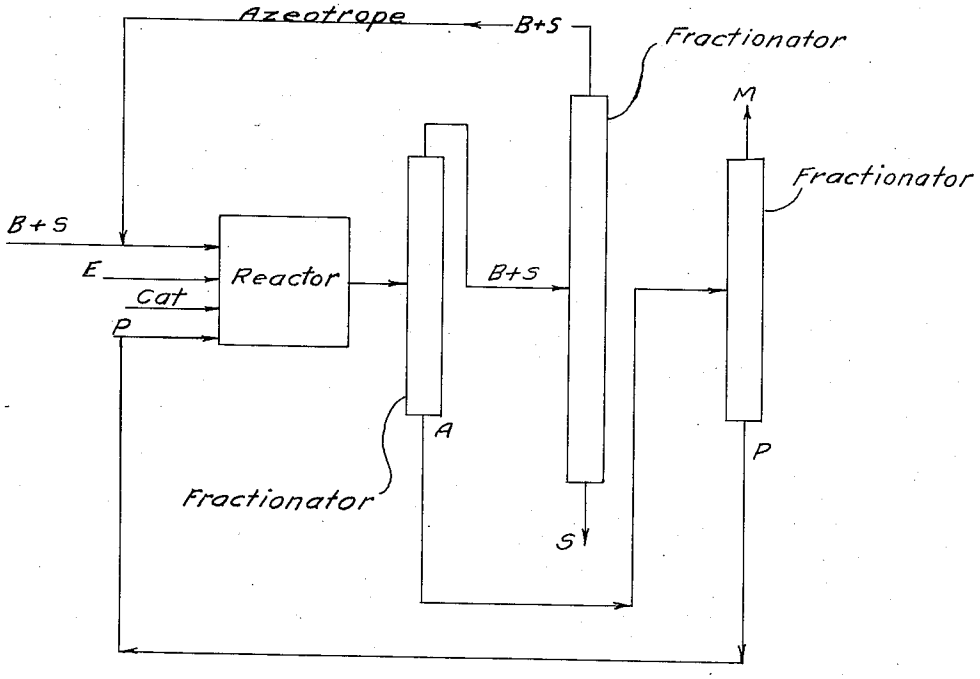
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ALKYLATION OF AROMATIC HYDROCARBONS

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LEGEND:

A – ALKYLATE
B – AROMATIC
E – ALKYLATING AGENT
M – MONOALKYLAROMATIC
P – POLYALKYLAROMATIC
S – SATURATES

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ALKYLATION OF AROMATIC HYDROCARBONS

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This invention relates to the production of alkylated aromatic hydrocarbons from fractions obtained in the refining of mineral oils.

The refining of mineral oils, such as petroleum, hydrogenated coal, shale oil, etc. is increasingly being effected by processes which result in the production of substantial amounts of aromatic compounds. The separation and recovery of the aromatic compounds presents a serious practical problem as they are often associated with saturated compounds, such as paraffins, having the same or very close boiling points. Often these compounds form azeotropes with the aromatic hydrocarbons and separation by fractional distillation becomes impossible or economically unattractive. As a result, the value of the aromatic hydrocarbons is substantially their fuel value and in some cases even less. For many purposes a fraction of a mineral oil is of less value when substantial amounts of aromatic hydrocarbons are present. For example, the presence of aromatic hydrocarbons increases soot formation on combustion and makes fuel fractions unsuitable for certain uses such as in jet engines.

