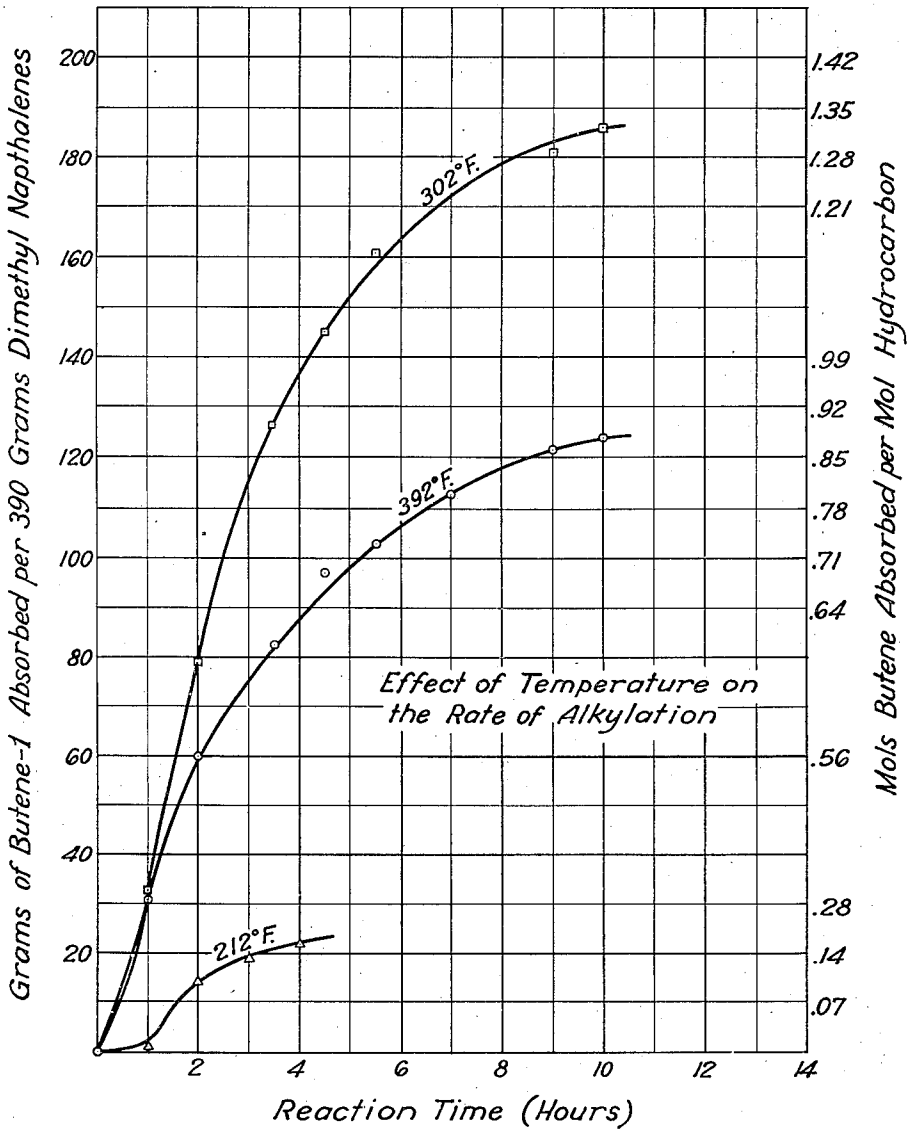
Feb. 22, 1949. F. T. WADSWORTH ET AL 2,462,792

ALKYLATION PROCESS

Filed Aug. 9, 1945



Inventors:—
Francis T. Wadsworth
Robert J. Lee
By Sam B. Becker
Attorney

Patented Feb. 22, 1949 2,462,792

UNITED STATES PATENT OFFICE

2,462,792

ALKYLATION PROCESS

Francis T. Wadsworth, Texas City, and Robert J. Lee, La Marque, Tex., assignors to Pan American Refining Corporation, New York, N. Y., a corporation of Delaware

Application August 9, 1945, Serial No. 609,882

6 Claims. (Cl. 260—671)

1

This invention relates to a process for the conversion of hydrocarbons. More particularly it relates to a process for the alkylation of polycyclic hydrocarbons. In one specific embodiment this invention relates to the alkylation of polymethyl naphthalenes with olefins.

