

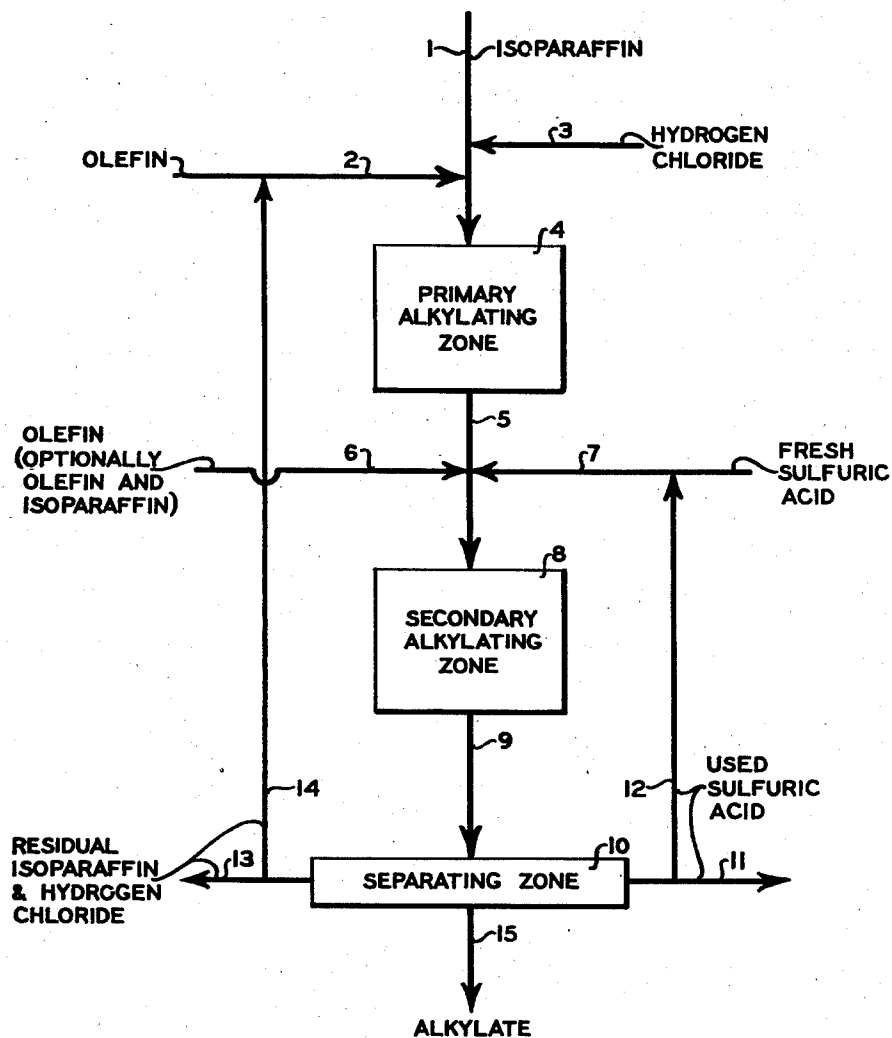
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TREATMENT OF HYDROCARBONS

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TREATMENT OF HYDROCARBONS

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This invention relates to the treatment of isoparaffin hydrocarbons to produce higher molecular weight alkyl derivatives thereof. More specifically the process is concerned with a method of alkylating isoparaffin hydrocarbons by olefins in the presence of catalysts to produce a motor fuel of relatively high antiknock value.

In one specific embodiment the present invention comprises a process for alkylating isoparaffin hydrocarbons by olefinic hydrocarbons to produce a substantially saturated gasoline of high octane number which comprises subjecting a mixture of an isoparaffin hydrocarbon and an olefinic hydrocarbon to contact in the presence of hydrogen chloride with a catalyst composite comprising essentially aluminum chloride and a substantially inert carrier in a primary alkylating zone to form a mixture comprising essentially the unconverted isoparaffin hydrocarbon and a substantially saturated alkylate as a major reaction product containing a relatively smaller proportion of unavoidably formed alkyl chlorides; separating said mixture from said catalyst composite; directing said mixture and an additional quantity of olefinic hydrocarbons to contact with sulfuric acid in a second alkylating zone to form a mixture of partially spent sulfuric acid, hydrogen chloride, unconverted isoparaffin, and a substantially saturated high antiknock alkylate of motor fuel boiling range substantially free from alkyl chlorides; recycling at least a part of said partially spent sulfuric acid to the second alkylating zone; and recycling said unconverted isoparaffin and said hydrogen chloride to commingle with the fresh isoparaffin-olefin mixture being charged to the primary alkylating zone.

