

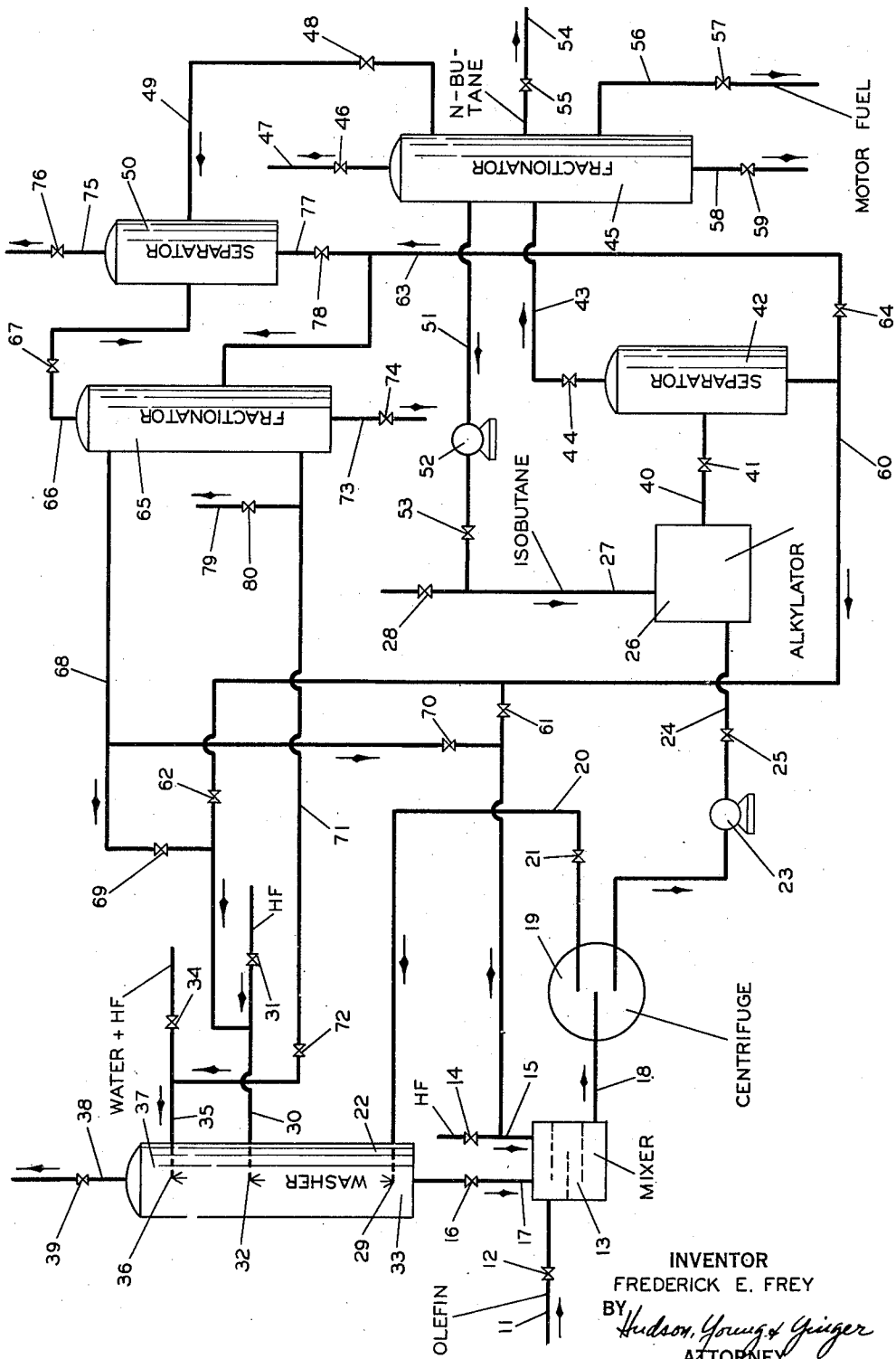
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ALKYLATION PROCESS

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ALKYLATION PROCESS

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This invention relates to a process for the conversion, by an alkylation reaction in the presence of a liquid catalyst, of relatively low-boiling hydrocarbons to higher-boiling hydrocarbons. More particularly, it relates to the efficient utilization of a comparatively inert hydrocarbon stream containing a relatively small proportion of olefins as a source of olefins for use as the alkylating agent.