One object of our invention is to provide a process for the alkylation of alkyl polycyclic hydrocarbons with olefins wherein side reactions are minimized. Another object of our invention is to provide a process for the alkylation of alkyl polycyclic aromatic hydrocarbons with olefins under conditions conducive to the production of high yields of alkylation products, which conditions avoid destruction of the alkylation catalyst. An additional object of our invention is to provide a process for the alkylation of aromatic hydrocarbons, especially naphthalene and its derivatives, under conditions and with a catalyst adapted to avoid or minimize the production of condensed ring compounds, such as binaphthyls and the like. Still another object of this invention is to provide a process for the employment of substantially anhydrous toluene sulfonic acids under carefully controlled conditions for the alkylation of polycyclic hydrocarbons with olefins. An additional object of our invention is to provide novel alkylated polycyclic aromatic hydrocarbons. Further objects will become apparent as the description of our invention proceeds.

Briefly, we have discovered that polycyclic hydrocarbons, such as naphthalene, methyl naphthalenes and polymethyl naphthalenes can be alkylated with olefins in the presence of substantially anhydrous toluene sulfonic acids to produce high yields of alkylated polycyclic hydrocarbons having molecular weights equal to the molecular weights of the olefins and polycyclic hydrocarbons which have participated in the alkylation reaction. Particularly, we have discovered operating conditions for this alkylation process which are conducive to the obtainment of high yields of desired alkylates at high alkylation reaction rates. The operating conditions which we use obviate undesirable side reactions of the type hitherto encountered in alkylation processes of this nature, viz., olefin polymerization and excessive catalyst destruction. We can use a wide variety of alkyl polycyclic hydrocarbons in our process. Suitable sources of alkyl polycyclic aromatic hydrocarbons for use in our process are synthetic hydrocarbon fractions obtained by the catalytic conversion of petroleum oils with catalysts comprising at least one metal oxide selected from groups 2 to 6, inclusive, of the periodic table, particularly silica, although polycyclic hydrocarbons from other sources, e. g., coal tar, can also be used.

2

Specifically, a suitable process for the production of alkyl polycyclic aromatic hydrocarbons is the hydroforming process. In this process a petroleum naphtha, which may be a virgin or cracked naphtha or mixture of both, is converted to aromatic hydrocarbons by contact with a solid, porous dehydrogenation catalyst at a temperature in the range of about 850° F. to about 1050° F., preferably in the presence of hydrogen. Suitable catalysts are oxides of metals of groups 2 to 6 of the periodic system, particularly oxides of 6th group metals such as chromium and molybdenum, preferably supported by alumina or magnesia. Excellent catalysts can be prepared by depositing about 4 to about 10% of molybdenum oxide upon an activated alumina. Suitable space velocities for hydroforming fall within the range of about 0.2 to about 4 volumes of the liquid charge stock per hour per volume of catalyst space. About 0.5 to about 8 mols of hydrogen can be charged to the process with each mol of naphtha feed stock. In addition to a high octane number naphtha, the hydroforming process produces a fraction which boils above the naphtha range, for example, in the range of about 425 to about 650° F., which is known as hydroformer bottoms. We can use the entire hydroformer bottoms or selected fractions thereof as feed stock for our process.

Hydroformer bottoms comprises a complex mixture of alkyl- and polyalkyl polycyclic aromatic hydrocarbons, including relatively large proportions of mono- and polymethyl naphthalenes. Although the constitution of hydroformer bottoms fractions may vary to a minor extent, depending upon the specific catalyst, the age of the catalyst, the specific constitution of the feed stock, etc., remarkably uniform hydroformer bottoms can be produced in a commercial hydroformer plant.

A representative hydroformer bottoms fraction exhibits the following physical properties:

A.P.I. gravity	11.0
Refractive index N_D^{20}	1.5911
Specific dispersion	264
Specific gravity $\frac{20°}{4°}$C	.989

A.S.T.M. distillation (°F.):

Initial	448
10%	465
20%	472
30%	477
40%	484
50%	490
60%	501
70%	516
80%	545
90%	620
Max.	[1] 750

[1] 92% off.

