

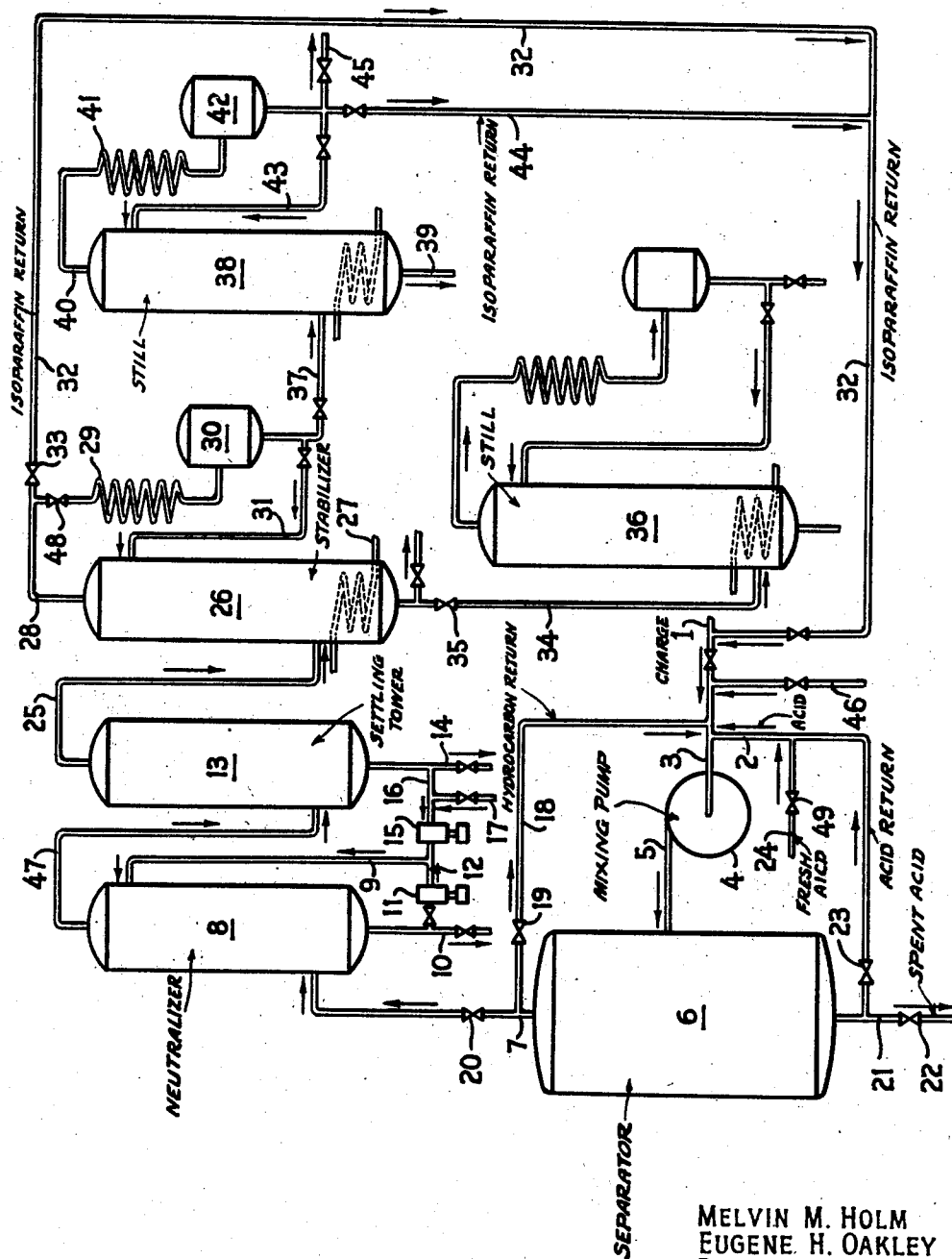
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REACTION OF HYDROCARBONS

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REACTION OF HYDROCARBONS

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This invention relates to an improved process for the manufacture of high antiknock motor fuel hydrocarbons by the reaction of paraffinic hydrocarbons with olefinic hydrocarbons.