Prior to this invention, the feeds to practical hydrofluoric acid alkylation processes have comprised relatively large proportions of reactive ingredients; for example, the feed used for the alkylation of isobutane with butylenes ordinarily contains a total of fifty per cent or more of isobutane plus butylenes. Heretofore, a feed having a relatively high proportion of inert diluent material has required equipment of excessive size.

An object of my invention is to provide a relatively simple, low-cost hydrocarbon-conversion process wherein a relatively inert fluid stream containing comparatively small proportions of olefin hydrocarbons may be utilized efficiently as a source of alkylating agent for converting relatively low-boiling hydrocarbons to higher-boiling hydrocarbons.

A further object of my invention is the elimination of large volumes of relatively inert material from an alkylation process in an early step, thereby increasing the capacity of the equipment.

Further objects and advantages of my invention will be apparent from the following description and the accompanying drawing.

Olefin hydrocarbons are very soluble in concentrated or anhydrous hydrofluoric acid, and polymerization of olefins in concentrated hydrofluoric acid occurs rapidly at atmospheric temperatures. Consequently, in the prior art of alkylation of hydrocarbons, there is a theory that the olefins must not come in contact with hydrogen fluoride except in low concentrations of olefins and in the presence of a large excess of alkylatable material; that is, the olefins or other alkylating agents have usually been added slowly with vigorous agitation to a mixture comprising hydrogen fluoride and an alkylatable hydrocarbon under alkylating conditions. I have found that, in a process for alkylating saturated hydrocarbons with olefin hydrocarbons in the presence of concentrated or anhydrous hydrofluoric acid, the olefins can be advantageously absorbed, under certain specific conditions which will be described hereinafter, by hydrofluoric acid prior to contacting, under alkylating conditions, with an alkylatable hydrocarbon. The resulting acid

solution, when used as an alkylating agent, produces in high yield a product of high octane number suitable for use as aviation-grade motor fuel. I have found that objectionable polymerization of the olefins absorbed in the hydrofluoric acid is averted effectively by controlling the acid-to-olefin ratio, the temperature, the acid concentration, and the period of residence of the olefin in the acid prior to the contacting with an alkylatable hydrocarbon under alkylating conditions. Hence, by the process of the invention disclosed herein, hydrocarbon streams comprising relatively small proportions of olefins may be utilized advantageously as a source of alkylating agent in a process for the conversion of relatively low-boiling hydrocarbons to higher-boiling hydrocarbons.

Understanding of some aspects of my invention will be aided by reference to the accompanying drawing, which is a schematic flow-diagram of one arrangement of apparatus for practicing the instant invention.

A liquid or liquefied hydrocarbon stream containing small proportions of olefins (for example, one to ten per cent of propylene and/or butylenes) is admitted through inlet 11 having valve 12 to mixing chamber 13, wherein it is contacted for a short time with concentrated hydrofluoric acid, admitted through valve 14 and inlet 15, and/or valve 16 and conduit 17. The mixer may be very simple; for example, a small chamber having several baffles, a length of pipe with or without baffles, a small pump, or a small zone through which both streams are made to pass at a high rate; in some cases, sufficient mixing and efficient absorption of olefins is obtained without a separate mixing apparatus by simply passing the two streams through the same or closely adjacent inlets to a centrifuge or other separating means.

