raffinate under alkylation conditions.

5. In a two-stage alkylation process comprising an absorption zone where a mixed feed stock containing olefins and paraffins is contacted with sulfuric acid to form an extract phase and a raffinate phase and a first alkylation zone wherein the said extract is reacted with isoparaffin under alkylating conditions in the presence of sulfuric acid catalyst, the improvement comprising withdrawing the raffinate from the absorption zone and passing it to a second alkylation zone, withdrawing from the first alkylation zone fluid which has taken part in the alkylation reaction and separating it by settling into a first portion including a major amount of hydrocarbons and a second portion including a major amount of acid, passing the first portion to said second alkylation zone and reacting it with the raffinate under alkylation conditions.

6. In a two-stage alkylation process comprising an absorption zone where a mixed feed stock containing olefins and paraffins is contacted with sulfuric acid to form an extract phase and a raffinate phase, and a first alkylation zone wherein the said extract is reacted with isoparaffin under alkylating conditions in the presence of sulfuric acid catalyst, the improvement comprising withdrawing raffinate from the absorption zone and passing it to a second alkylation zone, withdrawing from the first alkylation zone the fluid which has taken part in the alkylation reaction and passing it to the second alkylation zone and reacting it with the raffinate under alkylation conditions.

ERNEST W. BOWERMAN.