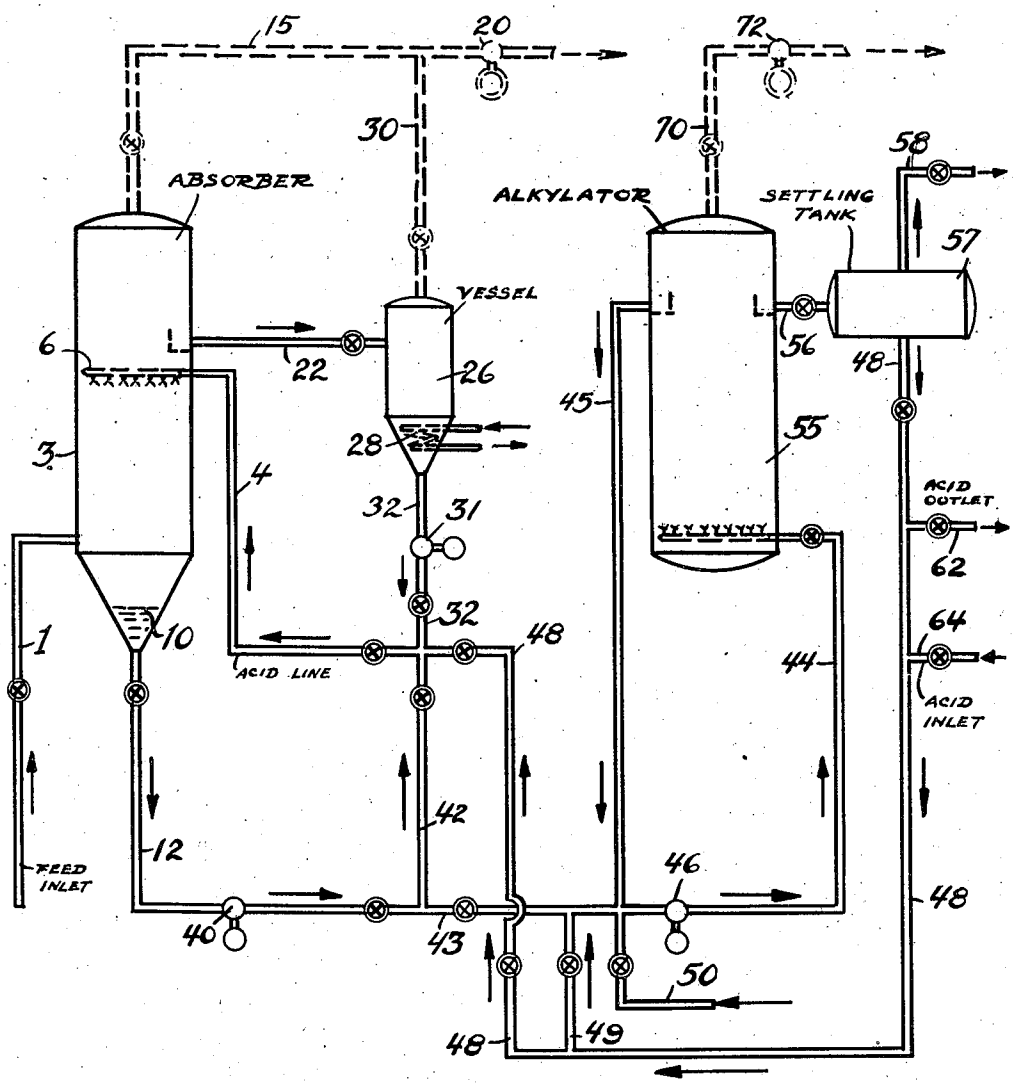
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CHEMICAL PROCESS

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CHEMICAL PROCESS

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The present invention relates to improvements in the art of synthesizing hydrocarbons and, more particularly, it relates to the alkylation of isoparaffins with olefins in the presence of alkylation catalysts, such as sulfuric acid.

In the conventional practice of alkylating isoparaffins with olefins, the normal procedure involves contacting the isoparaffin(s) with the olefin(s) in the presence of an alkylation catalyst, such as sulfuric acid, in a suitable vessel provided with means for mixing, agitation, and temperature control. A modification of this process, known as the two-stage alkylation process, involves dissolving the olefins in the acid catalyst, say, sulfuric acid, and then conducting the olefin-acid solution to an alkylation zone maintained under proper conditions of temperature, pressure, and the like, in which zone the solution is contacted with isoparaffin. Experience has shown that, in order to obtain the best results, the molal ratio of isoparaffin to olefin should be such that the isoparaffin is in large excess.

In its essence, my present invention is a two-stage alkylation process, in the first stage of which the olefins to be alkylated are dissolved in sulfuric acid under conditions such that the degradation of the olefin is at a minimum, and that the contamination of paraffins present in the olefinic feed stock is at a minimum. The solution of olefins and sulfuric acid is then subsequently used for alkylation according to known methods.