It will be noted that the hydroformer bottoms have a rather narrow boiling range except for the last 20%. Distillation of the bottoms with fire and steam accompanied by some fractionation was carried out, 8 volume percent distillate fractions of the bottoms being separated. The refractive indices and specific dispersions of the distillate fractions of the hydroformer bottoms are shown in the following table:

Fraction	Percent of Total Polymer	Refractive Index, N_D^{20}	Specific Dispersion
1	0–8	1.5346	192
2	8–16	1.5582	224
3	16–24	1.5638	224
4	24–32	1.5652	223
5	32–40	1.5720	235
6	40–48	1.5775	243
7	48–56	1.5828	248
8	56–64	1.5871	248
9	64–72	1.5917	256
10	72–80	1.6012	258

The precise chemical characterization of hydroformer bottoms or specific fractions thereof constitutes a difficult analytical problem. The general nature of the hydrocarbons present in hydroformer bottoms was revealed by extraction of the bottoms with nitromethane, which is a solvent having high solvent capacity for polycyclic and alkyl polycyclic aromatic hydrocarbons under conditions of temperature and solvent/oil ratios under which it dissolved substantially no non-aromatic or monocyclic aromatic hydrocarbons. The hydroformer bottoms were fractionally extracted and the boiling points, refractive indices and specific dispersions of the extracts were determined. From the data so obtained, together with distillation analyses and chemical characterization, it appears that the hydroformer bottoms have the following composition (by volume):

	Per cent
Paraffins	6–10
Monocyclic aromatics and tetralins	15–20
Naphthalene	1–3
Methylnaphthalenes	20–25
Alky [1] naphthalenes	25–35
Anthracene and alkylated anthracenes	6–8

[1] Dimethyl and higher alkyl groups.

It is to be remembered that the above values are only approximate and are given as our best estimate of its composition.

A variety of olefins which may be either normally gaseous or liquid, can be employed in our alkylation process. Normally gaseous olefins constitute a preferred feed stock in our process when it is desired to produce alkylates having value as plasticizers for high molecular weight resins and plastics, for example, natural rubber, butadiene rubbers such as butadiene-styrene copolymerizates (GR–S) or butadiene-acrylonitrile copolymerizates (GR–N), polystyrene, polyvinyl halide resins, cellulose and cellulose derivatives, etc. We can use olefins such as propylene, butylenes, amylenes, hexenes, and the like. We can

also use mixtures containing two or more olefins and/or other hydrocarbons, such as are found in petroleum refinery hydrocarbon fractions.

The catalyst employed in our alkylation process is a substantially anhydrous toluene sulfonic acid. The catalyst may be ortho-, meta-, or para-toluene sulfonic acid, but we prefer to use a "technical" toluene sulfonic acid which contains more than one isomer and may contain all three. We have found that the substantially anhydrous toluene sulfonic acids are much more soluble in hydrocarbons than hydrous toluene sulfonic acids and can be used as homogeneous catalysts under conditions where hydrous toluene sulfonic acids are quite immiscible with hydrocarbon feed stocks. Furthermore, anhydrous toluene sulfonic acids appear to induce higher reaction rates than the hydrated acids. In fact, in many instances, hydrated toluene sulfonic acid has been found to be substantially devoid of catalytic alkylation activity. Typical toluene sulfonic acids which we have employed as catalysts for the alkylation of alkyl polycyclic aromatic hydrocarbon with olefins have the following properties:

Neutralization equiv. (theory: 172)	177.5
Density, grams/ml. at 84.9° F	1.3043
Refractive index:	
(*a*) Of 11.4% aqueous solution	1.352
(*b*) Calculated to 100% toluene sulfonic acid	1.507
Crystallizing point, °F. (approx.)	95
Water content, weight percent (by refluxing with toluene, 3.5 hours.)	1.05
Physical appearance	viscous liquid or semi-crystalline mass depending on temperature; dark reddish brown color
Assay (toluene sulfonic acids)	94.0% (min.)
Free H_2SO_4	1.0% (max.)
Toluene	0.2% (max.)
Water	2.0% (max.)
Sulfones	3.0% (max.)
Para toluene sulfonic acid	80% (approx.)
Ortho toluene sulfonic acid	20% (approx.)

