Feb. 10, 1948. A. C. BYRNS 2,435,708

PROCESS FOR THE PRODUCTION OF SYNTHETIC ISOPARAFFINIC OIL

Filed June 8, 1942 2 Sheets-Sheet 1

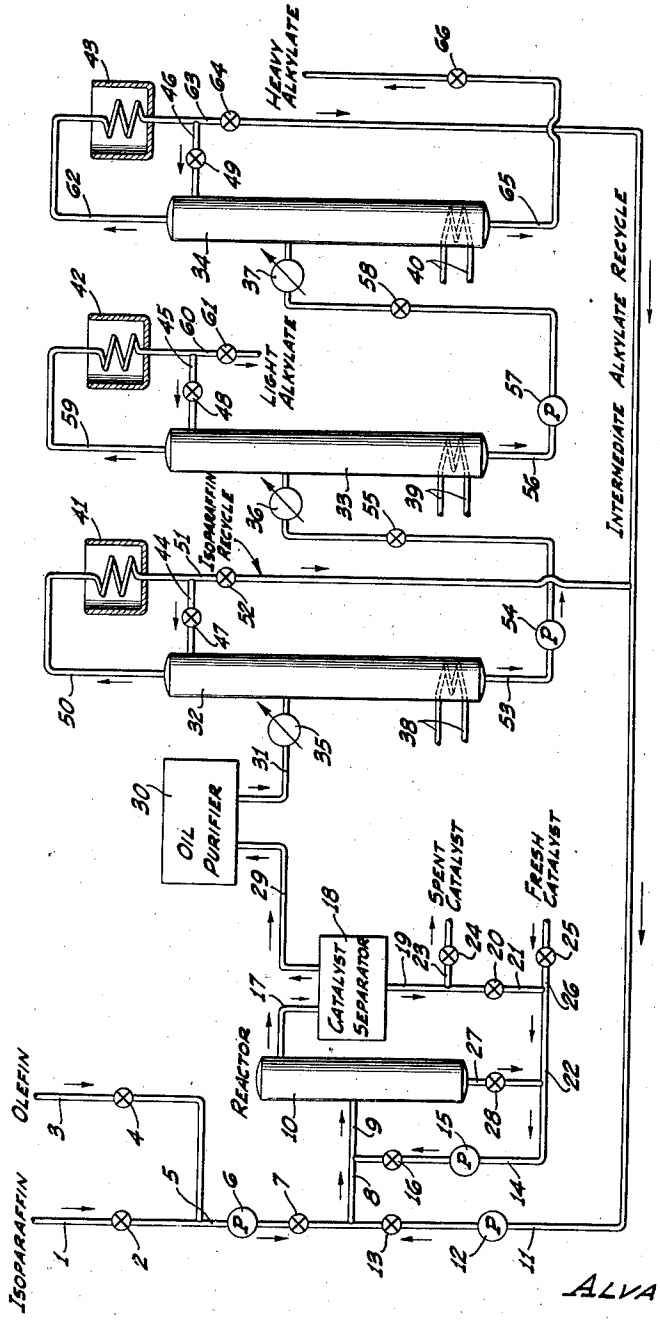


Fig. 1.