One object of my present invention, therefore, is to carry out the alkylation of an isoparaffin with an olefin in the presence of sulfuric acid in a two-stage operation, including an absorption stage and an alkylation stage proper, under such conditions that, in the absorption stage, the feed stock containing both paraffins and olefins is treated under conditions such that there is a maximum recovery of olefins, without degradation, for the process and a minimum contamination of the paraffins with esters and other contaminating material.

In the usual two-stage process of alkylating isoparaffins with olefins, the olefin charging stock ordinarily contains substantial quantities of paraffins, and the charging stream containing the olefins is usually in the liquid phase. During the absorption, at least a portion of the sulfuric acid reacts with the olefins to form alkyl sulfates. The monoalkyl sulfates are relatively insoluble in liquefied paraffins, but the dialkyl sulfates have an appreciable solubility in said liquefied paraffins. Consequently, when a separation is effected between the extract and the raffinate in the absorption zone, the paraffinic raffinate is contaminated with appreciable quantities of dialkyl sulfates. It is an important object of my present invention to remove the alkyl sulfates, principally the dialkyl sulfates, from the paraffins withdrawn from the absorption zone, so the paraffins may be utilizable as a gasoline blending stock or as a charging stock to a thermal polymerization process or other hydrocarbon reactions, including gas reversion, naphtha reforming in the presence of added butane, and the like.

My invention will be best understood by reference to the accompanying drawing which shows diagrammatically a form and arrangement of apparatus elements in which my invention may be carried into practical effect.

I shall now set forth a specific embodiment of my invention and, in so doing, I shall refer to the accompanying drawing in order to provide a better understanding thereof, but it is to be understood that the precise details I am about to set forth do not constitute a limitation on my invention.

Referring in detail to the drawing, a charging stock comprising a liquefied mixture of normally gaseous hydrocarbons containing 15% of normal butylene with substantially no isobutylene, the remainder being butane, isobutane, and minor quantities of C_3 and C_5 hydrocarbons enters the system through line 1. The best feed stock for an operation of the type I am about to describe is one which is substantially free of isoolefins. The charging stock preferably is not at a temperature greater than atmospheric. The feed stock is charged into an absorber 3 where it contacts sulfuric acid, discharged from line 4 into said absorber, preferably through a system of jets or sprays 6, preferably disposed in the upper portion of the absorber. The source of this acid will be hereinafter more fully described and identified. The absorption acid is discharged into the absorption zone 3 in such amount with respect to the olefin entering the absorber that the molal ratio of acid to olefin is approximately 1 to 1. The temperature prevailing in the absorber is approximately 25° F. to 30° F., and the pressure is from about 10 to 25 lbs./sq. in. gauge. Since the dissolution of olefins in sulfuric acid, as is well known, is a phenomenon in which heat is liberated, and since it is necessary to maintain a temperature within the absorber at a value not greater than about 30° F., it is necessary to provide means for disposing of the heat released during the dissolving of the olefins. I propose to

absorb substantially all of such heat released by permitting at least a portion of the paraffins to evaporate within the absorber 3. It will be understood, of course, that the same result, that is to say, the refrigeration or heat absorption, could be accomplished by external cooling means. In the absorber, as indicated, a substantial quantity of the olefin content of the charging stock is dissolved in the acid and collects in a well or sump 10 disposed in the bottom of the absorber, as shown in the drawing. It is pointed out that the quantity of acid-olefin solution or emulsion maintained in the absorber 3 is the minimum amount necessary to prevent escape of undissolved hydrocarbons as acid extract through line 12.

As previously indicated, a portion of the paraffin discharged into absorber 3 is vaporized and these hydrocarbons are withdrawn overhead as vapor through line 15. These hydrocarbons may be then compressed in compressor 20, and then may be rejected from the system and delivered to a gasoline blending plant, a thermal polymerization plant, or the like, or charged to fractionating equipment in order to recover any isoparaffins present for use in the alkylation system.

Referring again to the absorber, the unvaporized paraffinic fraction is withdrawn through line 22, and discharged into a vessel 26 having disposed therein a heating coil 28 through which hot water or other heating fluid may be circulated in order to vaporize the paraffin. The vaporized paraffins are then withdrawn through line 30 and discharged into line 15 for utilization with the paraffins in line 15. Since the alkyl sulfates in the hydrocarbon fed to vaporizer 26 are subject to polymerization and excessive decomposition if heated strongly, it is important to maintain the temperature therein below 50° F., preferably below 30° F. Conveniently, the low temperature in vaporizer 26 or absorber 3 or both may be obtained by operating compressor 20 in such manner as to reduce the pressure in these vessels and thereby permit evaporation of the hydrocarbons at the low temperature. The paraffins contained in line 22 have dissolved therein an appreciable quantity of dialkyl sulfates, say, about 3% by wt., and a much less quantity of monoalkyl sulfates. As previously pointed out, the solubility of dialkyl sulfates in butane or other paraffin hydrocarbons is appreciable and, consequently, after removal of the butane by evaporation from vessel 26, the bottoms withdrawn by pump 31 in line 32 will be composed substantially of the comparatively nonvolatile dialkyl sulfates formerly dissolved in the paraffin hydrocarbons. These dialkyl sulfates are recycled to the absorption tower 3 through line 4 where they suppress the formation of additional quantities of dialkyl sulfates from fresh feed olefins entering the said absorber.

