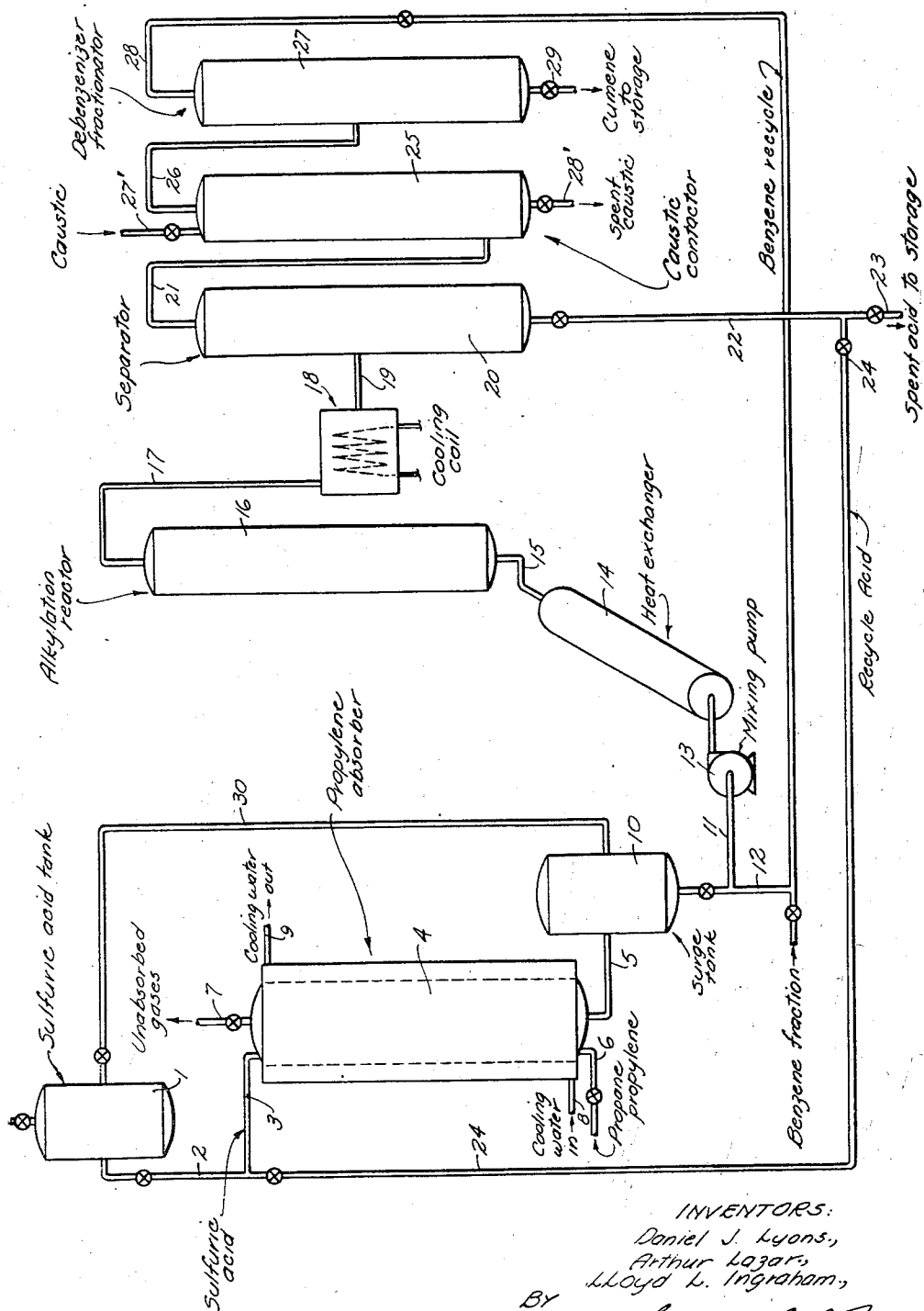


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ALKYLATION OF AROMATIC HYDROCARBONS WITH SULFURIC
ACID CATALYST AVOIDING SULFONATION OF PRODUCT
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ALKYLATION OF AROMATIC HYDROCARBONS WITH SULFURIC ACID CATALYST AVOIDING SULFONATION OF PRODUCT

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3 Claims. (Cl. 260-671)

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This invention relates to the alkylation of benzene and its homologues to produce alkyl derivatives of benzene, and in a more specific form to the manufacture of aromatic hydrocarbons having superior antiknock characteristics when incorporated into motor fuel.