The present invention effectively removes aromatic hydrocarbons from mineral oil fractions containing them in a form in which they have enhanced value as raw materials for chemical reactions. Essentially, the present invention is based on a discovery that in spite of the complexity of the mixtures of many mineral oil fractions, it is possible to alkylate the aromatic hydrocarbons almost quantitatively without affecting the other constituents. When this is done, the hydrocarbons are transformed into products whose boiling points differ very markedly from those of the accompanying more saturated hydrocarbons, and separation by distillation becomes a simple matter. It is not known why the large variety of other types of hydrocarbons present in the mineral oil fractions do not react with the alkylating agents and no theory on why the alkylation can be effected, even when a relatively small percentage of the aromatic hydrocarbons are associated with preponderant amounts of other hydrocarbons, is advanced. The results are in direct conflict with ordinary alkylation procedures where relatively pure aromatic hydrocarbons or derivatives have been considered essential as raw materials. It is thus possible, by means of the present invention, to accomplish a combined result of freeing mineral oil fractions from unwanted aromatic hydrocarbons and at the same time to recover these aromatic compounds in a form in which their value is enhanced and they constitute suitable materials for various industrial chemical purposes such as aviation gasoline additives, synthetic rubber intermediates, intermediates for various plastics, oxidation to hydroperoxides for use as polymerization catalysts or further syntheses, sulfonation for production of synthetic detergents, and the like.

Another advantage of the present invention is that alkylated aromatic compounds are produced in a high degree of purity with the elimination of one or more steps which were formerly considered necessary. In the past, when pure alkylated aromatic compounds were desired, the aromatic compounds were first recovered and purified and then were alkylated. Although the present invention eliminates steps of separating and/or purifying the aromatic hydrocarbons, the same end result of pure alkylated aromatic hydrocarbons is obtained. The elimination of the step or steps involved in the separation or purification of aromatic hydrocarbons constitutes a marked saving in the cost of production of the alkylated aromatic hydrocarbons.

While the present invention may be used with any suitable alkylating agent such as the various alkyl halides, for instance methyl, ethyl, amyl, and benzyl chlorides, butyl bromide, etc., alcohol such as isopropyl, butyl, or amyl alcohols and the like, the use of olefins is so much cheaper that they constitute the preferred type of alkylating agent. Typical examples of readily available economical olefins are ethylene, propylene, the butenes, the octenes and the like. The reaction proceeds in the presence of a catalyst and for this purpose known types of alkylating catalysts may be used. Aluminum chloride, being both cheap and effective, constitutes the preferred catalyst. However, other catalysts such as ferric chloride, hydrogen fluoride, stannic chloride, boron trifluoride, zinc chloride, sulfuric acid, phosphorus pentoxide, phosphoric acid, and contact catalysts, such as alumina and silica may be used.

Among the most important fractions in the refining of minerals oils are petroleum reformates or platformates, light cycle gas oil, etc. In many cases these fractions contain substantially only aromatic hydrocarbons and saturated hydrocarbons. However, in some instances these are associated with olefins. The latter may constitute undesirable constituents because we have found that side reactions involving the olefins may also take place when alkylating a mixture containing them. In general, amounts below about 0.2% of the total fraction are unobjectionable for any use and for certain usages much larger amounts will do no harm. Where desired the olefins may be removed by conventional means, such as acid treatment, prior to alkylation. In other words, it is not necessary that the processes of the present invention be applied to mineral oil fractions in the form in which they are ordinarily obtained and includes the alkylation of such fractions which have been subjected to various preliminary treatments to alter their composition.

Azeotropic mixtures which are frequently obtained as end-products of fractionation procedures or as certain cuts are very effectively treated by means of the process of the present invention. These azeotropic mixtures are often much richer in aromatics than are the ordinary fractions from the refining of mineral oils. The content of aromatics may even exceed that of other constituents. It is an important advantage of the present invention that a satisfactorily complete removal and recovery of the aromatic hydrocarbons is obtainable over a very wide range of concentrations. This flexibility of the process of the present invention is an important practical advantage.

A problem is presented due to the fact that the amount of alkylating agent required almost always results in the production of polyalkylated compounds in addition to monoalkylated compounds. Separation of the polyalkylated compounds presents no problem for their boiling points will ordinarily be even further removed from that of the original mixture than is the case with monoalkylates. However, they are often not useful. Many reactions, such as the oxidation to certain hydroperoxides in the syntheses of phenolic compounds requires that the alkylated aromatic hydrocarbon have but a single alkyl group, usually a secondary group. This problem, fortunately, is easily solved in most cases by effecting a separation of mono and polyalkylated aromatic hydrocarbons by distillation or by other well known means. Fortunately, alkylation results in a fairly definite equilibrium mixture when sufficient alkylating agent is used, and as is the case with equilibrium mixtures the equilibrium may be reached from either end, and, thus, when polyalkylated aromatic hydrocarbons are mixed with further feed they are dealkylated to the extent that the equilibrium mixture results. In many cases, therefore, it is desirable to mix the feed with separated polyalkylated compounds. This is another instance where the original mineral oil fraction is advantageously subjected to pretreatment before the alkylating step which constitutes the principal feature of the present invention.