In the embodiment shown, the effluent from mixer 13 is passed by way of conduit 18 to centrifuge 19, wherein it is separated into two liquid phases. The resulting hydrofluoric acid phase, which contains dissolved olefins, is forced as by gravity or by pump 23, through conduit 24 and valve 25 to alkylator 26, wherein it is rapidly mixed with a reactive paraffin hydrocarbon, such as isobutane or isopentane, admitted through conduit 27 having valve 28. Instead of centrifuge 19, it is possible in some cases to use a simple separating tank wherein separation is effected by gravity, or both centrifuge 19 and mixer 13 may be replaced by a Podbielniak-type helical supercontactor. However, the arrangement shown of a small mixer and conventional centrifuge is

usually preferred because the absorption and separation is accomplished much more rapidly than could be done with a gravitational separator, and the apparatus is simpler and less expensive than a Podbielniak-type contactor.

The other or hydrocarbon phase from centrifuge 19 which contains small proportions of organic fluorides and dissolved hydrogen fluoride, is passed via conduit 20 and valve 21 to acid washer 22. In this washer, it is distributed by suitable means 29 near the bottom of the washer, and it rises, by virtue of its relatively low density, countercurrently to downwardly flowing substantially pure concentrated hydrofluoric acid, introduced near the middle of the washer through inlet 30, valve 31, and distributing means 32. The organic fluorides are absorbed from the hydrocarbon phase by the hydrofluoric acid, which, after a short settling period in space 33 at the bottom of the washer, is passed through valve 16 and conduit 17 for use as olefin-absorbing liquid in mixer 13.

Although, as the hydrocarbon rises through the bottom half of washer 22, the countercurrently flowing concentrated hydrofluoric acid extracts organic fluorides, appreciable quantities of hydrofluoric acid remain dissolved in the hydrocarbon. The hydrocarbon continues rising in the upper half of the washer, wherein it is contacted with a countercurrently flowing aqueous phase, introduced as water or as a dilute solution of hydrofluoric acid of up to about 40 per cent in strength, preferably a constant-boiling mixture, through valve 34, inlet 35, and distributing means 36. The water or solution extracts the dissolved hydrofluoric acid from the hydrocarbon phase. The hydrocarbon phase, after a short settling period in space 37 at the top of washer 22, wherein it is separated from the aqueous phase, is withdrawn through outlet 38 having valve 39; if desired, this material may be passed to a fractionator, not shown, to recover isobutane for alkylation.

The quantity of water or aqueous dilute hydrofluoric acid introduced is preferably about one-twentieth to one-tenth of the volume of hydrocarbon treated; a much larger proportion introduces excessive amounts of water into the system, whereas a much smaller proportion does not effect substantially complete recovery of hydrofluoric acid from the hydrocarbon. The quantity of concentrated hydrofluoric acid introduced at the middle of the washer preferably is from one-fourth to two times the volume of hydrocarbon treated, and should be at least five times the volume of aqueous solution introduced at the top of the washer. Smaller amounts do not always completely remove alkyl fluorides from the hydrocarbons or are diluted too much by the aqueous solution from the top of the washer, whereas larger amounts produce an unnecessarily high ratio of acid to hydrocarbon in the alkylator.

In some instances, when the concentration of olefins in the feed is relatively high, and/or when the acid-to-olefin is low, the temperature of the extraction system is raised appreciably by the heat of solution of olefins in the hydrofluoric acid. Preferably, in such cases, cooling to about atmospheric temperature, to decrease the solubility of hydrogen fluoride in the hydrocarbon layer, may be practiced. A suitable cooling means, for example, consists of one or more cold-water coils situated within mixer 13 and/or washer 22.

The preferred time interval for passage of olefins and hydrogen fluoride from the inlet of mixer 13 by way of conduit 18, centrifuge 19, pump 23, conduit 24, and valve 25, to the inlet of alkylator 26 is in the range of 5 to 60 seconds; the preferred temperature is in the range of 30 to 150° F.; and the preferred ratio of hydrogen fluoride to olefin is in the range of 10:1 to 50:1 by weight or more. These variables are mutually interdependent; for example, at the lower temperature and the lower acid rate or longer time interval, approximately the same results are obtained as at higher temperatures and a higher acid rate or a shorter time interval. Good results can be obtained outside the ranges given, but these ranges are preferred for practical reasons, as follows: The preferred time intervals are obtainable with conventional equipment, especially centrifuging equipment, whereas shorter time intervals require more costly equipment; the preferred temperatures are near atmospheric and are therefore obtainable with little or no refrigeration; the preferred acid-to-olefin ratios are suitable for operation of the alkylation step. The exact optimum conditions for any particular case may be readily determined by trial.