We have found that although we may use as little as 1 mol percent, it is desirable to use at least 3 mol percent, preferably 10 mol percent of toluene sulfonic acid based on the alkyl polycyclic hydrocarbon employed as feed stock. Increased concentration of toluene sulfonic acid in the reaction zone increases the rate of the alkylation reaction. Thus, the employment of 10 mol percent of toluene sulfonic acid induced a higher rate of alkylation than 3 mol percent. We can use 20 mols of toluene sulfonic acid per 100 mols of alkyl polycyclic hydrocarbon, or even more.

The rate of alkylation is also affected by the specific olefin feed stock. We have found that the rate of alkylation is reduced with increasing molecular weight of the olefin feed stock. Thus, propylene alkylates an alkyl polycyclic aromatic hydrocarbon at a considerably faster rate than butene-1, and butene-1 alkylates more rapidly than pentene-1. Data illustrating the effects of catalyst concentration and specific olefins on the rates of alkylation are set forth in Table I. In the experiments which yielded the data set forth in Table I, a well-stirred solution of technical toluene sulfonic acid in a fraction of hydroformer bottoms boiling in the range of about 480 to 530° F. was in each case maintained at 265° F., while the pure olefin was introduced in slight excess of the reaction rate. The fraction of hydroformer bottoms that was used comprised a substantial proportion of dimethyl naphthalenes. The maximum rate of olefin introduction was 0.006 cubic foot per minute for a 15 mol aromatic hydrocarbon charge containing 10 mol percent of technical toluene sulfonic acid. The data presented in Table I show that 10 mol percent toluene sul-

fonic acid induced an enhanced rate of alkylation as compared with 3 mol percent of toluene sulfonic acid.

TABLE I

Effect of catalyst concentration and nature of olefin on the alkylation of dimethyl naphthalenes

Temperature: 265° F.—Charge stock: 480–530° F. fraction of hydroformer bottoms

Time Hours	Mols of Olefin Absorbed/Mol of Hydrocarbon/Hour			
	3% Catalyst		10% Catalyst	
	Propylene	Butene-1	Butene-1	Penetene-1
1	.226			
2	.118		.279	
3	.084			
4	.102			
7		.033		
8.5	.060			
9				
10			.148	
12				.048
14			.074	
17				
20	.084			
22		.039		
24				
25	.009			
27				
30		.017		
34				
37.5		.012		
41				
49				
47.5		.010		
Total mols of olefin/mol of Aromatic	1.81	1.82	2.04	.58
Total time	25	47.5	14	12

The optimum temperatures for the use of substantially anhydrous toluene sulfonic acid catalysts for alkylating alkyl polycyclic hydrocarbons with olefins lie within the range of about 265

to about 300° F. We have found that in admixture with alkyl polycyclic hydrocarbons and olefins, toluene sulfonic acids begin to decompose at a substantial rate at temperatures above about 300° F., although in the absence of polycyclic hydrocarbons and olefins considerably higher decomposition temperatures are indicated. It is probable that decreased alkylation rates observed at temperatures in excess of 300° F. are attributable to the decomposition of toluene sulfonic acids. However, we do not intend to be bound by any theory regarding the alkylation reactions.

Representative data indicating the effect of temperature on the rate of alkylation of alkyl polycyclic hydrocarbons with olefins are illustrated in the graph on the accompany drawing. The data were obtained by again alkylating a fraction of hydroformer bottoms boiling in the range of about 480 to about 530° F., comprising a substantial proportion of dimethyl naphthalenes, using a concentration of 10 mol percent of technical toluene sulfonic acid per mol of dimethyl naphthalene in the feed stock. Butene-1 was introduced into the alkylation zone at a rate slightly in excess of its absorption (reaction) rate. From the graph on the accompanying drawing it will be evident that alkylation proceeded at a slow rate at 212° F. and at a rapid rate at 302° F. However, at 392° F., the alkylation rate was appreciably lower than the rate at 302° F. The optimum alkylation rate is achieved and the recovery of toluene sulfonic acid catalyst for recycle to the alkylation zone is maximum at temperatures in the range of about 265 to about 300° F.