It is an advantage of the present invention that the process proceeds with any mineral oil fraction regardless of the origin or of the treatment by which the fraction is produced. By far the most important mineral oil

fractions from the standpoint both of quantity and cost are the fractions obtained in the refining of petroleum. However, the process is equally effective with similar fractions obtained by the refining of hydrogenated coal, shale oil, products from the pyrolysis of tar sands, etc., and it should be understood that throughout the present specification and claims the term "mineral oil" will be used to cover any of the essentially hydrocarbon fractions obtained from mineral sources as contrasted with the predominantly glyceride or organic acid character of oils derived from vegetable and animal sources.

It is possible to effect alkylation in a single step. In some cases, however, a cyclic process presents advantages, and in such a case polyalkylates may be recycled at any point. The dealkylation of the polyalkylates requires highly active alkylation catalysts which is an additional reason why aluminum chloride, which is one of the most active, is preferred in practice. When the alkylation is carried out in several stages, with an excess of the aromatic constituent present in most of the stages, the production of the ordinarily more desirable monoalkylated products is favored. Fractionation resulting in the removal of the monoalkylate formed prior to the next stage then makes it possible to produce a high content of monoalkylated aromatic hydrocarbon. As in most chemical reactions, the preferred compromise between completeness of monoalkylation and operating costs and equipment throughput will be chosen in each instance. It is an advantage of the present invention that it is very flexible and that the best compromise from an overall economic standpoint can easily be chosen in every instance. The relatively pure alkylated aromatic hydrocarbons obtained as final products normally need no further purification, although in some instances where a product of the highest purity is necessary they may be subjected to further purification by conventional means.

Referring to the accompanying drawing, which shows diagrammatically a preferred flow sheet for carrying out the process of the present invention, a mixture of aromatic hydrocarbons and saturated hydrocarbons which form an azeotrope are charged to a reactor, and a portion of the aromatic constituents thereof alkylated with an appropriate alkylating agent in the presence of a suitable catalyst. After alkylation, the mixture is discharged from the reactor and passed into a first fractionator from which the unalkylated aromatic and saturated hydrocarbons are removed as an overhead fraction, and the alkylated aromatics are removed as a bottom fraction. The azeotrope and excess saturates over those needed to form the azeotrope are separated by close fractionation in a second fractionator, the azeotrope is recycled to the reactor, and the saturates essentially completely uncontaminated by aromatics are removed. The alkylated fraction is charged to a third fractionator from which the monoalkylaromatics are removed as a final product and from which the polyalkylaromatics are removed for recycling to the reactor. The drawing is illustrative only as disclosing a continuous cyclic process for recovering from the mixture all of the aromatic hydrocarbons as monoalkylaromatics and all of the saturated hydrocarbons substantially free of aromatic hydrocarbons. Obviously, the invention may be carried out batch-wise in a single highly efficient fractionator, if desired, and the same result obtained.

The invention is further illustrated by the following specific examples, the parts being by weight unless otherwise specified. Temperatures are in degrees centigrade. In the examples which give an azeotrope of the unreacted aromatics as one of the products the description is based on the first stage of a cyclic process, the aromatic hydrocarbon-containing-azeotrope being recycled.

Example 1

13 parts of anhydrous aluminum chloride is added at 100° C. to 1490 parts of the naphthalene-dodecane azeotrope, which contains about 43% by weight of naphthalene. The resulting mixture is thoroughly agitated while propylene is passed through it until 210 parts is absorbed. During this operation, the temperature is maintained at 100° C. by cooling. The catalyst is then decomposed with water and the product fractionated with the following results:

Fraction:	Weight, parts
Naphthalene-dodecane azeotrope	477
Dodecane	578
Monoisopropyl naphthalene	272
Polyisopropyl naphthalene	340
Residue	33

The naphthalene-dodecane azeotrope with or without the polyisopropylnaphthalene is recycled for further alkylation. The final overall yield of alkylnaphthalene is about 94%.