In alkylator 26, under suitable alkylating conditions, such as 30 to 150° F., a pressure sufficient to maintain all components in the liquid phase, and for a time of about one to thirty or more minutes, the olefin-in-acid phase is agitated with an alkylatable hydrocarbon, such as isobutane or isopentane, introduced through conduit 27 having valve 28 in an amount of about two to ten times the amount of olefin by weight.

The resulting mixture passes as the effluent from alkylator 26 through conduit 40 and valve 41 to separator 42, wherein, by cooling and/or gravitational or centrifugal means, it is separated into two liquid phases.

Of these phases, the lighter or hydrocarbon phase is passed by way of conduit 43 and valve 44 to fractionation unit 45, in which it is separated by fractional distillation into the following six fractions: (1) A relatively minor fraction of noncondensable gases, which is removed through outlet 46 having valve 47; (2) a relatively minor fraction, comprising an azeotropic mixture of hydrogen fluoride and light hydrocarbons, such as propane or butane, which passes via valve 48 and conduit 49 to separator 50; (3) a comparatively large fraction, comprising unreacted readily alkylatable hydrocarbons, such as isobutane or isopentane, which is recycled via conduit 51, pump 52, valve 53, and conduit 27 to alkylator 26; (4) a fraction comprising relatively difficultly alkylatable hydrocarbons, such as normal butane, which is withdrawn through outlet 54 having valve 55; (5) a substantial fraction of highly-branched paraffinic reaction products boiling within the gasoline range, which is withdrawn through outlet 56 having valve 57; and (6) a high-boiling bottom fraction, comprising heavy polymers and other by-products, which is withdrawn through outlet 58 having valve 59.

The heavier or hydrofluoric acid phase from separator 42 is recycled to mixer 13 and/or washer 22 by way of conduit 60 and valve 61 and/or valve 62, respectively. Preferably, however, a part of it is passed through conduit 63 and valve 64 to acid-fractionation unit 65, wherein it is separated into the following four fractions: (1) A minor fraction, comprising an azeotropic mixture of hydrofluoric acid and low-boiling hydrocarbons, such as propane or butane, which is

passed through conduit 66 having valve 67 to separator 50; (2) a major fraction of substantially pure anhydrous hydrogen fluoride, which is recycled through conduit 68 and valve 69 and/or valve 70 to washer 22 and/or mixer 13, respectively; (3) a fraction, comprising a constant-boiling mixture of water and hydrogen fluoride, which is passed through conduit 71, valve 72, and inlet 35 to the top of washer 22, wherein it is used to extract HF from the olefin-depleted hydrocarbon phase as already described; (4) a bottom fraction, comprising hydrocarbon residue and high-boiling by-products, which is withdrawn through outlet 73 having valve 74. If desired, any excess constant-boiling mixture may be withdrawn from the system, as through outlet 79 and valve 80, and this excess may be treated, in a separation step not shown, for the recovery of hydrogen fluoride.

Separator 50 is shown as a separation means, in which, by cooling and gravitational or centrifugal means, the azeotropic mixtures of hydrofluoric acid and low-boiling hydrocarbons from fractionators 45 and 65 separate into two liquid phases; the lighter or hydrocarbon phase is withdrawn through outlet 75 having valve 76, and the heavier or hydrofluoric acid phase is passed by way of conduit 77 and valve 78 to fractionator 65. Alternatively, instead of going to separator 50, either or both of the azeotropic mixtures may be recycled to alkylator 26, by means that are not shown but that can be readily supplied by those skilled in the art; this alternative is preferred when the low-boiling hydrocarbon in the azeotropic mixture is a relatively easily alkylatable hydrocarbon, such as an isoparaffin.