It is known that isoparaffinic hydrocarbons can be reacted with olefinic hydrocarbons to make isoparaffinic hydrocarbons having a number of carbon atoms equal the sum of the carbon atoms of the initial isoparaffin and olefin. For example, the alkylation of isobutane with a butene to make isooctane by contact and vigorous agitation with sulfuric acid is disclosed by British Patent No. 479,827. The product of such alkylation reactions will be referred to herein as an "alkymer."

In the manufacture of motor fuel by means of the alkylation of isoparaffins with olefins, especially in the manufacture of aviation gasoline, it is necessary that the product meet certain quality standards, such as those relating to high antiknock value, bromine number, gravity and boiling range, but due to numerous difficulties encountered in the operation of an alkylation process for the production of good quality motor fuel, it has heretofore been impossible to obtain a product having as high a quality as is desired.

It is one object of the present invention to manufacture isoparaffinic motor fuel hydrocarbons having a high antiknock value.

It is another object of this invention to provide a new and improved process for the alkylation of isoparaffins with olefins to produce saturated high antiknock motor fuel hydrocarbons.

Still another object of this invention is to provide a new and improved process for the alkylation of isoparaffins with olefins to produce saturated high antiknock motor fuel hydrocarbons, the product of which process contains a high proportion of such hydrocarbons boiling in the aviation gasoline boiling range.

Another object of this invention is to provide a new and improved process for the alkylation of isoparaffins with olefins to produce an alkymer product having a better bromine number and a better gravity.

Other and further important objects of this invention will become apparent from the following description and appended claims.

Briefly, the process of this invention comprises the alkylation of isoparaffins with olefins by contact with sulfuric acid as the alkylation catalyst in which the alkyl acid sulfate concentration, which results from the reaction between olefin and sulfuric acid, is maintained below cer-

tain critical values so that a good quality product is obtained.

In effecting the alkylation of isoparaffins with olefins the alkylation catalyst, such as sulfuric acid, is continuously mixed with the olefin or olefins and the isoparaffin or isoparaffins to be alkylated. This mixture is agitated to assist the alkylation reaction and then passed to a separating zone where the catalyst, such as sulfuric acid, separates from the hydrocarbons.

According to this invention the concentration of alkyl acid sulfate, resulting from the reaction of sulfuric acid and olefin, is maintained below certain critical values, which are related to the quality of the product, and especially the antiknock value, bromine number and yield of aviation gasoline cut in the product. This concentration of alkyl acid sulfate in the sulfuric acid catalyst is maintained at a maximum of about two per cent by weight of the sulfuric acid when operating at a temperature below about 40° F. However, even at temperatures below about 40° F., for a maximum use of the sulfuric acid as an alkylation catalyst, it is preferable that the concentration of alkyl acid sulfate be not more than about one per cent by weight of the acid. For operation at temperatures above about 40° F. the alkyl acid sulfate concentration should in no case be above about one per cent by weight of the acid, and preferably at a value below about one per cent to minimize side reactions.

This invention may be better understood by reference to the accompanying drawing where one specific embodiment exemplifying the invention is shown in the figure. In this embodiment a mixture of normally gaseous hydrocarbons containing an isoparaffin to be alkylated and the olefins may be introduced through line 1, while the catalyst, sulfuric acid, is introduced through line 2. The mixture of catalyst, olefins and isoparaffin are rapidly passed through line 3 to a mixing or agitating device such as a mixing pump 4. In this mixing pump the catalyst and the hydrocarbons, including the olefins and isoparaffin, are thoroughly mixed to assist the alkylation reaction, and then the resulting mixture discharged through line 5 into a separator 6 in which the sulfuric acid catalyst separates from the hydrocarbons by gravity.

From separator 6 hydrocarbons, and any unseparated sulfuric acid, are withdrawn through line 7 controlled by valve 20 and may be passed into a neutralizer 8, in which the hydrocarbons are contacted with a neutralizing agent, such as a caustic alkaline material, or the like, intro-

duced to 8 through line 9, to remove any acid present in the hydrocarbons. Used caustic which has settled in 8 may be withdrawn through line 10, or may be recirculated by pump 11 through lines 12 and 9. From the neutralizer 8, the hydrocarbons may be passed through line 47 to a settling tower 13, where alkali settles out from the hydrocarbons and is withdrawn through line 14 or may be recirculated to the neutralizer 8 by pump 15 through lines 16 and 9. Fresh caustic may be added through line 17, communicating with lines 16 and 9, as needed.