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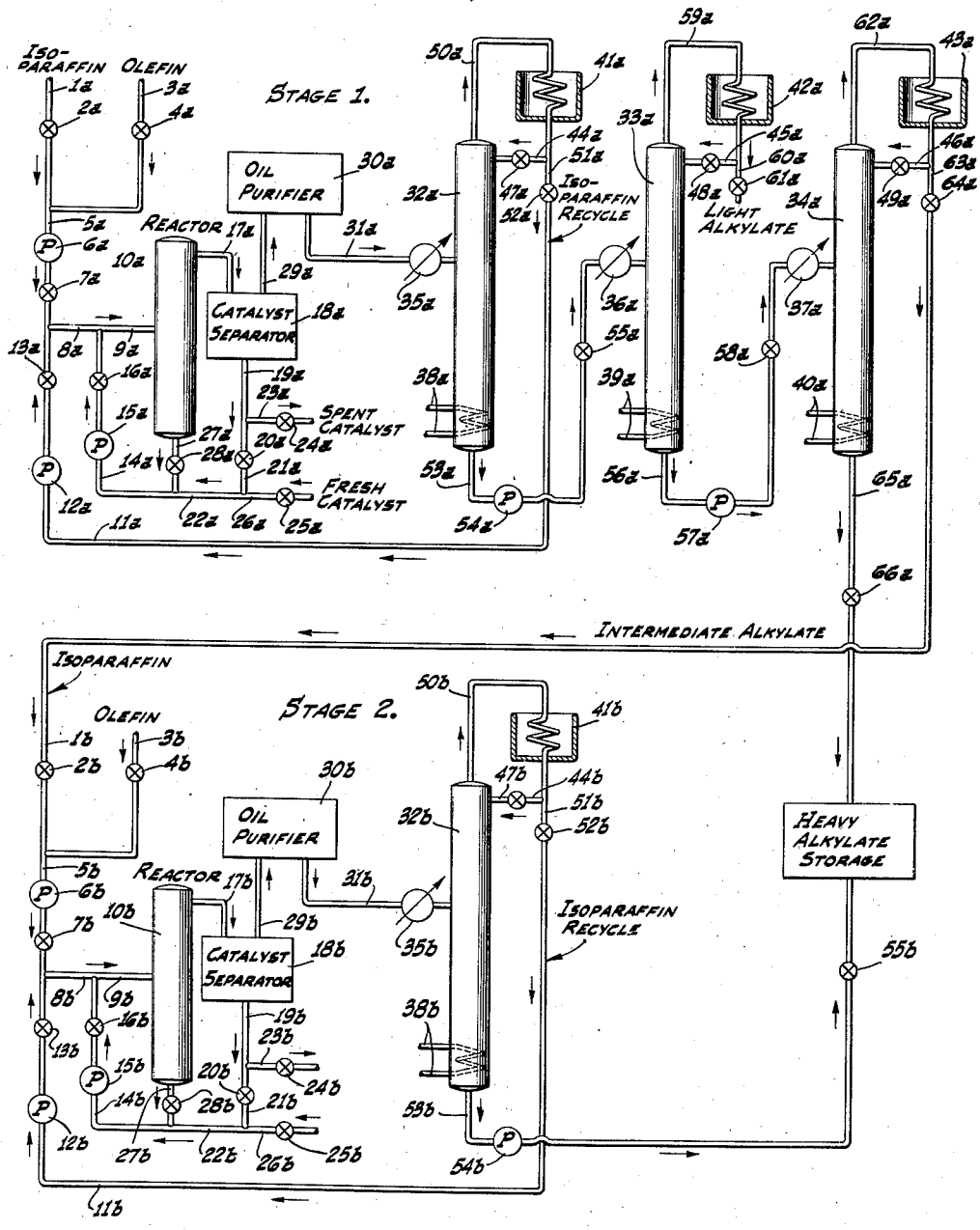


Fig. 2.

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PROCESS FOR THE PRODUCTION OF SYNTHETIC ISOPARAFFINIC OIL

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4 Claims. (Cl. 260—683.4)

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This application relates to a process for production of synthetic light oils; more particularly to an alkylation process for the production of predominately isoparaffinic oils boiling largely in the range of 400° F. to 800° F.

Hitherto processes involving production of isoparaffinic material by alkylation reactions have been devoted almost exclusively to the manufacture of "light alkylate" boiling in the gasoline range, particularly in the aviation gasoline boiling range of about 100° F. to 300° F. Many ingenious inventions have been made to suppress the production of heavier material such as "intermediate alkylate," for example material boiling from about 300° F. to 400° F. and generally used only for motor fuel blending, and "heavy alkylate" boiling above 400° F. and frequently considered of no value except as cracking stock. Many of these inventions also have had beneficial effects on catalyst life and quality of the light alkylate.

It is the object of the present invention to provide novel modifications in the present alkylation procedures whereby the production of heavy alkylate, which has been found to have valuable application in insecticide sprays, hydraulic oils, etc., is not suppressed, but enhanced or even made the primary aim of the process, without having objectionable effects on catalyst life and quality of the light alkylate which may be produced concurrently.