It is an object of the invention to provide a method whereby benzene and homologues of benzene may be alkylated to form alkyl derivatives of the same.

Another object is to provide a process for alkylating benzene and its homologues, involving the use of sulphuric acid, in which sulphonation and polymerization is avoided.

An object of a specific embodiment of the invention is to recover, as a high antiknock component for motor fuels, the benzene content of petroleum.

Other objects will be apparent from the following description.

In the manufacture of modern aviation gasoline, especially that intended for use in military aviation, it has become common to include a small percentage of isopropyl benzene (cumene) or of certain other alkyl derivatives of benzene. These aromatic compounds have proven to be very effective in improving the antiknock quality of aviation gasoline, especially during periods of operation on rich fuel-air mixtures. Although cumene and similar aromatic hydrocarbons have been found in petroleum in certain localities, the proportions so present are too small for successful separation or for supplying the required amounts. Accordingly, methods have been developed for synthesizing cumene from benzene.

It is known that benzene and propylene will react, in the presence of concentrated sulphuric acid as a catalyst, to form cumene in a manner which may be considered superficially similar to the alkylation of isoparaffins, with propylene or with other olefins. However, the chemical reactions involved are quite dissimilar and the alkylation of benzene with sulphuric acid as a

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catalyst creates difficult problems of control due to the formation of sulphonic acids from the benzene, and due to alkyl-sulfates which do not participate in the alkylation reaction and thus remain in the finished product either as such or as sulphates of polyolefins. In the alkylation of isoparaffins the formation of alkyl sulphates is readily controlled by maintaining large amounts of the isoparaffin in the reacting mixture. However, when benzene, or an alkyl derivative of benzene, is brought into contact with sulphuric acid of the customary alkylation strength, sulphonation of a substantial proportion of the original aromatic hydrocarbon material occurs. Likewise, in the presence of sulphuric acid of alkylation strength, sulphonation of the alkylated aromatic portion occurs even more readily. The resulting aromatic sulphonic acids are difficult to separate economically from the desired alkylated aromatic and, in any event, represent substantial losses of material.

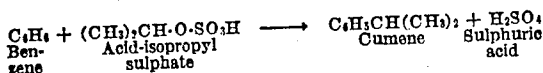
In order to avoid the above difficulties, various processes have been proposed using phosphoric acid, or mixtures of phosphoric acid and sulphuric acid, as catalyst. Some of these involve high temperatures with concomitant high pressures, and all of them present difficulties in the recovery of the high-priced phosphoric acid.

Some success on a commercial scale has been obtained in the alkylation of benzene with propylene using certain solid catalysts. These involve the use of high temperatures in the range of 500° F., require extended time for regenerating the catalyst, in some instances are limited to a single use of the catalyst, and generally produce low conversion of the benzene for each pass through the reactors and subsequent fractionation equipment.

According to the present invention benzene and its homologues are alkylated using alkyl sulphate as the alkylating agent. When an acid-alkyl sulphate, or a dialkyl sulphate containing even a small amount of acid-alkyl sulphate, is brought into contact with benzene or a homologue of

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benzene, alkylation proceeds rapidly at atmospheric temperature without further catalyst and without substantial formation of aromatic sulphononic acids. In the presence of stoichiometric amounts, or excess, of the aromatic hydrocarbon the alkyl sulphate is almost completely consumed with the liberation of sulphuric acid, as is illustrated by the following equation showing the reaction of benzene with acid-isopropyl sulphate:



This reaction under atmospheric, or slightly higher than atmospheric, temperature forms substantially theoretical yields of alkylated aromatic hydrocarbon, but does not proceed to the point where the alkylated aromatic is subject to any substantial degree of sulphonation by the sulphuric acid liberated in the reaction.