Some of the hydrocarbons withdrawn from the separator 6 through line 7 may be passed into line 18 controlled by valve 19 and thence recirculated through the mixer 4 and separator 6. These hydrocarbons will include some of the alkylmer product produced and a substantial quantity of unreacted isoparaffin.

Spent acid may be removed from the system from the lower part of separator 6 through line 21 controlled by valve 22, or recirculated through line 2 controlled by valve 23. Fresh acid may be added to the system through line 24, controlled by valve 49, which communicates with line 2.

From the upper part of settler 13, hydrocarbons, which include the alkylmers and unreacted normally gaseous hydrocarbons, may be removed through line 25 and passed to an alkylmer stabilizer 26, having therein heating coil 27 or equivalent heating means. If the olefinic or isoparaffinic gases charged to the system contain normal paraffin, the mixture of normal and isoparaffin, such as normal and isobutane, may be removed from the stabilizer 26 overhead through line 28 controlled by valve 48; condensed in condenser 29, and collected in receiver 30. Some of the condensate in receiver 30 may be returned to the upper part of stabilizer 26 as reflux through line 31. On the other hand, should the normally gaseous hydrocarbons charged to the system contain no normal paraffin, such as normal butane, the isoparaffin, such as isobutane, may be passed directly from the stabilizer 26 through line 32 controlled by valve 33 and charged back to the mixing zone through line 1. Moreover, the mixture of normal and isoparaffin may be passed directly to mixer 4 through lines 32 and 3, if desired. The material being returned through line 32 may be liquified, when desired, by any known means, such as a condenser or compressor, not shown.

The alkylmer product may be withdrawn from stabilizer 26 through line 34 controlled by valve 35 and passed into a still 36 where the alkylmer product may be distilled into any desired cuts, although it will usually be desirable to take off an aviation gasoline cut overhead from this still.

It is a significant feature of this invention that when the concentration of alkyl acid sulfate in the sulfuric acid catalyst is maintained below a value of about one per cent, the alkylmer product has a higher antiknock value and a lower bromine number than when this concentration becomes higher than this value, and the alkylmer product taken off overhead from still 36 gives a higher yield of high antiknock motor fuel hydrocarbons boiling in the aviation gasoline boiling range (initial boiling point about 80° F. and 90% off at about 275° F.).

The mixture of isoparaffin and normal paraffin, such as isobutane and normal butane, in receiver 30 may be passed through line 37 to an isoparaffin still 38 from which normal paraffin is removed as

bottoms through line 39 and isoparaffin is taken off overhead through line 40, condensed in cooler 41 and collected in receiver 42. Some isoparaffin from receiver 42 may be returned to the isoparaffin still as reflux through line 43, if desired. From receiver 42 isoparaffin may be returned to the mixing zone through lines 44 and 32, or withdrawn from the system through line 45, as desired.

Usually the normally gaseous hydrocarbons 10 charged to the system will comprise a mixture of olefins, isoparaffin and normal paraffin and such mixture may be introduced through line 46. Should olefins and isoparaffins be charged separately, the olefins may be introduced through line 46 and isoparaffin through line 1.

In accordance with this invention the concentration of alkyl acid sulfate in the sulfuric acid in the zone in which the alkylation reaction is effected, especially in mixer 4, is maintained at least below about one per cent, preferably, for all temperatures of operation, but may be as high as about two per cent for temperatures below about 40° F. This concentration may be maintained below such critical values by introducing fresh acid through line 24, by controlling the feed rate of the charge passing through line 3 to be alkylated, which effects a control of the ratio of olefin to sulfuric acid, by controlling the degree of contacting or mixing in mixer 4, or by controlling the ratio of isoparaffin to olefin in line 3 where the olefin first contacts the sulfuric acid and in the mixer 4, or by controlling any number or all of these factors together to maintain the desired alkyl acid sulfate concentration in the sulfuric acid. The ratio of isoparaffin to olefin may be controlled by the addition of a greater quantity of isoparaffin through line 32, line 44, line 1 or line 18, or by lowering the quantity of olefin supplied either through line 1 or line 46. Thus, should the concentration of alkyl acid sulfate in the sulfuric acid become too high as indicated by a direct measurement, by the degradation of the product, or by any other means, it can be lowered by any of the foregoing methods or means.