The data in Table II are advanced as practical illustrations of the results obtainable by our improved alkylation process, but are not intended unduly to limit our invention.

TABLE II

Preparation and properties of propylated and butylated alkyl naphthalenes

Example	1	2	3	4	5
Product	mono and dibutyl	dibutyl	crude mono and dibutyl.	mono and dibutyl	dipropyl.
Reactor	5 liter glass	5 liter glass	2 gallon steel	50 gallon steel	3 liter glass.
Alkylation Conditions:					
Mol percent toluene sulfonic acid catalyst.	3	10	10	10	8.
Pressure	Atm	Atm	30 p. s. i. g	30 p. s. i. g	70 mm. Hg.
Temperature, °F	265–285	265–285	265–285	265–285	260–265.
Time, hours	80	14	18	84	92 (in excess).
Mols olefin absorbed/mol hydroformer bottoms.	1.2	2.04	1.51	1.25	2.14.
Charge Stock:					
Olefin	Butene-1	Butene-1	Mixed B–B [1]	Mixed B–B [1]	Refinery propylenes (47.9% propylene).
Hydroformer bottoms fraction, boiling range (°F.) at 1 atm.	482–527	437–554	437–554	437–554	437–554.
Total Product Yields, Wt. Percent Based on Charge:					
Unreacted	26	32.5	21.2	14.5	7.6
Monoalkylated	38.7	Trace	97.7	25.1	17
Dialkylated	60.4	123.7		80.2	106.1
Polyalkylated and Bottoms	17.9	16.8	35.1	25.2	7.3
Total	143	173	154	145	138
Dialkylated Product, Wt. Percent of Theoretical Yield.	35.2	72.0	56.8	46.7	69.1.
Product	1	3 2	3	4	5.
Boiling Range, °F	{248–338/1 mm; {563–680/760 mm	336–383/2 mm	541–633/760 mm	{608–622/760 mm; {284–338/1 mm	612–653/772 mm. 293–318/1 mm.
n_D^{25}	1.5630	1.5550	1.5464	1.5620	1.5592.
d_4^{25}	0.9489	0.9320	0.921	0.944	0.9390.
Color	Light Yellow	Light Yellow (1½ ASTM).	Light Red (4½ ASTM).	Light Yellow (1½ ASTM).	Light Yellow (1½ ASTM).
Weight percent Aromatics by sulfonation [2].	98.6	96.6		92.0	98.5.
Iodine No. (Wijs)	0.0	0.7	0.7	0	0.
Viscosity at 100 °F., Centistokes	24.9	63.8	42.1	39.7	46.5.
Saybolt Viscosity, Universal (seconds/100°F.)	118	295	195	184	215.

[1] Refinery butane-butylene stream containing 41% olefins.
[2] Method tends to give low values in the high ranges of aromatic content.
[3] Average molecular wight 256. The theoretical molecular weight of a dibutyl dimethyl naphthalene is 268.

In Table II, the hydroformer bottoms fraction boiling in the range of 437 to 554° F. comprised predominantly a mixture of mono-, di-, and trimethyl naphthalenes. The hydroformer bottoms fraction boiling at 482 to 527° F. comprised predominantly dimethyl naphthalenes. Details of operating procedures used in obtaining the data set forth in Table II will be set forth below.