I have found that the rate of polymerization of olefins in hydrofluoric acid is reduced considerably if some water is present in the acid. However, although alkylation with hydrofluoric acid containing up to about 10 per cent water produces in high yield a product of good quality, both the quality and the yield may be somewhat inferior to those obtained by alkylation with acid containing less water. Therefore, it is advantageous to have a higher concentration of water present in the acid phase of the olefin-extraction step than in the acid phase of the alkylation step. This desirable end can be attained in a modification of my process in which the hydrofluoric acid introduced in the absorption step is of relatively lower concentration, such as 65 to 90 per cent by weight, the balance being water, and in which a proportion of substantially anhydrous hydrofluoric acid large enough to raise the average concentration to the desired value, at least to 90 per cent and preferably higher, is introduced in the alkylation step. This modification is advantageous, for instance, if means for carrying out the absorption and separation steps within the preferred short time interval are not available. Usually, however, in order to simplify the operation and to maintain a high acid-to-olefin ratio in the absorption operation, it is preferable to introduce all the hydrogen fluoride, in concentration sufficient to obtain efficient operation of the alkylation step, into the washing or mixing steps, and to depend upon control of the time, temperature, and acid-to-olefin ratio to avert undesirable polymerization reactions.

The olefin-containing feed to the absorption step of this process should be liquid, and the pressures and the temperatures in the mixing, centrifuging, and washing equipment must be so controlled as to maintain all components in the liquid

phase. Preferably, therefore, so that relatively low operating pressures may be used, the average boiling-point of the olefin-containing feed is of the order of, or higher than, that of butanes. The specific olefin in the feed, in accordance with the prior art of hydrofluoric acid alkylation, is preferably one having three to five carbon atoms per molecule or a mixture of these. Although pure propylene is a relatively low-boiling hydrocarbon, it dissolves readily in, or is readily extracted from a gaseous mixture by, relatively higher-boiling hydrocarbons, such as normal butane, normal pentane, normal hexane, or the like. Thus, a solution of propylene in a higher-boiling hydrocarbon may be advantageously used as a feed to the absorption step of this process, thereby eliminating the necessity for using a high operating pressure to maintain propylene in the liquid phase.

To illustrate some of the many aspects of my invention, the following specific examples are given:

Example I

A butane fraction containing 11.2 per cent of unsaturated hydrocarbon is contacted, at 71° F. and at sufficient pressure to maintain the liquid phase, with concentrated hydrofluoric acid in a small mixer; the resulting mixture is centrifuged to separate out an acid phase containing dissolved olefins, which is immediately passed to an alkylator, and a hydrocarbon phase from which, first, organic fluorine is recovered by washing with countercurrently flowing concentrated hydrofluoric acid, and, second, dissolved hydrogen fluoride is recovered by washing with a countercurrently flowing aqueous solution of hydrogen fluoride. The effluent hydrocarbon stream is free from unsaturates and contains less than 0.002 per cent by weight of organic fluorine and less than 0.02 per cent by weight of dissolved hydrogen fluoride. The acid from the washing operations is added to the mixer, thus preventing the loss of fluorine as hydrogen fluoride or as organic fluorine in the hydrocarbons from which the olefins have been extracted. The total average time of mixing, centrifuging, and introduction into the alkylator is about 15 to 30 seconds. The alkylating conditions are: 95° F., five minutes contact time, pressure sufficient to maintain the liquid phase, and rapid agitation with excess isobutane. The effluent from the alkylator is separated by gravity into an acid phase and a hydrocarbon phase. Half of the acid phase is recycled directly to the mixer, and half is passed to an acid-fractionating unit. From this unit are withdrawn a substantially anhydrous hydrofluoric acid fraction and a constant-boiling water-hydrogen fluoride fraction; these fractions are recycled to the first and second above-described washing operations, respectively. The hydrocarbon phase is fractionated to recover isobutane, which is recycled to the alkylator, and relatively high-boiling hydrocarbons suitable for use as motor fuel.