Example 2

818 parts of the benzene-cyclohexane azeotrope, containing about 55% by weight of benzene, is heated to 74° C., and there is added to it 9 parts of anhydrous aluminum chloride. The mixture is thoroughly agitated and propylene passed into it until 242 parts are absorbed. The reaction mixture is allowed to reflux during this operation, and the temperature gradually rises to approximately 90° C. The catalyst is then decomposed with water and the product fractionated as follows:

Fraction:	Weight, parts
Benzene-cyclohexane azeotrope	322
Cyclohexane	223
Cumene	228
Diisopropylbenzene	152
Triisopropylbenzene	108
Residue	25

The recovered azeotrope may be recycled, affording complete separation of the benzene and cyclohexane; the former is recovered in 96% yield as useful alkyl derivatives.

Example 3

800 parts of a mixture, consisting of 50% toluene and 50% mixed octanes, is heated to 100° C. and 16 grams of anhydrous aluminum chloride added. With vigorous agitation, 272 parts of butylene is gradually introduced, the temperature being held at 100° C. The catalyst is then destroyed with water and the product fractionally distilled, giving the following fractions:

Fraction:	Weight, parts
Toluene octane mixture (containing approximately 20% toluene).	498
Monobutyltoluene	252
Higher boiling products (mainly dibutyltoluenes).	322

Thus, in a single step, approximately 75% of the toluene is separated and recovered in the form of synthetically useful alkyl derivatives.

Example 4

A sample of platformate, obtained from the aromatization of a fraction of C_6 hydrocarbons, was subjected to an acid treatment to remove small amounts of olefinic materials. The product of this operation was analyzed by silica-gel adsorption and found to contain about 61.8% benzene by weight, the remainder being paraffin hydrocarbons having a refractive index, $n_D^{20}=1.38–1.39$. The overall boiling range was 8.6° C. To 650 parts of this material at 70° C. is added 13 g. of anhydrous aluminum chloride. With vigorous agitation, propylene gas is added until 302 parts has been absorbed. After destroying the catalyst with water, the reaction product is fractionally distilled, giving the following fractions:

Fraction:	Weight, parts
C_6 hydrocarbons, 24% benzene	328
Cumene	216
Diisopropylbenzene	250
Triisopropylbenzene	100
Residue	57

About 80% of the original benzene was alkylated.

Example 5

To 640 parts of the starting mixture of Example 4 is added 6 parts of anhydrous aluminum chloride at 70° C. With vigorous agitation, ethylene gas is added until 30 parts have been absorbed. After destroying the catalyst with water, the product is fractionated, giving 562 parts of C_8 hydrocarbons distillate and 108 parts of alkylated benzene residue. The recovered C_8 hydrocarbons are subjected to a second alkylation with 30 parts of

ethylene, under identical conditions with the first. Distillation of this product gives 484 parts of C_6 hydrocarbons and 108 parts of alkylated benzene. A third, fourth, and fifth alkylations are similarly carried out giving a final product of 250 parts of C_6 hydrocarbons, essentially aromatic free, and a total of 540 parts of alkylate. Fractionation of the combined alkylates gives 478 parts of ethylbenzene, 33 parts of diethylbenzene, and 29 parts of residue.

Thus the benzene in the original mixture is converted to ethylbenzene with an overall yield of 90%.

Example 6

A light cycle gas oil, of petroleum origin, having the following properties: specific gravity—0.8569, refractive index at 20° C.—1.4825, distillation range—216.7–241.8° C. was fractionally distilled in an efficient fractionating column at 98% reflux. The naphthalene containing fraction distilled over at a head temperature of 212.5° C. to 215.5° C. and amounted to 18.7% by weight of the charge. An analysis of this naphthalene concentrate by silica gel adsorption showed it to contain, by weight, 47% of aliphatic hydrocarbons having an average refractive index of 1.43, 30% of benzenoid hydrocarbons having an average refractive index of 1.51, and 23% of naphthalene. The fact that its distillation range was 4° C. below that of pure naphthalene (218° C.) indicates it to be an azeotropic mixture.