Example 1

A sample of butylated hydroformer bottoms was prepared by alkylation at 265° F. of a 3 mol percent solution of technical toluene sulfonic acid in dimethylnaphthalenes (482–527° F. fraction from hydroformer bottoms). The solution was placed in a 5 liter, 3 neck flask fitted with an efficient mechanical stirrer, a water condenser and a gas distributor which introduced the gas through small holes beneath the surface of the liquid. The gas was metered in at a rate slightly faster than that at which it was absorbed. Alkylation was continued until 1.2 mols of olefin per mol of hydroformer bottoms, calculated as dimethylnaphthalene, had been absorbed. Beyond this point the absorption of butylenes was slow. Alkylation was then stopped and when flask contents had cooled the catalyst was washed out with dilute alkali and then with water. When vacuum distillation of the dried mixture was attempted, the presence of a white crystalline solid was noted in the distillate; some had also solidified in the condenser. It is believed that this solid is formed by the decomposition of esters of toluene sulfonic acid at the high pot temperatures. The distillation was continued, however, at total take-off, allowing the remaining esters to decompose until the temperature reached 410° F. at 3 to 4 mm. mercury pressure. The toluene sulfonic acid was washed out of the distillate with dilute alkali and nonalkylated and unreacted hydrocarbons were removed by topping this distillate through a 60 x 2.5 cm. column packed with ⅛ inch Fenske helices to an overhead temperature of 450° F. at 200 mm. mercury pressure. The product was diluted with isopentane and decolorized by filtering through clay. After solvent removal the mixed mono- and dibutyl dimethylnaphthalene yield based on crude butylated product was 75 weight percent. Physical properties were determined and are listed in Table II under product 1.

Example 2

Product 2 of Table II was prepared by the alkylation of a wider cut of hydroformer bottoms (mono-, di-, and tri-methylnaphthalenes, boiling range 437–554° F.) with pure butene-1, using 10 mol percent of anhydrous toluene sulfonic acid catalyst. In this preparation, butylation was continued until the product contained an average of two butyl groups per naphthalene nucleus. The product was washed with water, dried and then flash distilled up to 374° F. at 1 mm. mercury pressure absolute. Free toluene sulfonic acid catalyst was washed out of the distillate with dilute alkali and the product was topped on a 3 x 30 cm. column packed with ¼ inch metal helices at a reflux ratio of 12:1 to an overhead temperature of 383° F. at 2 mm. mercury pressure. Molecular weight determinations gave values corresponding to dibutyl dimethylnaphthalene.

Example 3

For this alkylation a refinery stream of butanes-butylenes was used in place of pure butene-1, and found to be satisfactory. The refinery stream, containing 41% of olefins, was dispersed well beneath the surface of the liquid aromatic hydrocarbons by means of a distributor tube. The exhaust gas, from which most of the olefins had been removed, was allowed to escape from a pressure reducing valve located at the top of the reactor. After the injection of the olefinic gas stream was discontinued, the contents of the alkylation reactor were maintained with stirring at the reaction temperature between 3 and 4 hours. The reactor contents were thereafter withdrawn, cooled, and free toluene sulfonic acid was removed by washing with an aqueous solution of caustic soda. The specific constants listed in Table II for product 3 are for the crude unfractionated material which contains a small amount of unreacted feed stock; hence they are at slight variance with other product samples.

Example 4

The liquid charging stock was 17.5 gals. (66.7 kg.) of a mixed mono-, di-, and trimethyl naphthalene fraction of hydroformer bottoms. To this charging stock there was added 10 mol percent (7.35 kg.) of technical toluene sulfonic acid. The butane-butenes gas stream was first introduced at the rate of 0.2 cubic feet per minute. Shortly thereafter the rate was increased to 0.5 cubic feet per minute. A small proportion of polymer having an average molecular weight of 126 was produced. The mol ratio of olefin converted to polymer to olefin converted to alkylate was 0.0645. The products were worked up in the manner described in Example 3 and were then fractionated.

Example 5

Table II indicates that dipropylation of a hydroformer bottoms fraction can be effected under conditions similar to those employed with butylenes to yield a similar product. Upon completion of the desired alkylation reaction, propylene injection was discontinued and the reaction mixture was stirred at the alkylation temperature for an additional 4 hours to decompose esters of toluene sulfonic acid which are present in the alkylation reaction mixture. Thereafter the reaction mixture was allowed to cool to room temperature and finished as described in Example 3.

From the data of Table II, it will be seen that mono- or dialkylation of hydroformer bottoms fractions can be accomplished quite readily under mild reaction conditions in the presence of substantially anhydrous toluene sulfonic acids. The specific catalyst used was a mixture of technical toluene sulfonic acids, whose properties have been described above. It will also be observed that petroleum refinery mixtures of butenes-butanes can be used as alkylating agents with substantially as good results as those obtained when pure butene-1 is used.