The invention is believed to reside not in any individual step of the process per se, but rather in the advantageous combination of steps which cooperate to produce the desired final result, namely, conversion of isoparaffin and olefinic hydrocarbons, including ethylene, into good yields of substantially saturated, high antiknock value products boiling within the range of gasoline and substantially free from alkyl chlorides heretofore present in alkylation products formed in the presence of an aluminum chloride-hydrogen chloride catalyst. The process has the advantage that both ethylene and higher molecular weight olefins may be used to alkylate isoparaffins while at the same time overcoming the objection to the aluminum chloride alkylation step previously mentioned, namely, chlorination of the reaction product.

According to the present invention any of the isoparaffin hydrocarbons may be alkylated including isobutane and its homologs though obviously under somewhat modified conditions of operation when alkylating isoparaffins of different reactivities. The olefins employed may be normally gaseous or liquid but are preferably of lower molecular weight than hexenes and consist essentially of ethylene, propene, butenes, and pentenes.

One method of preparing supported aluminum chloride used as catalyst in the primary alkylation stage of the process consists in compositing aluminum chloride and a granular supporting material by some means such as by mixing these materials in an apparatus which will withstand some pressure and then in heating at an elevated temperature and under a superatmospheric pressure until the aluminum chloride has been adsorbed by the supporting material which may comprise various types of activated carbon, diatomaceous earth, celite particles, silica, crushed firebrick, aluminum silicate, porous clays, fuller's earth, bentonite, montmorillonite, and in general, any refractory porous substance which has no undesirable reactivity with substantially anhydrous aluminum chloride.

Aluminum chloride is adsorbed by the granular material and accordingly is not easily lost by sublimation as is the case with unsupported aluminum chloride. Also the supported catalyst has the advantage that aluminum chloride is diluted by the carrier employed and therefore the reaction is catalyzed less energetically than in the presence of unsupported aluminum chloride and consequently the destructive tendency of unsupported aluminum chloride to decompose an alkylation product is substantially diminished.

The proportions of adsorbent carrier and aluminum chloride may be varied as desired to make catalyst composites of different activities. It has been found possible and practical in the case of aluminum chloride to make stable granular catalysts resistant to disintegrating influences by using approximately 0.2 to about 0.8 part by weight of anhydrous aluminum chloride per part by weight of adsorptive support or carrier. These materials, after thorough mechanical mixing in the desired proportions, are placed in a pressure vessel which is preferably made of or lined with a suitable corrosion resistant material, the vessel is placed under a superatmospheric pressure by the introduction of hydrogen or of another inert gas, and then the vessel and

contents are heated up to approximately 480° F. for several hours. The heating may also be carried out in the absence of an added gas or hydrogen chloride may be introduced prior to the heating either in the presence or in the absence of an added gas as hydrogen.

After such a treatment of the original mixture, a product is obtained in the form of a dry granular composite of aluminum chloride and carrier. From the appearance of the composite the aluminum chloride seems to have disappeared although it is actually in the pores and on the surface of the adsorbent as evidenced by the violent reaction of the granules of the composite with water and the catalytic activity in organic reactions. This procedure is typical of the preparation of a large number of similar catalysts using different combinations of the metal chloride on the supports already mentioned.

Alkylation of an isoparaffin as isobutane by ethylene may be effected readily in the presence of aluminum chloride and hydrogen chloride although such an alkylation proceeds only with difficulty in the presence of sulfuric acid. Alkylation in the presence of supported aluminum chloride may be carried out at a temperature within the limits of approximately 30° and 300° F. and under a pressure of from substantially atmospheric to approximately 1000 pounds per square inch or more in the presence of about 0.5% to about 10% by weight of hydrogen chloride. It has been found that the reaction product from this step contains not only alkylation products but various percentages of alkyl chlorides up to 6% or 8% or even more, which, if not removed, cause the alkylation reaction product to have a chlorine content often of as much as 3% by weight. Some means of removing these alkyl halides is essential if the alkylation product is to be utilized as a motor fuel since otherwise corrosion problems may be serious.

The present invention proposes to react these alkyl halides with additional quantities of isoparaffin, such as isobutane, in a second alkylating step and, when desired, in the presence of additional olefinic hydrocarbons utilizing sulfuric acid as alkylating catalyst. This second alkylating treatment in the presence of sulfuric acid at from about 0° to about 150° F. under a pressure of up to about 500 pounds per square inch causes isoparaffins to be alkylated by olefins and also by alkyl chlorides. This conversion of the alkyl chlorides also yields hydrogen chloride and produces a substantially saturated alkylate with a relatively low chlorine content.

