

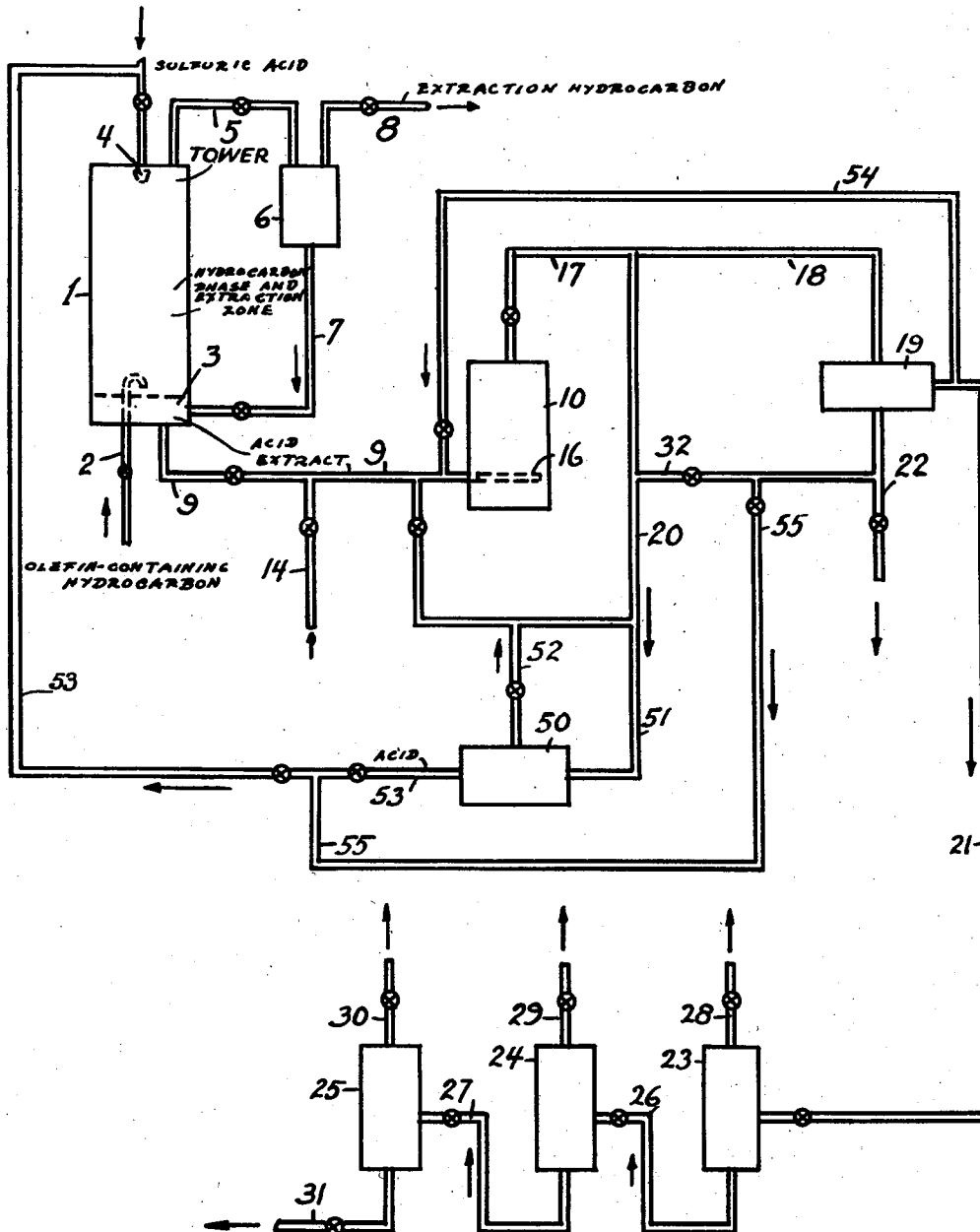
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REFINING MINERAL OIL

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REFINING MINERAL OIL

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The present invention is concerned with the refining of mineral oil. The invention is more particularly concerned with an improved process for producing hydrocarbon constituents boiling in the motor fuel and aviation fuel boiling ranges from relatively low boiling hydrocarbon constituents. In accordance with the present process, relatively low boiling olefins are absorbed in a mineral acid catalyst in an initial stage wherein the catalyst comprises the discontinuous phase and is injected into said stage by means of sprays or jets. The acid phase, comprising a solution of olefins, is then passed to a secondary stage and contacted with a tertiary hydrocarbon under conditions to alkylate the same.