The acid-alkyl sulphate for the alkylation may readily be prepared by reacting the desired olefin with sulphuric acid in accordance with generally known conditions to reduce the amount of polymerization of the olefin to a minimum. The strength of the sulphuric acid may be between 65% and 100% H_2SO_4 and the absorption of the olefin by the sulphuric acid should be conducted at a temperature range known to reduce polymerization of the olefin to a minimum. For the absorption of propylene a safe temperature range has been found to be not in excess of 60° F. when the absorbing acid has a strength between 92-100% H_2SO_4 . With weaker acid, such as 80-90% H_2SO_4 , absorption temperatures up to 80° F. are permissible. However, to obtain optimum yields in the subsequent alkylation and, in particular, to avoid any sulphonation of aromatics during the alkylation, the preferred strength of sulphuric acid to be used in preparing the acid-alkyl sulphate should not exceed 90% H_2SO_4 . By using sulphuric acid of this low a concentration the sulphuric acid released during the alkylation is always below the sulphonation strength.

Although, broadly, the invention comprehends the alkylation of benzene and benzene homologues with an alkyl sulphate prepared separately and by any method of preparation, a preferred embodiment includes the formation of the alkyl sulphate in one stage of the process under selected conditions to avoid the formation of polymers of the olefin and, in a separate subsequent stage, the alkylation of the aromatic hydrocarbon with the alkyl sulphate under different conditions selected to avoid the formation of sulphonated aromatics. In this manner the disadvantages of the usual method of alkylating aromatics with olefins by a sulphuric acid catalyst are avoided.

To this end, as stated above, the olefin is reacted with sulphuric acid, preferably of 80-90% strength, at a temperature not exceeding 80° F. until substantially all the sulphuric acid is converted to acid-alkyl sulphate. The acid-alkyl sulphate thus formed is introduced into a body of the aromatic hydrocarbon to be alkylated at a temperature between about 60° F. and 150° F. while maintaining an excess of the aromatic present. For best results the molal ratio of the aromatic present to the acid-alkyl sulphate introduced should be greater than about 2:1 in order

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that the acid-alkyl sulphate may be consumed without formation of poly-alkyl-aromatics. In cases where di-alkyl, tri-alkyl, or tetra-alkyl-aromatics are desired, the ratio of aromatic hydrocarbon to alkyl sulphate may be changed accordingly. With ratios above about 2:1 the yield of alkylated aromatic is chiefly the mono-alkyl derivative. With lower ratios, substantial amounts of poly-alkyl derivatives are formed.

For the preparation of the alkyl sulphate the olefin need not be in highly concentrated form, but may be in mixture with substantial amounts of paraffinic hydrocarbons. For example, if it is desired to alkylate benzene with propylene to form cumene, the propylene may be obtained from a C_3 fraction derived from petroleum refinery cracking plant gases. In such a case the entire C_3 fraction may advantageously be passed through an absorber containing sulphuric acid of the desired strength and at the desired temperature. The propylene is absorbed by the sulphuric acid with the formation of acid-isopropyl sulphate and the non-reactive hydrocarbons are discharged from the absorber for any desired use. The absorption is controlled to bring about a conversion of substantially all the sulphuric acid to alkyl sulphate. The acid-isopropyl sulphate thus formed is passed to the reactor wherein benzene (or homologue of benzene) is to be alkylated.

In commercial operations it is generally inconvenient to operate the "absorber," wherein the olefin is converted to alkyl sulphate, and the "reactor," wherein the benzene is alkylated with the alkyl sulphate, at all times at such respective rates that the absorber will produce alkyl sulphate only at the rate required by the reactor. Accordingly, an accumulator tank for the alkyl sulphate may advantageously be placed between the absorber and the reactor. As it is disadvantageous to store acid-alkyl sulphate for any substantial period of time due to its tendency to deteriorate, when such accumulator tank is used the reaction in the absorber should be carried out with the addition of sufficient olefin to produce the more stable dialkyl sulphate. It has been found that di-alkyl sulphate may be stored at atmospheric temperature for appreciably long periods of time without substantial decomposition or deterioration. The di-alkyl sulphate may readily be rendered suitable for alkylation according to the invention by the addition of sulphuric acid prior to its introduction into the reactor. The quantity of sulphuric acid so added may be upwards from about 10%, more or less, but the total sulphuric acid, including that combined with the olefin, should not substantially exceed a ratio of 2 mols of sulphuric acid per mol of olefin absorbed.