For the second alkylating treatment sulfuric acid employed as catalyst may be of a concentration from about 90% to 100% and also fuming sulfuric acid may be used. The amount of olefin to be added to the mixture of isoparaffins and alkyl chloride charged thereto should be within the approximate limits of 1% and 5% of the total isoparaffin content of the mixture. The resulting product may be separated into a substantially saturated alkylate and a mixture of unconverted isoparaffins and hydrogen chloride, the latter mixture being recycled to further treatment in the primary alkylating step in the presence of aluminum chloride or of supported aluminum chloride.

The present invention is not merely a sulfuric acid treating process for removing chlorinated products from a material of gasoline boiling range but it is a process wherein such dechlorination is accomplished with the additional bene-

ficial effect of converting the undesirable alkyl chlorides into increased quantities of high anti-knock motor fuel, the total yield of alkylation product being increased because of the increased alkylation of the isoparaffins by said alkyl chlorides.

For the purpose of illustrating the combination of steps characteristic of the present invention the attached drawing shows a typical process flow for producing gasoline of high octane number from iso-paraffinic and olefinic hydrocarbons.

Referring to the drawing, an isoparaffinic hydrocarbon such as isobutane may be introduced through line 1 and therein commingled with an olefin admitted through line 2 and hydrogen chloride added by way of line 3. The commingled mixture of isoparaffin, hydrogen chloride, and an olefin such as ethylene may be directed from line 1 to primary alkylating zone 4 which may comprise a reactor or group of reactors containing as filling material a composite of aluminum chloride and an adsorptive carrier such as activated charcoal. Depending upon the reactivity of the isoparaffinic and olefinic hydrocarbons charged to contact with an aluminum chloride-containing alkylation catalyst in the presence of hydrogen chloride, primary alkylating zone 4 may be maintained at some temperature within the approximate limits of about 30° and about 300° F. and under a pressure of from substantially atmospheric to approximately 1000 pounds per square inch. The mixture charged to alkylating zone 4 should preferably contain between about 1 and about 25 mole per cent of olefinic hydrocarbon in order that alkylation may be the predominant reaction and that polymerization of the olefinic material may be avoided.

From primary alkylating zone 4 the reaction product comprising essentially unconverted isoparaffin, alkylation product, alkyl chlorides (which may be present up to the extent of 6% to 8% or even more), and hydrogen chloride are directed through line 5, and therein commingled with an additional quantity of olefinic material higher than ethylene or a mixture of olefinic and isoparaffinic hydrocarbons introduced through line 6 and with fresh sulfuric acid of a concentration between about 90% and about 100% or more introduced through line 7. The commingled mixture in line 5 is then directed to secondary alkylating zone 8 which comprises a suitable reactor or group of reactors maintained at a temperature between about 30° and about 300° F. and under sufficient pressure to maintain in liquid phase a substantial proportion of the hydrocarbons introduced thereto.

From about 1%, to about 5% by volume of olefinic hydrocarbons should be present in the hydrocarbon mixture introduced to secondary alkylating zone 8 in order that olefin polymerization may be avoided and that the formation of a substantially saturated alkylate may be the major reaction in secondary alkylating zone 8. The alkyl chlorides introduced thereto react with isoparaffinic hydrocarbons in the presence of sulfuric acid to form higher boiling paraffinic hydrocarbons, hydrogen chloride being liberated simultaneously.

The entire mixture of reaction products is directed from secondary alkylating zone 8 through line 9 to separating zone 10 which may comprise a series of steps although in the diagrammatic drawing it is shown as a single step for purposes of simplification. Used sulfuric acid may be di-

rected from separating zone 10 through line 11 to a reactivating treatment, not shown, or to other use or waste. When desired, at least a portion of the used sulfuric acid may be recycled from line 11 through lines 12, 7, and 5 to further use in secondary alkylating zone 8. Residual isoparaflinic hydrocarbon admixed with used hydrogen chloride may be withdrawn from separating zone 10 through line 13 to storage or to other use. When desired, at least a portion of the mixture of residual isoparaflin and hydrogen chloride may be recycled from line 13 through lines 14, 2, and 1 to further use in primary alkylating zone 4 in the presence of supported aluminum chloride. The substantially saturated alkylate separated from other products in separating zone 10 may be discharged therefrom through line 15 to storage.