The relative proportions of materials in the various steps are as follows: Acid-to-olefin ratio in mixer and centrifuge, 15:1; isobutane-to-olefin ratio in feeds entering alkylator, 8:1; acid directly recycled from alkylator to mixer, 50 per cent; ratio of concentrated acid in first washing operation to aqueous solution in second washing operation, 8:1.

The yield of debutanized alkylate is about 167 per cent based on the weight of olefins in the feed. Upon rerunning, 96 per cent of this alkylate is ob-

tained as an aviation-gasoline cut having an octane number of 91, which is raised to about 100.2 by the addition of one cc. of tetraethyl lead per gallon of gasoline.

Example II

A process similar to that described in Example I is carried out with the following changes: A simple gravity settling chamber is used instead of the centrifuge. The temperature of mixing and absorption is 35° F. instead of 71° F. The average time interval for mixing, separation, and introduction to the alkylator is about two minutes instead of about 15 to 30 seconds. One and one-half times as much acid is used, of which one-third is introduced in the washing steps and two-thirds in the mixing step. A yield of debutanized alkylate of 155 per cent by weight of unsaturates in the feed is obtained. Upon rerunning, 94 per cent of 89 octane aviation gasoline is obtained.

It will be evident to those skilled in the art that my invention effects a substantial reduction in the size of equipment required for hydrofluoric acid alkylation, or a substantial increase in the capacity of existing plants. My invention makes possible the recovery and utilization as alkylating agent, of olefins present only in small proportions, such as five per cent or even less, in hydrocarbon streams. My invention provides for substantially complete recovery from the olefin-depleted hydrocarbon stream of dissolved hydrogen fluoride.

Obviously, there are many variations and modifications of my invention, only a few of which are described herein. For example, washer 22 may be replaced by a series of washers in which the olefin-depleted hydrocarbon effluent from mixer 13 is contacted in succession with concentrated hydrofluoric acid, one or more aqueous acid solutions in the order of decreasing concentration, and finally, if desired, pure water. An acid effluent from one washer may be used as the extracting liquid in a washer using a more concentrated solution of acid. The one or more concentrated acid extracts, which contain dissolved alkyl fluorides, may be passed to mixer 13. If desired, the one or more dilute acid extracts, which are substantially pure aqueous solutions of hydrogen fluoride, may be passed to a fractionating unit to be separated into a constant-boiling mixture, which may be recycled to the appropriate washer, and into the component in excess.

In another modification, part or all of the aqueous acid solution introduced into washer 22 through distributing means 36 may be withdrawn, by means not shown in the drawing, at a point just above distributing means 32, and may be recycled to distributing means 36 or passed to an acid fractionator, such as fractionator 65, for separation into substantially pure hydrofluoric acid and a maximum-boiling aqueous solution. Fractionator 65 may be any system capable of producing the separations indicated. It may, for example, comprise the following: A first column from which high-boiling organic material is withdrawn as a kettle product and from which the overhead effluent is passed to a separator for separation into two liquid phases; and a second column, in which the hydrofluoric acid phase from this separator is fractionated into an overhead effluent of substantially anhydrous hydrofluoric acid and a kettle product of a constant-boiling aqueous hydrofluoric acid, either or both of which may be used as already described. Additional

pumps, valves, fractionators, coolers, and the like, such as are well known in the art, may be used wherever they are desirable or convenient. It is intended that the foregoing specific examples and description of particular apparatus and operating conditions should illustrate the principles of my invention and the preferred modes of practicing it, but that the scope of the invention should be limited only by the following claims.