From a comparison of the data in Table II it will be observed that the butylated product is characterized by high viscosity (100–300 seconds Saybolt Universal at 100° F.) and low volatility or high boiling range at 1–2 mm. mercury pressure.

Our alkylation process can be operated batch wise, multistage, or continuously. The toluene sulfonic acid catalyst can be separated from the alkylation products intermittently or continuously, and recycled to the alkylation reactor. A particularly suitable method for recovering the toluene sulfonic acid catalyst from the reaction mixture, especially where relatively large quantities of catalyst are used, e. g., 10 to 20 mol percent, comprises diluting with a saturated aliphatic material in the liquid state, e. g., a hydrocarbon such as liquid propane, butanes, pentanes, hexanes, heptanes, cyclohexane, etc., or mixtures containing two or more of these hydrocarbons, paraffinic naphthas, kerosene, gas oil or the like. Upon the addition of a sufficient volume of saturated aliphatic material, usually between about 0.25 and about 3 volumes per volume of the alkylation reaction mixture, the toluene sulfonic acid catalyst separates as a lower layer in substantially anhydrous condition and can be recycled as an alkylation catalyst without modification. Layer separation can be effected conveniently at temperatures within the range of about 50 to about 150° F. e. g., at room temperature. The small proportion, e. g., 1 to 3% of toluene sulfonic acid which remains in solution in the alkylate can be removed by washing with water or alkalies prior to fractionating the alkylate. Unconverted feed stocks can be recovered and recycled in proper proportions to the alkylation reactor. Over-alkylation can be avoided by recycling products of undesirably high molecular weight to the alkylation reactor.

Although our invention has been described with specific reference to the alkylation of hydroformer bottoms, it is not thus limited and can be applied to the alkylation of alkyl polycyclic hydrocarbons from different sources. Thus, it may be applied to alkyl polycycylic hydrocarbons derived from certain crude petroleum oils by extraction with selective solvents. Alkyl polycyclic hydrocarbons derived from coal tars, e. g., alkyl naphthalene fractions, are desirable feed stocks for our improved alkylation process. Alkyl polycyclic aromatic hydrocarbons are also present to a considerable extent in cracked cycle stocks produced by cracking high boiling petroleum oils such as gas oils, preferably with catalysts. Cracking with solid cracking catalysts comprising one or more oxides of metals selected from groups 2–6, inclusive, e. g., silica, of the periodic table may be effected at temperatures of the order of about 850 to 1050° F. and pressures of atmospheric to 50 p. s. i. or even higher. A suitable cracking catalyst is active silica promoted with about 5 to about 30% of active alumina or magnesia. Also, activated clays may be used as catalysts. Alkyl polycyclic aromatic hydrocarbons may be concentrated from cracked cycle stocks by a variety of selective solvents. Suitable selective solvents include nitromethane, nitroethane, ethylene glycol monoethyl ether, diethylene glycol monoethyl ether, diethylene triamine, dipropylene glycol, methanol, ethylene glycol monomethyl ether, diethylene glycol monoethyl ether, morpholine ethanol, triethylene tetramine, tetraethylene pentamine, etc.

The physical properties of aromatic hydrocarbons extracted by a selective solvent from a cycle stock produced by catalytically cracking 35° A. P. I. Mid-Continent gas oil are:

A.P.I. gravity	9.6
Refractive index N_D^{20}	1.5960
Specific dispersion	267
Specific gravity $\frac{20°}{4°}$C	1.007

A.S.T.M. distillation (°F.):

Initial	420
10%	464
20%	478
30%	494
40%	512
50%	526
60%	544
70%	570
80%	600
90%	658
Max	732