The following example is introduced to show results which may be expected in one specific operation of the process, although with no intention of unduly limiting the generally broad scope of the invention.

1000 volumes of charging stock containing ethylene, isobutane, and hydrogen chloride is passed per hour through 100 volumes of a granular catalyst composite consisting of 24 parts by weight of aluminum chloride and 36 parts by weight of celite particles used as a filler in a reactor maintained at 145° F. under a pressure of 400 pounds per square inch. The charging stock is formed by commingling just before entering the catalyst chamber a mixture containing 6% by weight of ethylene, 0.2% propene, 3.0% propane, 76.7% isobutane, 13.5% normal butane, and 0.6% pentane with another mixture containing 2% by weight of propane, 79% isobutane, 14% normal butane, and 5% hydrogen chloride, the last dissolved in the hydrocarbons.

While 5400 volumes of the ethylene-containing mixture and 515 volumes of the hydrogen chloride-containing mixture are charged over a period of 6 hours, 367 parts by weight of a substantially paraflinic hydrocarbon product is obtained containing 0.41% by weight of chlorine. Analysis by fractional distillation of the paraflinic hydrocarbon product shows a composition of approximately 12% by volume of pentane, 66% hexane, 3% heptane, 15% octane, 2% nonane, and 2% of higher boiling material with an end boiling point of 300° F. The yield of paraflinic hydrocarbon product is equivalent to approximately 206% by weight of the ethylene charged.

The mixture of unconverted isobutane and paraflinic hydrocarbon products containing chlorine resulting from the primary alkylation in the presence of hydrogen chloride and of the aluminum chloride-celite catalyst is admixed with approximately 15% by weight of normal butene and subjected to contact with sulfuric acid of 95% concentration at 45° F. under a pressure of 200 pounds per square inch. This treatment forms a saturated product substantially free from chlorine, the yield of said product being increased by the amount of alkylate formed from the isobutane and normal butenes which react in the presence of sulfuric acid. The average boiling range of the product resulting from the alkylation in the presence of sulfuric acid is generally higher than that of the alkylate formed in the presence of aluminum chloride because of the fact that some of the primary alkylation products undergo further reaction with normal butenes during the alkylation catalyzed by sulfuric acid. The final alkylation product resulting from suc-

cessive alkylation in the presence first of supported aluminum chloride and next in the presence of sulfuric acid has an octane number of approximately 92 and a chlorine content of not more than 0.01% by weight.

The novelty and utility of the process of this invention are evident from the preceding specification and example, although neither section is intended to unduly limit its generally broad scope.

We claim as our invention:

1. A process for alkylating isoparaflinic hydrocarbons with olefinic hydrocarbons to produce high antiknock motor fuel which comprises subjecting a mixture of a major proportion of an isoparaflinic hydrocarbon and a relatively smaller proportion of an olefinic hydrocarbon to a primary alkylating treatment in the presence of both an aluminum halide catalyst and a hydrogen halide, separating the reaction products from the catalyst, and subjecting the reaction products of the primary alkylating treatment to a secondary alkylating treatment in the presence of sulfuric acid to form a substantially saturated alkylate.

2. A process for alkylating isoparaflinic hydrocarbons with olefinic hydrocarbons to produce high antiknock motor fuel which comprises subjecting a mixture of a major proportion of an isoparaflinic hydrocarbon and a relatively smaller proportion of an olefinic hydrocarbon to a primary alkylating treatment in the presence of both an aluminum halide catalyst and a hydrogen halide; separating the reaction products from the catalyst; subjecting the reaction products of the primary alkylating treatment to a secondary alkylating treatment in the presence of sulfuric acid; separating from the resulting reaction products a substantially saturated alkylate, a mixture containing hydrogen halide and unreacted isoparaflin, and partially spent sulfuric acid; and recycling to the primary alkylating treatment at least a portion of the mixture containing hydrogen halide and unreacted isoparaflin.

3. A process for alkylating isoparaflinic hydrocarbons with olefinic hydrocarbons to produce high antiknock motor fuel which comprises subjecting a mixture of a major proportion of an isoparaflinic hydrocarbon and a relatively smaller proportion of an olefinic hydrocarbon to a primary alkylating treatment in the presence of both an aluminum halide catalyst and a hydrogen halide; separating the reaction products from the catalyst, subjecting the reaction products of the primary alkylating treatment to a secondary alkylating treatment in the presence of sulfuric acid; separating from the resulting reaction products a substantially saturated alkylate, a mixture containing hydrogen halide and unreacted isoparaflin, and partially spent sulfuric acid; recycling to the primary alkylating treatment at least a portion of the mixture containing hydrogen halide and unreacted isoparaflin; and recycling to the secondary alkylating treatment at least a portion of the partially spent sulfuric acid.