Although the alkylation reaction may be effected with the isoparaffins and olefins in the gas phase, it is preferred to operate with these hydrocarbons in the liquid phase. The sulfuric acid used may be of any concentration known to effect the alkylation reaction, but it is preferred to use sulfuric acid of concentration between about 95 per cent and about 98 per cent. The temperature may be any temperature known for the alkylation reaction with sulfuric acid as the catalyst, but it is preferred to operate with a temperature of from about 15° F. to about 150° F. Although the process of this invention may be used to effect the alkylation of any isoparaffin with any olefin known to be capable of such reaction, it is especially suitable for the alkylation of normally gaseous isoparaffins with normally gaseous olefins, such as are usually present in gases obtained from a cracking operation, for example, the alkylation of isobutane or isopentane with propylene or any of the butylenes.

Having thus disclosed our invention relating to the improved process of alkylating isoparaffins with olefins to produce high antiknock motor fuel hydrocarbons, we claim:

1. Process of alkylating isoparaffins with olefins which comprises contacting isoparaffin and olefin with sulfuric acid of alkylating concentration and maintaining the concentration of alkyl

acid sulfate in the acid below about one per cent by weight of the acid.

2. Process of alkylating isoparaffins with olefins which comprises contacting isoparaffin and olefin with sulfuric acid of alkylating concentration at temperatures below about 40° F. and maintaining the alkyl acid sulfate concentration in the sulfuric acid below about two per cent by weight of the acid.

3. Process of making high antiknock motor fuel hydrocarbons which comprises catalytically alkylating normally gaseous isoparaffins with normally gaseous olefins by means of sulfuric acid of alkylating concentration as a catalyst and maintaining the concentration of alkyl acid sulfate in the sulfuric acid below about one per cent by weight of the sulfuric acid.

4. Process of reacting isobutane with butylene to produce isooctane therefrom which comprises alkylating isobutane with butylene by contact with sulfuric acid of alkylating concentration and maintaining the butyl acid sulfate concentration in the acid below about one per cent by weight of the acid.

5. Process of reacting isoparaffins with olefins to form alkymers therefrom which comprises alkylating isoparaffin with olefin by contacting and agitating the isoparaffin and olefin with sulfuric acid of alkylating concentration and maintaining the concentration of alkyl acid sulfate in the sulfuric acid below about one per cent to produce a good quality product by controlling the degree of contacting of the isoparaffin with the sulfuric acid, controlling the ratio of olefin to sulfuric acid, and controlling the ratio of isoparaffin to olefin.

6. Process of reacting isoparaffins with olefins to produce alkymers therefrom which comprises alkylating isoparaffin with olefin by contacting

and agitating the isoparaffin and olefin with sulfuric acid of alkylating concentration and maintaining the concentration of alkyl acid sulfate in the sulfuric acid below about one per cent to produce a good quality product by controlling the ratio of olefin to sulfuric acid.

7. Process of reacting isoparaffins having less than six carbon atoms per molecule with normally gaseous olefins to make a product high in antiknock value, low in bromine number and high in aviation gasoline content which comprises agitating said isoparaffins and said olefins with sulfuric acid of alkylating concentration in a reaction zone under conditions effective to alkylate isoparaffins with olefins, maintaining the concentration of alkyl acid sulfate in the sulfuric acid in said reaction zone below about one per cent by weight of the acid to make a product high in antiknock value, low in bromine number and high in aviation gasoline content.

8. Process of reacting isoparaffins having less than six carbon atoms per molecule with normally gaseous olefins to make a product high in antiknock value, low in bromine number and high in aviation gasoline content which comprises agitating said isoparaffins and said olefins with sulfuric acid of alkylating concentration in a reaction zone at a temperature below about 40° F. under conditions effective to alkylate isoparaffins with olefins, maintaining the concentration of alkyl acid sulfate in the sulfuric acid in said reaction zone below about two per cent by weight of the acid to make a product high in antiknock value, low in bromine number and high in aviation gasoline content.

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