The bottoms from the absorption tower 3 are withdrawn through line 12, as previously indicated, and thence pumped by pump 40 in part back to the absorption tower through lines 42 and 4, and the remainder are conducted through line 43 to the alkylation zone. It is pointed out at this time, however, that the ratio of bottoms or extract recycled through lines 42 and 4, to absorber 3, is about ten times the weight of the extract which is delivered to the alkylation zone. The large proportion of recycled extract to the absorber is desirable since the acid returned through line 48 from the alkylation stage, as will more fully appear hereinafter, has a higher titratable acidity than the recycled extract containing the mono- and dialkyl sulfates and this stronger acid would tend to cause undesirable polymerization if it, alone, were fed into the absorber.

The extract in line 43 proceeds to the alkylation unit through line 44 which, in conjunction with line 45, is a recycle line, and the confluents of the fresh charge plus the recycle are proportioned in the known manner; the mixed streams are pumped by pump 46 into the alkylator 55, where they are permitted to remain under known conditions for a proper time to effect the desired alkylation. The product from the alkylator is withdrawn through line 56 and delivered to a settling tank 57, from which the crude alkylate is withdrawn through line 58 and delivered to refining equipment to produce the finished product. The bottoms, that is to say, the acid layer, is withdrawn from the bottom of settling tank 57 through line 48, and recycled to absorber 3 as previously mentioned. It is pointed out that, as shown in the drawing and as is well known to those familiar with this art, a portion of the settled acid from settler 57 may be recycled through lines 48, 49, 43 and 44 to the alkylator 55. It is also pointed out that a portion of the acid withdrawn from settler 57 may be discarded through line 62 and be replaced by fresh strong acid introduced through line 64 in order to maintain the acid in the alkylation stage at the desired strength.

A part of the unreacted iso- and normal paraffins are evaporated in reactor 55 to absorb the heat of reaction and maintain the desired reactor temperature. The vaporized hydrocarbons are withdrawn overhead from alkylation reactor 55 through line 70, compressed in pump 72, and are then recycled, preferably after fractionation to remove normal paraffins in apparatus not shown along with extraneous isoparaffins through isoparaffin charging line 50. It is to be understood, of course, that, in the preceding description, I do not claim that the alkylation stage proper is anything other than the conventional method of carrying out this particular portion of my process. The invention resides, as stated, in the first, or absorption, stage of the process, particularly with regard to the method of suppressing the formation of additional quantities of dialkyl sulfate from the fresh olefin feed entering the system.

It will be understood that not only may I alkylate isobutane with normal butylene, but I may also alkylate other normally gaseous or normally liquid isoparaffins with other normally gaseous and/or normally liquid olefins.

Many modifications of my invention will readily suggest themselves to those who are familiar with this art without departing from the spirit thereof.

The present invention having been thus described and illustrated, what is claimed as new and useful and is desired to be secured by Letters Patent is:

1. In a two-stage alkylation process, including an olefin absorption stage and an alkylation stage proper, the improvement which comprises charging to the first stage a liquefied charging stock containing olefins for alkylation and paraffins, contacting said olefins with concentrated sulfuric acid whereby the olefin content of the charging stock is substantially completely reacted with the sulfuric acid to form dialkyl sulfates and monoalkyl sulfates, withdrawing the monoalkyl sulfates as bottoms from the absorption zone, and withdrawing dialkyl sulfates as the side cut from

the said absorption zone dissolved in paraffin hydrocarbons, separating the paraffin hydrocarbons from the dialkyl sulfates, and returning the separated dialkyl sulfates to the absorption zone to suppress further formation of the same.

2. The process set forth in claim 1 in which the heat liberated by the reaction between the sulfuric acid and the olefins is substantially completely absorbed by permitting at least a portion of the paraffin hydrocarbons to evaporate in the absorption zone.

3. The process set forth in claim 1 in which the absorption is carried out at a temperature not higher than about 30° F.

4. The process set forth in claim 1 in which a substantial portion of the monoalkyl sulfates withdrawn as bottoms from the absorption zone is recycled to the said absorption zone to dilute the acid concentration therein, and to prevent degradation of the olefin.

5. The process set forth in claim 1 in which, in order to provide intimate contact between acid and olefin hydrocarbons in the absorption zone, the said acid is discharged into the upper portion of the absorption zone in the form of droplets.

6. The process set forth in claim 1 in which the absorption is carried out countercurrently.

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