4. A process for alkylating isobutane with olefinic hydrocarbons to produce high antiknock motor fuel which comprises subjecting a mixture of a major proportion of isobutane and a relatively smaller proportion of an olefinic hydrocarbon to a primary alkylating treatment in the presence of both an aluminum halide catalyst and a hydrogen halide, separating the reaction products from the catalyst, and subjecting the reaction products of the primary alkylating treatment to

a secondary alkylating treatment in the presence of sulfuric acid to form a substantially saturated alkylate.

5. A process for alkylating isobutane with normally gaseous olefinic hydrocarbons to produce high antiknock motor fuel which comprises subjecting a mixture of a major proportion of isobutane and a relatively smaller proportion of a normally gaseous olefinic hydrocarbon to a primary alkylating treatment in the presence of both an aluminum halide catalyst and a hydrogen halide, separating the reaction products from the catalyst, and subjecting the reaction products of the primary alkylating treatment to secondary alkylating treatment in the presence of sulfuric acid to form a substantially saturated alkylate.

6. The process of claim 1 further characterized in that the aluminum halide is aluminum chloride and the hydrogen halide is hydrogen chloride.

7. The process of claim 1 further characterized in that the aluminum halide is supported on a relatively inert carrier.

8. A process for alkylating isoparaflinic hydrocarbons with olefinic hydrocarbons to produce high antiknock motor fuel which comprises treating a mixture comprising a major proportion of an isoparaflinic hydrocarbon and a relatively smaller proportion of a normally gaseous olefinic hydrocarbon under alkylating conditions of temperature and pressure with an alkylating catalyst comprising essentially an aluminum halide and a hydrogen halide, separating the other reactants from the aluminum halide, adding to said reactants an additional quantity of a gas containing gaseous olefins to form a mixture containing up to about 5% by weight of olefins in respect to the isoparaflin content of the mixture, and subjecting said mixture to further alkylating treatment in the presence of sulfuric acid to form a substantially saturated alkylate.

9. A process for alkylating isoparaflinic hydrocarbons with olefinic hydrocarbons to produce high antiknock motor fuel which comprises treating a mixture comprising a major proportion of an isoparaflinic hydrocarbon and a relatively smaller proportion of a normally gaseous olefinic hydrocarbon under alkylating conditions of temperature and pressure with an alkylating catalyst comprising essentially an aluminum

halide and a hydrogen halide; separating the other reactants from the aluminum halide; adding to said reactants an additional quantity of a gas containing gaseous olefins to form a mixture containing up to about 5% by weight of olefins in respect to the isoparaflin content of the mixture; subjecting said mixture to further alkylating treatment in the presence of sulfuric acid; separating from the resulting reaction products a substantially saturated alkylate, a mixture containing hydrogen halide and unreacted isoparaflin, and partially spent sulfuric acid; recycling to the primary alkylating treatment at least a portion of the mixture containing hydrogen halide and unreacted isoparaflin; and recycling to the secondary alkylating treatment at least a portion of the partially spent sulfuric acid.

10. A process for alkylating isoparaflinic hydrocarbons with olefinic hydrocarbons to produce high antiknock motor fuel which comprises subjecting a mixture of a major proportion of an isoparaflinic hydrocarbon and a relatively smaller proportion of an olefinic hydrocarbon to a primary alkylating treatment in the presence of both hydrogen chloride and aluminum chloride to form a mixture comprising essentially hydrogen chloride, unconverted isoparaflinic hydrocarbon, and a substantially saturated alkylate as a major reaction product containing a relatively small proportion of alkyl chlorides; separating said mixture from said aluminum chloride catalyst; adding to said mixture an additional quantity of a gas containing gaseous olefins to form a commingled mixture containing up to about 5% by weight of olefins in respect to isoparaflin; subjecting said commingled mixture to further alkylating treatment in the presence of sulfuric acid; separating from the resulting reaction products a substantially saturated alkylate, a mixture containing hydrogen halide and unreacted isoparaflin, and partially spent sulfuric acid; recycling to the primary alkylating treatment at least a portion of the mixture containing hydrogen halide and unreacted isoparaflin; and recycling to the secondary alkylating treatment at least a portion of the partially spent sulfuric acid.

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