To 1300 parts of this concentrate were added 13 parts of anhydrous aluminum chloride and the mixture heated to 100° C. With vigorous stirring, propylene gas was introduced until 90 parts had been absorbed. After an additional reaction time, until substantial equilibrium is reached, the catalyst was destroyed with water and the product fractionally distilled. The composition was found to be the following.

	Per cent
Napthalene concentrate (distilling at 212–216° C.), 216–220° C.	64.6
Aliphatic hydrocarbons (n_D^{20}=1.43), 140–146° C. at 25 mm.	11.8
Alkyl benzenoid hydrocarbons (n_D^{20}=1.51), 150° C. at 25 mm.	7.6
Isopropylnaphthalene (n_D^{20}=1.59)	6.0
Polyakylated hydrocarbons	7.0
Residual tar	3.0
	100.0

It may be observed that this complex azeotropic mixture was broken up in a manner similar to the simple binary azeotropes described in earlier examples. The naphthalene concentrate may be recycled to further alkylations, thus insuring complete separation of the starting material into alkylated aromatic and aliphatic hydrocarbons.

We claim:

1. A process of separating a mixture of aromatic hydrocarbons and saturated hydrocarbons which form an azeotrope therewith and recovering substantially all of the aromatic hydrocarbons in the form of monoalkyl derivatives and all of the saturated hydrocarbons substantially free of aromatic hydrocarbons, which comprises alkylating said mixture in the presence of an alkylation catalyst with less than 2 moles of an alkylating agent per mole of aromatic hydrocarbon, separating the reaction product by distillation into an azeotrope fraction, a fraction of saturated hydrocarbons substantially uncontaminated with aromatic hydrocarbons, a fraction of monoalkylaromatics and a fraction of polyalkylaromatics, the fraction of saturated hydrocarbons having a distillation range between the boiling point of the azeotrope and that of the monoalkylaromatics and recycling said azeotrope fraction and said polyalkylaromatic fraction to the alkylation step so as to recover substantially all of the aromatic hydrocarbons as monoalkylaromatics and all of the saturated hydrocarbons substantially free of aromatic hydrocarbons

2. A process according to claim 1 in which the alkylation catalyst is a Friedel-Crafts catalyst and in which the alkylation agent is a normally gaseous olefin.

3. A process according to claim 2 in which the catalyst is aluminum chloride and in which the olefin is propylene.

4. A process according to claim 1 in which the aromatic hydrocarbons in the azeotropic mixture are mononuclear aromatic hydrocarbons.

5. A process according to claim 4 in which the alkylation catalyst is a Friedel-Crafts catalyst and in which the alkylation agent is a normally gaseous olefin.

6. A process according to claim 5 in which the catalyst is aluminum chloride, in which the olefin is propylene, and in which the mononuclear aromatic hydrocarbon in the azeotropic mixture is benzene.

7. A process according to claim 6 in which the azeotropic mixture is a benzene-cyclohexane azeotrope.

8. A process according to claim 1 in which the aromatic hydrocarbons in the azeotropic mixture are polynuclear aromatic hydrocarbons.

9. A process according to claim 8 in which the alkylation catalyst is a Friedel-Crafts catalyst and in which the alkylation agent is a normally gaseous olefin.

10. A process according to claim 9 in which the catalyst is aluminum chloride, in which the olefin is propylene, and in which the polynuclear aromatic hydrocarbon in the azeotropic mixture is naphthalene.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,741,472	Michel	Dec. 31, 1929
2,010,948	Egloff	Aug. 13, 1935
2,260,279	D'Ouville et al.	Oct. 21, 1941
2,371,163	Francis et al.	Mar. 13, 1945
2,377,243	Kimberlin, Jr.	May 29, 1945
2,398,563	Smith et al.	Apr. 16, 1946
2,450,652	Francis et al.	Oct. 5, 1948

OTHER REFERENCES

Haensel: Oil and Gas Journal, March 30, 1950, pages 82–85 (4 pages).