Briefly the invention resides in separating the desired heavy alkylate from the product of a primary alkylation process and realkylating lower boiling fractions from the primary alkylation either with the same olefin stock used in the primary alkylation or with a second olefin stock. In one modification of the invention, using the same olefin feed stock in a single-stage process and assuming both light alkylate and heavy alkylate products are desired as products, these fractions are separated from the total alkylate production leaving the intermediate alkylate which is recycled to produce additional heavy alkylate. If the light alkylate is not desired as a product, it may also be recirculated with the intermediate alkylate. In another modification of the invention any desired fraction of the original total alkylate boiling below the boiling range of the desired heavy alkylate is subjected to a second alkylation with a second olefin stock which may or may not be the same as the original olefin stock, and the product of the second alkylation is fractionated to produce heavy alkylate, for example boiling above 400° F. and lighter fractions which may or may not be recirculated through the second alkylation stage.

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To illustrate the invention, certain aspects are shown in the accompanying drawings, which for the purpose of clarity refer primarily to the alkylation of isobutane with mixed butenes and pentenes using concentrated sulfuric acid as the catalyst, and wherein

Fig. 1 illustrates a one-stage operation, and

Fig. 2 illustrates a two-stage operation.

Referring to Fig. 1, an isoparaffin stream, e. g. isobutane, flowing through line 1 controlled by valve 2, is mixed with an olefin stream, e. g. a mixed butene-pentene stream passing through line 3 controlled by valve 4. The mixture of isoparaffin and olefins is passed through line 5 and pump 6 controlled by valve 7, and thence through lines 8 and 9 to reactor 10. A recycle stream of isoparaffin, in this example isobutane and "intermediate alkylate" is introduced also into line 8 through line 11 and pump 12 controlled by valve 13, and flows through lines 8 and 9 to reactor 10. Another stream containing catalyst, H_2SO_4 in this example, is introduced also into line 9 through line 14 and pump 15 controlled by valve 16, and flows with the other two streams through line 9 to reactor 10. From reactor 10, which is equipped for proper cooling and mixing of catalyst, reactants, and recycle oil, two streams containing both catalyst and alkylated product are drawn. One stream is passed through line 17 into catalyst separator 18, where it is separated into a catalyst phase and an oil phase. The catalyst phase is passed through line 19, valve 20, and lines 21 and 22 to line 14 ahead of pump 15. Spent catalyst may be withdrawn from line 19 through line 23 and valve 24, and new catalyst may be introduced into line 22 through valve 25 and line 26, in order to maintain the catalyst at proper strength. The second stream from reactor 10 is passed through line 27 and valve 28 also to line 14 ahead of pump 15. The oil phase from separator 18 is passed successively through line 29 to oil purifier system 30, where it is freed from traces of catalyst, by caustic washing in this example. The oil from purifier 30 is passed successively through line 31 to a series of three fractionating towers 32, 33, and 34, equipped with feed preheaters 35, 36, and 37, bottoms reboilers 38, 39 and 40; overhead vapor condensers 41, 42, and 43; and reflux return lines 44, 45, and 46, fitted with control valves 47, 48, and 49, respectively. Column 32 is operated so as to produce an overhead consisting principally of the isoparaffin feed stock, isobutane in this example, which is passed through

line 50, condenser 41, line 51 and valve 52 to recycle line 11 ahead of pump 12. The bottoms from column 32 pass through line 53 and pump 54 controlled by valve 55 through preheater 36 to column 33; and the bottoms from column 33 pass through line 56 and pump 57 controlled by valve 58 through preheater 37 to column 34. The overhead from column 33 passes through line 59, condenser 42, line 60 and control valve 61 to storage. This overhead "light alkylate" consists in this example of liquid alkylate boiling below about 300° F., which may be fractionated for removal of normal butane and normal pentane if present, and blended into high quality aviation gasoline. The overhead from column 34 passes through line 62, condenser 43, line 63 and control valve 64 to line 51 and 11, ahead of pump 12. This overhead "intermediate alkylate" consists in this case of material boiling above 300° F. and below the initial boiling point of the desired "heavy alkylate" bottoms from this column (34) which latter material is drawn off through line 65 and valve 66.