The procedure of forming the neutral alkyl sulphate in the absorber and converting at least some of it to acid-alkyl sulphate prior to the alkylation has been found useful also in other cases where there is a substantial lapse of time between the production of the alkyl sulphate and its use; for example, in installations where the absorber is located at some distance from the reactor. Even where no time lapse is involved such procedure may be useful for reducing the amount of control necessary in operating the absorber and the process as a whole. The reaction in the absorber may be allowed to go to completion and the desired amount of sulphuric acid may be added as required.

Experiment Number	1—	2	3	4	5	6	7	8	9	10	11	12
Formation of alkyl Sulphate:												
Strength of acid used, per cent H_2SO_4	98.6	98.6	98.6	84.3	98.6	89.1	85.5	83.6	86.3	86.3	86.3	86.3
Volume of acid used, cc.....	1,000	540	180	671	800	800	1,000	1,000	1,500	1,500	1,500	1,500
Propylene charged, gms.....	1,576	426	170	483	743	493	387	303	693	693	587	693
Mol ratio H_2SO_4 to C_3H_6	1:2	1:1	1:1.2	1:1	1:1.2	1:0.9	1:0.6	1:0.6	1:0.6	1:0.6	1:0.6	1:0.6
Vol. alkyl sulfate reactant-catalyst, cc.....	3,100	1,130	380	1,303	1,670	1,520	1,450	1,550	2,515	2,515	2,515	2,515
Specific gravity of reactant-catalyst.....	1.104	1.32	1.28	1.26	1.206	1.292	1.414	1.389	1.349	1.349	1.349	1.349
Per cent monoisopropyl sulfate in reactant-catalyst.....	0	100	87	100								
Per cent Diisopropyl sulfate in reactant-catalyst.....	100	0	13	0								
Alkylation:												
Alkyl sulfate charge, cc.....	465	1,100	414	535	395	496	680	687	580	580	580	580
Hydrocarbon charge, cc.....	1,000	2,000	2,000	1,000	1,000	1,000	750	1,000	1,000	1,000	1,000	1,000
Boiling range of hydrocarbon, ° F.....	176	148-180	148-180	176	176	176	176	176	176	176	176	176
Per cent Benzene in hydrocarbon.....	100	20.2	20.2	100	100	100	100	100	100	100	100	100
Contact time, minutes.....	35	30	30	52	16.5	46	57	70	35	44	74	78
Temperature of agitator, ° F.....	76			114	110	110	110	130	145	130	110	100
Mol ratio—benzene to alkyl sulfate.....	2:1	1:2	1:1.1	2.5:1	2.9:1	2.9:1	2.1:1	2.4:1	3:1	3:1	3:1	3:1
Yields:												
Volume of product, cc.....	1,255	2,350	2,100	1,210	1,165	1,225	965	1,260	1,195	1,205	1,215	1,215
Per cent Alkylate in product.....	53.3	34.6	22.0	45.6	33.5	42.5	56.0	48.0	41.9	45.0	44.2	42.0
Per cent Isopropyl benzene ¹	54.3	10.7	9.5	48.3	32.6	45.9	63.7	54.2	43.6	47.0	49.8	43.7
Per cent Diisopropyl benzene ¹	8.6	10.7	10.2	4.6	1.8	1.2	3.2	2.5	2.4	2.9	none	2.1
Per cent Boiling above 410° F.....	none	15.0	none	none	none	none	none	none	none	none	none	none
Per cent Bottoms ¹	4.0	4.3	4.1	4.2	4.7	4.9	5.2	3.8	4.1	4.1	3.9	5.2
End point of product.....	402	420	388	390	402	394	390	383	386	375	360	398
Recovered acid—Volume, cc.....	265	660	240	300	215	235	465	420	465	360	355	360
Recovered acid—Specific gravity.....	1.56	1.56	1.55	1.760	1.544	1.730	1.768	1.764	1.618	1.768	1.767	1.771
Recovered acid—Acid strength in per cent H_2SO_4	73.5	73.8	72.0	83.0	66.4	82.0	84.2	83.3	70.3	82.6	84.4	84.4

¹ Based on the volume of hydrocarbon charge to alkylation.