I claim:

1. In a process for alkylating a low-boiling isoparaffin with a low-boiling olefin, the improvement which comprises contacting an olefin-containing hydrocarbon mixture with liquid aqueous hydrofluoric acid having a hydrogen fluoride concentration in the range of 65 to 90 per cent by weight and with a ratio of hydrogen fluoride to olefin of at least 10:1 by weight, separating a resulting liquid hydrofluoric acid phase and a resulting hydrocarbon phase containing minor amounts of organic fluorine compounds and free hydrogen fluoride, successively contacting said separated hydrocarbon phase with liquid hydrofluoric acid to remove said organic fluorine compounds and with highly aqueous hydrofluoric acid to remove free hydrogen fluoride, adding resulting extract phases to the first said aqueous hydrofluoric acid, admixing with the first said resulting liquid hydrofluoric acid phase sufficient hydrogen fluoride to raise the hydrogen fluoride concentration to an alkylating strength above 90 per cent by weight and also admixing a low-boiling isoparaffin, maintaining in an alkylation zone the resulting admixture under alkylation conditions to effect an alkylation of said isoparaffins with olefins dissolved in said aqueous hydrofluoric acid, and recovering from effluents of said treatment a hydrocarbon fraction containing alkylated isoparaffins so produced.

2. The process of removing olefins from a hydrocarbon material containing low-boiling olefin and paraffin hydrocarbons, which comprises contacting such an olefin-containing hydrocarbon mixture with liquid aqueous hydrofluoric acid having a hydrogen fluoride concentration in the range of 65 to 90 per cent by weight and with a ratio of hydrogen fluoride to olefin of at least 10:1 by weight, separating a resulting liquid hydrofluoric acid phase and a resulting hydrocarbon phase containing minor amounts of organic fluorine compounds and free hydrogen fluoride, successively contacting said separated hydrocarbon phase with liquid hydrofluoric acid to remove said organic fluorine compounds and with highly aqueous hydrofluoric acid to remove free hydrogen fluoride, and adding resulting extract phases to concentrated hydrofluoric acid to form the aforesaid aqueous hydrogen fluoride having a concentration of 65 to 90 per cent by weight and recovering as effluents of said process an olefin-free hydrocarbon material and an aqueous liquid hydrofluoric acid containing dissolved olefins.

3. In a process for alkylating a low-boiling isoparaffin with a low-boiling olefin, the improvement which comprises intimately contacting at a temperature in the range of 30 to 150° F. an olefin-containing liquid hydrocarbon mixture with liquid aqueous hydrofluoric acid having a hydrogen fluoride concentration in the range of 65 to 90 per cent by weight and with a ratio of hydrogen fluoride to olefin in the range of 10:1 to 50:1 by weight, separating a resulting liquid hydrofluoric acid phase from unabsorbed inert liquid hydrocarbons, admixing with said aqueous hydrofluoric acid phase sufficient hydrogen flu-

oride to raise the hydrogen fluoride concentration to above 90 per cent by weight and also admixing a low-boiling isoparaffin, maintaining in an alkylation zone the resulting admixture under alkylation conditions to effect an alkylation of said isoparaffin with olefins dissolved in said aqueous hydrofluoric acid, and recovering from effluents of said treatment a hydrocarbon fraction containing alkylated isoparaffins so produced.

4. In a process for alkylating a low-boiling alkylatable hydrocarbon with a low-boiling olefin, the improvement which comprises contacting an olefin-containing hydrocarbon mixture with liquid aqueous hydrofluoric acid having a hydrogen fluoride concentration in the range of 65 to 90 per cent by weight and with a ratio of hydrogen fluoride to olefin of at least 10:1 by weight, separating a resulting liquid hydrofluoric acid phase and a resulting hydrocarbon phase containing minor amounts of organic fluorine compounds and free hydrogen fluoride, successively contacting said separated hydrocarbon phase with liquid hydrofluoric acid to remove said organic fluorine compounds and with highly aqueous hydrofluoric acid to remove free hydrogen fluoride, adding resulting extract phases to the first said aqueous hydrofluoric acid, admixing with the first said resulting liquid hydrofluoric acid phase sufficient hydrogen fluoride to raise the hydrogen fluoride concentration to an alkylating strength above 90 per cent by weight and also admixing a low-boiling alkylatable hydrocarbon, maintaining the resulting admixture under alkylation conditions to effect an alkylation of said alkylatable hydrocarbon with olefins dissolved in said aqueous hydrofluoric acid, and recovering from effluents of said treatment a hydrocarbon fraction containing alkylated hydrocarbons so produced.