It is well known in the art to react relatively low boiling olefins such as olefins containing from 2 to 5 carbon atoms in the molecule with saturated hydrocarbons containing a tertiary carbon atom hereinafter referred to as tertiary hydrocarbons. These reactions are generally conducted by employing a feed stock containing olefins and tertiary hydrocarbons and contacting the same under suitable conditions with a so-called alkylating catalyst. In general, the operation is conducted under conditions in which the mole ratio of the tertiary hydrocarbons to the olefins is relatively high. Temperature and pressure conditions vary considerably. For example, the alkylating temperature may range from about -20° F. or lower to temperatures as high as 100° F. or higher. However, in general the alkylating temperatures are in the range from about 20° F. to about 70° F. Although a number of substances may be employed as alkylating catalysts such as aluminum chloride and the like, the preferred materials comprise mineral acids, particularly sulphuric acid or fluorosulfonic acid. In the case of sulphuric acid the preferred concentration is from about 88% to about 100%.

It is also known in the art to carry out this operation employing two stages. In the first stage the olefins are absorbed in sulphuric acid, the acid stream removed, passed to a secondary stage and alkylated in a conventional manner. I have, however, now discovered that providing a two-stage alkylating operation be conducted wherein in the initial stage the sulphuric acid is maintained as the discontinuous phase unexpected desirable results are obtained. In accordance with the preferred modification of my invention the sulphuric acid is sprayed into the liquid or gaseous hydrocarbon feed stream. By operating in this manner rapid separation and removal of the acid extract is secured. The acid extract may then be immediately treated in a secondary stage with an isoparaffin under conditions to alkylate the same. My invention may be readily understood by reference to the at-

tached drawing illustrating one embodiment of the same.

For the purpose of description it is assumed that the feed stream comprising olefin hydrocarbons is a conventional refining cut comprising constituents containing about 4 carbon atoms in the molecule. The olefin containing hydrocarbons are introduced into absorption zone or extraction tower 1 by means of feed line 2 at a point above the acid extract phase 3. Conditions are adjusted so that zone 1 is substantially full of hydrocarbons which constitute the continuous phase. The mineral acid alkylating catalyst which for the purpose of description is taken to be a concentrated sulphuric acid is sprayed or jetted into the top of zone 1 by means of spraying device 4. The sulphuric acid constitutes the discontinuous phase. The extracted hydrocarbons are removed from zone 1 by means of line 5, passed through zone 6 where any entrained acid separates which is recycled to the bottom of extraction tower 1 by means of line 7. The extracted hydrocarbons are removed by means of line 8 and further handled as desired. The acid extract containing dissolved therein the olefins is removed from zone 1 by means of line 9 and passed to alkylation zone 10. The tertiary hydrocarbon comprising isobutane is introduced into the acid solution of olefins by means of line 14. The entire mixture is then passed into alkylation zone 10 by means of jets or equivalent means 16. Temperature and pressure conditions as well as time of contact in alkylation zone 10 are adapted to secure the maximum yield of the desired product. The reaction mixture of acid emulsion is removed from alkylation zone 10 by means of line 17. A portion of the acid emulsion is segregated from the main emulsion stream by means of line 18 and passed into separation zone 19. The main emulsion stream is recycled to alkylation zone 10 by means of line 20 through jets 16.

The portion of the emulsion stream passed to separation zone 19 separates into a hydrocarbon layer which is removed by means of line 21 and into an acid layer which is removed by means of line 22. The hydrocarbon layer is passed successively into distillation zones 23, 24, and 25 by means of lines 26 and 27. Temperature and pressure conditions are adjusted in zone 23 to remove overhead by means of line 28 isobutane which is preferably recycled to the alkylation zone. Temperature and pressure conditions in zone 24 are adjusted to remove overhead by means of line 29 normal butane constituents which may be disposed of as desired. The total alkylate product passed to distillation zone 25 is fractionated to segregate a desired aviation product which is removed overhead by means of line 30 and a heavy alkylate product which is removed by means of

line 31 and handled as desired. The acid separated from zone 19 is preferably recycled by means of line 32 but may be withdrawn from the system. The acid introduced into zone 1 may comprise fresh acid as well as recycle acid. A preferred method of segregating acid for recycling to absorption zone 1 is to pass at least a portion of the emulsion into a second separation zone 50 by means of line 51 wherein a separation is made between acid and hydrocarbons. The hydrocarbons are recycled to zone 10 by means of line 52 while the acid is recycled to zone 1 by means of line 53. Another adaptation for securing sufficient acid for recycling is to pass a considerably larger quantity of the emulsion into separation zone 19 and to separate the acid and hydrocarbons. The hydrocarbon layer is removed and the product portion separated by means of line 21 as hereinbefore described, while the recycle portion is recycled to zone 10 by means of line 54. The acid separated in zone 19 is then recycled to zone 1 by means of line 55.