² In Experiment No. 1, carried out with the alkyl sulfate, free H_2SO_4 (75 cc.) had to be added to initiate the alkylation reaction.

In the accompanying table a series of twelve different experiments is given which shows the results obtained with a charging stock containing aromatics and with a reactant catalyst of varying composition. More specifically the propylation of benzene is involved and it is shown in what manner the propylation of benzene is affected by such variables as: (1) strength of H_2SO_4 used in preparing the catalyst reactant, (2) mol ratio of H_2SO_4 to propylene in the catalyst reactant, (3) ratio of mono- to di-isopropyl sulphate in the catalyst reactant, (4) mol ratio of benzene to propylene contained in the catalyst reactant, (5) contact time, (6) temperature.

The following conclusions can be drawn from the experiments described.

In all cases where sulphuric acid of high strength (98%) was used, the strength of the resulting spent acid is considerably below that of the original acid used in preparing the catalyst-reactant, which seems to indicate that the alkyl sulphate is not fully utilized for alkylation purposes and that possibly other undesirable reactions have taken place. Refer to experiments 1, 2, 3, and 5.

On the other hand, when the original acid strength was chosen between 83 and 89% H_2SO_4 , the resultant spent acid shows almost the strength of the original acid charged to the absorber for the preparation of the catalyst-reactant. The restoration of the acid concentration to such a high degree indicates that the alkyl sulphate catalyst-reactant is substantially used up in the alkylation reaction and that undesirable side reactions have been reduced to a minimum.

As far as the mol ratio of the alkyl sulphate to benzene is concerned, wide variations seem to be permissible. Satisfactory results were obtained with mol ratios of 3:1 of benzene to alkyl sulphate, as well as with mol ratios as low as 1:2. It is evident, however, that a low mol ratio of benzene to alkyl sulphate favors the formation of poly alkylated benzene; therefore, the preferable mol ratio would be closer to 3:1 in such cases where the manufacture of mono-iso-propyl benzene as a blending agent for aviation gasoline is aimed at in order to avoid formation of poly

alkylated high boiling aromatics which would be outside of the specified boiling range. On the other hand, if recovery of large percentages of di-iso-propyl benzene, tri-iso-propyl benzene, or tetra-iso-propyl benzene is desired, a low mol ratio of benzene to propylene is indicated.

The time-temperature relationship of the alkylation reaction is well indicated in Examples 9, 10, 11, and 12. These four experiments were carried out with catalyst-reactant from the same batch prepared from H_2SO_4 of 86.3% strength and using a constant mol ratio of 3:1 benzene to alkyl sulphate. It will be noted that the shortest contact time was required at the highest contact temperature, but under these particular conditions the alkylation reaction was less complete, as indicated by the low specific gravity of the spent acid resulting from the process. The most complete conversion appears to take place at 100° F. where the specific gravity comes back to 1.771, which is only slightly below the original gravity of 1.80.

Although the involved reactions may be carried out by batch treatment in closed vessels equipped with stirring devices and means for required temperature control, the invention is well suited for the use of continuous operation and various continuous apparatus will suggest themselves for conducting the reactions. The absorber may advantageously be a tower equipped with baffles or packing in which the sulphuric acid is caused to flow downward countercurrently to a rising stream of the olefin or olefin-containing hydrocarbon mixture. The necessary temperature control may be provided by coolers in the gas and/or sulphuric acid stream entering the tower or the tower may contain a cooling jacket or cooling coils. Likewise, for continuous operations, the alkylation may be conducted by forcing the mixture of aromatic and alkyl sulphate through a packed tower. In this case concurrent flow is preferred to insure uniform reaction, though countercurrent flow may be used when desired. If desired, the reactor may comprise a centrifugal pump, which acts as a mixer as well as providing the propulsion, followed by a reaction chamber of the turbulence mixer type. As the alkylation reaction proceeds readily at or

near atmospheric temperatures and is only slightly exothermic, temperature control in the reactor is very simple. Both the aromatic charge and the alkyl sulphate may be passed through heat exchangers to accomplish this temperature control.