The novel feature of this process lies in the recirculation of an "intermediate alkylate" fraction separated from the total alkylate product, to produce the desired "heavy alkylate." If a larger ratio of heavy alkylate to light alkylate is desired, part of the light alkylation production may be recycled with the intermediate alkylate; and if no light alkylate is desired, fractionating columns 33 and 34 may be eliminated by modifying the operation of column 32 so as to take overhead the light alkylate and the intermediate alkylate as well as the isobutane. This entire overhead is then recirculated, and the bottoms constitute the heavy alkylate production. It should be noted that such recirculation of isoparaffinic material does not tend to decrease catalyst life or quality of product. Heavy alkylate samples have been prepared as above by reacting light alkylate, intermediate alkylate, or total alkylate with butenes and pentenes in the proportions of about 5 volumes isoparaffin to one of olefin in the presence of 98% H_2SO_4 at temperatures between 32° F. and 140° F., and the products, after fractionation and acid-clay treatment, where necessary, have been found to be excellent ingredients for insecticide sprays, hydraulic oils, and the like. It has been found that in general, relatively low ratios of isoparaffin to olefin feed stocks, sulfuric acid catalyst strengths below say 95%, and reaction temperatures above about 50° F., tend to increase the production of heavy alkylate.

Another phase of the invention is shown in Figure 2 which illustrates a two-stage alkylation process, each stage having similar equipment to that of the single stage equipment of Figure 1. For convenience in reference, the various pieces of equipment of Figure 2 are numbered to correspond with the numbering of Figure 1 using additional letters *a* and *b* to distinguish first stage and second stage equipment respectively. For example, reactor 10 of Figure 1 corresponds to reactor 10*a* for the first stage of Figure 2 and reactor 10*b* for the second stage.

As a specific example of the two stage process using sulfuric acid as the catalyst in both stages, using isobutane and butene-pentene olefins as feed stocks for the first stage, using intermediate alkylate and commercial di-isobutene as feed stocks for the second stage; and producing both a "light alkylate" and a "heavy alkylate" fraction, the flow in stage I of Figure 2 is exactly as in Figure 1 except that the "intermediate alkylate" is charged to the reactor of the second stage. The single fractionating column of the second stage is used to produce a bottoms fraction of heavy alkylate of the desired initial boiling point which is combined with the heavy alkylate produced in the first stage, and an overhead stream which is recycled. The novelty here also resides in recirculation of an isoparaffinic fraction from a previous alkylation, freed from the isoparaffinic feed material and the desired heavy alkylate, but in this instance employment of a two stage process permits use of different olefin feed stocks, different catalysts, temperatures, flow rates, etc., in the two stages. Heavy alkylate fractions boiling in the range 400° F. to 800° F. have been prepared by reacting intermediate alkylate and commercial di-isobutylene in a volume ratio of 5 to 1 respectively with 98% sulfuric acid at temperatures between 32° F. and 140° F., and these products have been found suitable for application in spray oil and other compositions as were the similar fractions from the single stage process above. Many modifications of the above invention are possible. For example, in the two stage process, the "olefin" feed stock may be a polymer of a normally gaseous olefin, cracked wax olefins, or a mixture of hydrocarbons comprising olefins and aromatics such as cracked or dehydrogenated petroleum fractions; the isoparaffinic feed stock may be mixed isoparaffins or mixtures of normal and isoparaffins; the boiling ranges of the "light alkylate," "intermediate alkylate," and "heavy alkylate" fractions may be modifications of the above approximations; the catalysts may be sulfuric acid, hydrofluoric acid, aluminum chloride, or any other alkylation catalyst using different catalysts in the two stages if desired; the operating conditions may be varied to suit the stocks, catalysts and equipment; and the equipment may be modified to suit the catalysts, etc. Where the "olefin" feed stock for the second stage is a cracked gasoline, for example, it may be desirable to use two fractionating columns in the second stage instead of one, taking a gasoline overhead fraction, at least partially freed from aromatics and olefins, in the first column and sending the bottoms to the second column, where the desired heavy alkylate is taken as a bottoms fraction and the recycle isoparaffin stream is taken overhead. When the "olefin" fraction sent to the second stage contains aromatic hydrocarbons, there is likely to be an appreciable quantity of alkylated aromatics in the heavy alkylate production. In case this is undesirable such stocks should be avoided. The heavy alkylate production may be treated with sulfuric acid, clay, caustic, zinc chloride, etc., and fractionated to obtain premium grade stocks for production of spray oils, hydraulic oils, Diesel fuels, etc., boiling substantially within the range 400° F. to 800° F.