The alkylation products, particularly the mono- and dibutylated methyl naphthalenes, produced by the process of our invention are novel and useful. Because of their low volatility and high viscosity, they are especially adapted for use as plasticizers in high molecular weight resins and plastics such as natural rubbers, butadiene-styrene rubbers, butadiene-acrylonitrile rubbers, cellulose plastics, etc. Alkylated methyl naphthalenes, e. g., dipropyl, dibutyl, and diamyl dimethyl naphthalenes, can be used in combination with other plasticizers, e. g., ester type plasticizers such as dibutyl phthalate, in plasticizing rubbers, e. g., butadiene-acrylonitrile rubbers. Alkylated methyl naphthalenes, as produced by the process of our invention, can also be employed in compositions for impregnating wood and other fibrous materials to prevent or inhibit attack by termites or by marine organisms. Suitable impregnating compositions can contain creosote or coal tar in addition to the alkylated methyl naphthalenes. Alkylation products of our invention can also be used as insecticides, e. g., for chinch bugs and termites, alone or in combination with other insecticidal materials. The alkylated methyl naphthalenes can also be sulfonated to yield sulfonates whose salts, e. g., the sodium and potassium salts are wetting, re-wetting, detergent or emulsifying agents. The alkylated methyl naphthalenes can also be employed as lubricants alone or in combination with other lubricants. Alkylated methyl naphthalenes can be employed in quenching oils. As to the foregoing description of uses for the alkylation products which can be produced by our process, it will be understood that chemical derivatives of the alkylation products can also be employed, e. g., halogenated derivatives, alkoxy derivatives, chloromethyl derivatives, etc.

It will be evident that we have set forth a highly advantageous process for the alkylation of alkyl polycyclic hydrocarbons characterized by high yields of desirable alkylates, low catalyst consumption and the avoidance of undesirable side reactions.

We claim:

1. A process for the alkylation of polycyclic aromatic hydrocarbons which comprises introducing an olefin into an alkylation zone and contacting said olefin in said alkylation zone with polycyclic aromatic hydrocarbons and at least 3 mol percent of a substantially anhydrous toluene sulfonic acid at a temperature in the range of about 265 to about 300° F. under sufficient pressure to maintain a liquid phase in said alkylation zone, diluting alkylation reaction products with a saturated hydrocarbon, and separating a phase comprising substantially anhydrous toluene sulfonic acid.

2. A process for the alkylation of a polycyclic aromatic hydrocarbon which comprises contacting an olefin in an alkylation zone with a poly-

cyclic aromatic hydrocarbon and a substantially anhydrous toluene sulfonic acid catalyst at an alkylation temperature under sufficient pressure to maintain a liquid phase in said alkylation zone, diluting the alkylation reaction mixture with a saturated hydrocarbon and separating a distinct phase comprising substantially anhydrous toluene sulfonic acid.

3. The process of claim 2 wherein the olefin is a normally gaseous olefin containing at least three carbon atoms in the molecule.

4. The process of claim 2 which comprises the additional step of recycling substantially anhydrous toluene sulfonic acid recovered from the alkylation reaction mixture to said alkylation zone.

5. The process of claim 1 wherein the polycyclic aromatic hydrocarbons are contained in a fraction comprising a substantial proportion of methylnaphthalenes, said fraction boiling between about 437° F. and about 554° F. at 1 atmosphere.

6. The process of claim 2 wherein the polycyclic aromatic hydrocarbons are contained in a fraction comprising a substantial proportion of methylnaphthalenes, said fraction boiling between about 437° F. and about 554° F. at 1 atmosphere.

FRANCIS T. WADSWORTH.
ROBERT J. LEE.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
1,741,472	Michel	Dec. 31, 1929
2,014,766	Isham	Sept. 17, 1935
2,385,303	Schmerling	Sept. 18, 1945
2,386,892	Schaad	Oct. 16, 1945
2,390,835	Hennion et al.	Dec. 11, 1945
2,390,836	Hennion et al.	Dec. 11, 1945
2,395,976	Shankland	Mar. 5, 1946
2,411,578	Lieber	Nov. 26, 1946

Certificate of Correction

Patent No. 2,462,792. February 22, 1949.

FRANCIS T. WADSWORTH ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Columns 5 and 6, Table II, column numbered "4", opposite "Boiling Range, °F." for "608–622/760 mm" read *608–662/760 mm*;

and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 28th day of June, A. D. 1949.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.