For satisfactory alkylation, depending, of course, on the degree of agitation and other factors attained in the reactor, a time interval of ten minutes to one hour, or more, is required, following which the sulphuric acid formed by the reaction is separated from the alkylation product. Under optimum operating conditions the sulphuric acid withdrawn from the alkylation reaction contains a minimum amount of side reaction products and, therefore, may be returned to the absorber for the formation of further alkyl sulphate. It has been found that, when 65% to 90% H_2SO_4 was originally used for the formation of the alkyl sulphate, the acid obtained from the alkylation reactor is sufficiently free from sludge as to be useful for several cycles in the process.

The alkylated hydrocarbon layer obtained from the reaction is first neutralized by washing with an alkaline solution, and then distilled to fractionate out any unreacted aromatic which may be returned to the reactor for a subsequent alkylation cycle.

A particular embodiment of the invention resides in the efficient utilization of the aromatic content of certain petroleum fractions containing relatively small percentages of aromatic hydrocarbons. In the manufacture of aviation gasoline it is now common practice to separate a petroleum fraction containing predominantly C_6 and C_7 hydrocarbons. This material is further subjected to so-called "superfractionation" to obtain two fractions: one, predominating in isoparaffins, is used as an antiknock component of aviation fuels, while the other, predominately in normal paraffins, is generally disposed of by blending into low grade motor fuels. It has been found that the entire C_6 — C_7 fraction first mentioned above when derived from California petroleum contains approximately 7% of benzene. Upon superfractionation due to azeotropic effects caused by the presence of certain naphthenes this benzene is about equally divided between the isoparaffinic and normal paraffinic fractions. Thus, the normal paraffinic fraction contains, roughly, about 7% of benzene of high antiknock value which, in this manner, because of the limitations of commercial fractionating equipment, finds its way only into low grade motor fuel. In accordance with the invention it has been found that most of the benzene contained in the normal paraffinic fraction can be salvaged readily by alkylating it to cumene and di-isopropyl benzene which, due to their higher boiling points, may then be readily separated from the bulk of low antiknock hydrocarbons by distillation. The separated alkylated benzene may then be used as a valuable antiknock component of aviation gasoline.

If desired, the entire C_6 — C_7 fractions may be treated to obtain cumene and di-isopropyl benzene from its total benzene content. Likewise, the invention may be applicable to other hydrocarbon materials containing small amounts of benzene where it is desired to alkylate the benzene.

To this end the hydrocarbon fraction containing the benzene is treated with acid-isopropyl sulphate (or normal isopropyl sulphate containing some acid-isopropyl sulphate), prepared by absorption of propylene in sulphuric acid. In

this case it is generally desirable to add not over the stoichiometric amount of alkyl sulphate necessary to react with the benzene present. Upon thorough mixing for about ten minutes, more or less, the reaction will be completed and the resulting sulphuric acid is separated and the hydrocarbon fraction is neutralized and fractionated to recover the alkylated benzene.