5. In a process for alkylating a low-boiling alkylatable hydrocarbon with a low-boiling olefin, the improvement which comprises intimately contacting at a temperature in the range of 30 to 150° F. an olefin-containing liquid hydrocarbon mixture with liquid aqueous hydrofluoric acid having a hydrogen fluoride concentration in the range of 65 to 90 per cent by weight and with a ratio of hydrogen fluoride to olefin in the range of 10:1 to 50:1 by weight, separating a resulting liquid hydrofluoric acid phase from unabsorbed inert liquid hydrocarbons, admixing with said aqueous hydrofluoric acid phase sufficient hydrogen fluoride to raise the hydrogen fluoride concentration to above 90 per cent by weight, and also admixing a low-boiling alkylatable hydrocarbon, maintaining the resulting admixture under alkylation conditions to effect an alkylation of said alkylatable hydrocarbon with olefins dissolved in said aqueous hydrofluoric acid, and recovering from effluents of said treatment a hydrocarbon fraction containing alkylated hydrocarbons so produced.

drocarbon fraction containing alkylated hydrocarbons so produced.

6. In a process for alkylating a low-boiling isoparaffin with a low-boiling olefin, the improvement which comprises intimately contacting at a temperature in the range of 30 to 150° F. an olefin-containing liquid hydrocarbon mixture with liquid aqueous hydrofluoric acid having a hydrogen fluoride concentration in the range of 65 to 90 per cent by weight and with a ratio of hydrogen fluoride to olefin in the range of 10:1 to 50:1 by weight, separating a resulting liquid hydrofluoric acid phase from unabsorbed inert liquid hydrocarbons, admixing with said aqueous hydrofluoric acid phase sufficient hydrogen fluoride to raise the hydrogen fluoride concentration to above 90 per cent by weight and also admixing a low-boiling isoparaffin, maintaining in an alkylation zone the resulting admixture under alkylation conditions to effect an alkylation of said isoparaffin with olefins dissolved in said aqueous hydrofluoric acid, the time interval between the initial mixing of said olefin-containing hydrocarbon mixture with said aqueous hydrofluoric acid and introduction of the resulting aqueous hydrofluoric acid phase to said alkylation zone being between about 5 and about 60 seconds, and recovering from effluents of said treatment a hydrocarbon fraction containing alkylated isoparaffins so produced.

7. In a process for alkylating a low-boiling alkylatable hydrocarbon with a low-boiling olefin, the improvement which comprises intimately contacting at a temperature in the range of 30 to 150° F. an olefin-containing liquid hydrocarbon mixture with liquid aqueous hydrofluoric acid having a hydrogen fluoride concentration in the range of 65 to 90 per cent by weight and with a ratio of hydrogen fluoride to olefin in the range of 10:1 to 50:1 by weight, separating a resulting liquid hydrofluoric acid phase from unabsorbed inert liquid hydrocarbons, admixing with said aqueous hydrofluoric acid phase sufficient hydrogen fluoride to raise the hydrogen fluoride concentration to above 90 per cent by weight, and also admixing a low-boiling alkylatable hydrocarbon, maintaining in an alkylation zone the resulting admixture under alkylation conditions to effect an alkylation of said alkylatable hydrocarbon with olefins dissolved in said aqueous hydrofluoric acid, the time interval between the initial mixing of said olefin-containing hydrocarbon mixture with said aqueous hydrofluoric acid and introduction of the resulting aqueous hydrofluoric acid phase to said alkylation zone being between about 5 and about 60 seconds, and recovering from effluents of said treatment a hydrocarbon fraction containing alkylated hydrocarbons so produced.

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