It has been observed that in general synthetic isoparaffinic oils have some tendency to deteriorate in color and odor, or increase in acidity on continued storage, particularly if the storage conditions involve exposure to oxygen, heat, or catalytic surfaces. However, the addition of an antioxidant, particularly one of the efficient alkylated or arylated aminophenols, is usually very effective in retarding such deterioration. For example a heavy alkylate was fractionated to obtain a material boiling approximately from 450 to 600° F., and this fraction was treated with H_2SO_4 and clay, in a conventional manner to

obtain a stock for the following stability experiments:

One portion of the stock, containing no inhibitor, was placed in "light storage" in a 4 oz. clear glass bottle with a loose cotton stopper and exposed to sunlight for two weeks. A second portion, likewise uninhibited was placed in "dark storage" in a loosely capped tinned can for two weeks at a temperature of about 160° F. Both samples showed an increase of 0.2 to 0.3 mg. KOH per g. in acid number and development of pronounced odor. Serious color degradation also occurred in the "dark storage" test. Three similar pairs of samples of the same stock, containing 0.0025% BAP (monobenzyl p-aminophenol), 0.025% Universal Oil Products Co. Inhibitor No. 5, and about 0.01% hydroquinone, respectively showed no appreciable degradation in acid number, odor, or color in the above "dark storage" test. In "light storage," the BAP was similarly entirely effective; the U. O. P. No. 5 protected the acid number and odor while degrading the color appreciably, and the hydroquinone had apparently no appreciable effect at all.

It will be apparent to those skilled in the art that many modifications in addition to those mentioned above may be made without departing from the scope of the invention as defined by the following claims.

I claim:

1. A continuous two-stage process for production of synthetic isoparaffinic oils boiling largely in the range 400° F. to 800° F., comprising a first stage in which an olefin feed stock comprising normally gaseous olefins is reacted with an isoparaffinic feed stock containing isobutane in molal excess in the presence of alkylation catalyst and the reaction product is fractionally distilled to obtain an isobutane fraction, which is recirculated, the desired heavy alkylate fraction boiling largely between 400° F. and 800° F., as a residual fraction which is not recirculated and an isoparaffinic intermediate fraction having a boiling range between about 300° F. and 400° F.; and a second stage in which said intermediate fraction free from those materials comprising the isoparaffinic feed stock employed in the first stage is reacted with an olefin which is present in lower molal proportions than the isoparaffin,

employing an olefinic stock containing no aromatic hydrocarbons, and carrying out the reaction in the presence of an alkylation catalyst; and a third step in which the catalyst free product is fractionally distilled to obtain the desired fraction, boiling approximately within the range 400° F. to 800° F., as a residual fraction which is not recirculated and one or more lower boiling fractions at least one of which is recirculated to the second stage reactor.

2. A process according to claim 1 in which the olefin stock used in the second stage is a polymer of a normally gaseous olefin; the catalyst used in the first stage is concentrated sulfuric acid of 80% to 110% strength; and the reaction temperature for the first stage is between 32° F. and 140° F.

3. A process according to claim 1 in which the olefin stock used in the second stage is a product from cracking of paraffin wax; the catalyst used in the first stage is concentrated sulfuric acid of 80% to 110% strength; and the reaction temperature for the first stage is between 32° F. and 140° F.

4. A process according to claim 1, in which the catalyst employed in each stage is sulfuric acid having a concentration between 80% and 95% by weight, the ratio of isoparaffin to olefin to each stage lies between about 1:1 and 5:1, and the reaction temperature in each stage is between about 32° F. and 50° F.

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