The accompanying drawing illustrates, in diagrammatic form, apparatus and procedure suitable for carrying out the invention. Sulphuric acid from sulphuric acid storage tank 1 passes through line 2 where it is met by recycle acid from alkylation cycle in line 24, and passes through line 3 into top of propylene absorber 4. Propane-propylene feed enters through line 6 into the bottom of propylene absorber 4 wherein the propylene reacts with acid to form alkyl sulphate which is discharged through line 5 into surge tank 10. The unreacted gases in propylene absorber 4 are discharged through line 7. The propylene absorber is provided with a jacket through which is circulated cooling water as shown by lines 8 and 9. Free sulphuric acid may be drawn from tank 1 through line 30 into the alkyl sulphate surge tank when operations require such adjustment. The alkyl sulphate from surge tank 10 passes through line 11, meeting benzene fraction from line 12, then passing concurrently through heat exchanger 14, through line 15, and into alkylation reactor 16. From alkylation reactor 16, the mixture passes through line 17, through cooling coil 18 and line 19 into separator 20. The acid layer in separator 20 leaves through line 22 and thence to storage by line 23, or line 24, as recycle acid to charging line 3, as mentioned before. The hydrocarbon layer in separator 20 passes through line 21 to caustic contactor 25 where caustic enters line 27' and spent caustic leaves by line 28'. The neutralized hydrocarbon layer leaves contactor 25 through line 26 to debenzenizer fractionator 27 where cumene or alkyl aromatic fraction leaves by line 29 to storage and the unreacted benzene passes through 28 as recycle entering the system again through line 12.

In the appended claims the term "benzene hydrocarbon" is used to denote one or more hydrocarbons of the group consisting of benzene and those homologues of benzene which are susceptible of further alkylation.

We claim:

1. The method of alkylating benzene hydrocarbons with olefines in which the presence of water is utilized to dilute sulphuric acid present during the reaction below sulphonating strength, which comprises reacting an olefin with sulphuric acid of a concentration between 65% and 90% and in quantity not greater than two mols of acid per mol of olefin, contacting the reacted mixture with an excess of benzene hydrocarbon, while maintaining the temperature between about 60° F. and about 150° F., water at all times being present in sufficient quantity to dilute all sulphuric acid present during and formed by the reaction below 90% strength to avoid sulphonation, separating the contacted mixture into an oil layer and an acid layer, removing the acid layer, neutralizing the acidity of the oil layer, and fractionally distilling the neutral oil layer to separate alkylated hydrocarbons from unreacted hydrocarbons.

2. The method of claim 1 in which the concentration of the acid is between 80% and 90%.

3. A cyclic process for alkylating benzene hy-

drocarbons with olefines in which the presence of water is utilized to dilute sulphuric acid present during the reaction below sulphonating strength, which comprises flowing a stream of olefinic hydrocarbons through an absorption zone; flowing a stream of 65% to 90% sulfuric acid through said zone countercurrently to, and in contact with, said olefinic hydrocarbons, whereby at least half of said acid becomes combined with olefin forming alkyl sulphate, said alkyl sulphate containing water in sufficient quantity to dilute all sulphuric acid present during and formed by the reaction in the hereinafter specified alkylation zone below 90% strength, withdrawing any unreacted hydrocarbons from said zone; separately withdrawing alkyl sulphate, together with any free sulphuric acid, from said zone; flowing said alkyl sulphate into an alkylation zone maintained at a temperature between about 60° F. and about 150° F.; flowing a stream comprising an excess of a benzene hydrocarbon into said alkylation zone, whereby said alkyl sulphate reacts with said benzene hydrocarbon to form alkylated benzene hydrocarbons and free sulphuric acid; flowing the reacted mixture from said alkylation zone into a separation zone and therein continuously separating free acid from alkylated and unreacted hydrocarbons; flowing said alkylated and unreacted hydrocarbons from said separation zone to a neutralizing zone wherein acidity is neutral-

ized by contact with an alkali and thence to a fractionating zone; separating alkylated hydrocarbons from unreacted hydrocarbons in said fractionating zone; and continuously removing free sulphuric acid from said separating zone and recycling said free acid to said absorption zone.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,670,505	Gunther	May 28, 1928
1,938,162	Woolcock	Dec. 5, 1933
1,994,249	Ipatieff et al.	Mar. 12, 1935
2,001,907	Ipatieff	May 21, 1935
2,143,493	Stanley et al.	Jan. 10, 1939
2,276,171	Ewell	Mar. 10, 1942
2,349,415	Draeger et al.	May 23, 1944

OTHER REFERENCES

Guyot: "New Method . . ." Chem. Abst. vol. 14 (1920), pages 404-405 (2 pages).

Ipatieff et al.: "Influence of Sulfuric Acid . . . Benzene." J. A. C. S., 582, 919-922 (4 pages), (June, 1936). 260-671.