It is to be understood that the process of the present invention may be widely varied. The respective zones may comprise any suitable number and arrangement of units. The invention essentially comprises employing two stages wherein in the initial stage the alkylating catalyst is sprayed as the discontinuous phase into the hydrocarbon phase under conditions to absorb the olefins from the hydrocarbon layer comprising the continuous phase. The acid solution is combined with tertiary hydrocarbons and handled in a conventional manner for alkylating the hydrocarbons. Although the invention may be adapted for utilization in conjunction with any catalyst it is particularly adapted for use in operations in which the alkylating catalyst comprises sulphuric acid. When operating in accordance with the present process improved results are secured due to the fact that the acid extract rapidly separates from the hydrocarbon phase resulting in a minimum time of contact. Furthermore, improved results are secured by utilizing spray jets or equivalent means in order to thoroughly disperse the acid throughout the hydrocarbon phase. By incorporating the acid into the hydrocarbons as a discontinuous phase rapid separation of the acid is secured. This results in less emulsification and carryover of acid with the extracted hydrocarbons. Furthermore, due to the fact that the acid separates rapidly, immediate introduction of the acid into the alkylation zone is possible with the result that substantially no self-alkylation resulting in undesirable products is secured. This increases the yield of desired products and reduces acid consumption.

The preferred acid for use in the present invention comprises a sulphuric acid having a concentration in the range from 88% to about 100%. Although the feed hydrocarbon fraction to the initial stage may comprise vapors or liquid, it is preferred to inject and spray the acid throughout a hydrocarbon liquid phase.

The feed material to the initial stage is preferably one that is substantially completely free of hydrocarbon constituents containing a tertiary carbon atom. However, feed fractions segregated from the various refining operations may be passed to the initial stage and treated in accordance with the present process providing the ratio of tertiary hydrocarbons to olefins is relatively

low. It is desirable that if feed fractions of this character are passed to the initial stage that the ratio of isoparaffins to olefins not exceed 0.5 to 1.0 and preferably be less than 0.25 to 1.0.

The feed rates when employing feed fractions of this character and when employing a 98% sulphuric acid may vary over a wide range. In general, the amount of acid to olefins passed to the initial stage may vary in the range from 10 volumes of acid per volume of olefins to 100 volumes of acid per volume of olefins. A desirable feed ratio comprises 25 to 50 volumes of acid per volume of olefins.

The acid emulsion removed from the initial stage may be alkylated under any process. In general, it is preferred to employ temperatures in the range from about 0° F. to about 100° F. and to add sufficient isoparaffins so that the ratio of isoparaffins to olefins, based on free olefins, is in the range from 5 to 10 and higher to 1.

What I claim as new and wish to protect by Letters Patent is:

1. Process for alkylating tertiary hydrocarbons which comprises passing a feed stream containing olefins to an initial stage, absorbing said olefins in said initial stage with a mineral acid under conditions whereby the mineral acid is the discontinuous phase and in which the ratio of acid to olefin is between 10 and 100 to 1, withdrawing the acid solution and contacting the same in a secondary stage with added isoparaffinic hydrocarbons in the presence of an alkylating catalyst under alkylating conditions.

2. Process as defined by claim 1 in which said acid employed in said initial stage is a concentrated sulphuric acid.

3. Process as defined by claim 1 in which the feed to said initial stage comprises a feed stream which is substantially completely free of tertiary hydrocarbons.

4. Process as defined by claim 1 in which the absorbent in said initial stage comprises a sulphuric acid catalyst and wherein said catalyst is sprayed into a body of the hydrocarbon feed in said stage.

5. Improved process for the production of hydrocarbon constituents boiling in the motor fuel and aviation fuel boiling ranges which comprises passing a feed fraction containing less than 50% tertiary hydrocarbons based upon olefins into an initial stage, absorbing said olefins in said initial stage with a mineral acid catalyst under conditions wherein the acid is the discontinuous phase and in which the ratio of acid to olefin is between 25 and 50 to 1, removing the acid solution and passing the same together with added tertiary hydrocarbons and an alkylating catalyst to a secondary stage and subjecting the same to alkylating conditions.

6. Process as defined by claim 5 in which said acid employed in said initial stage is a concentrated sulphuric acid.

7. Process as defined by claim 5 in which the feed to said initial stage comprises a feed stream which is substantially completely free of tertiary hydrocarbons.

8. Process as defined by claim 5 in which the catalyst in said initial stage comprises a sulphuric acid catalyst and wherein said catalyst is sprayed into a body of the hydrocarbon feed in said stage.

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