

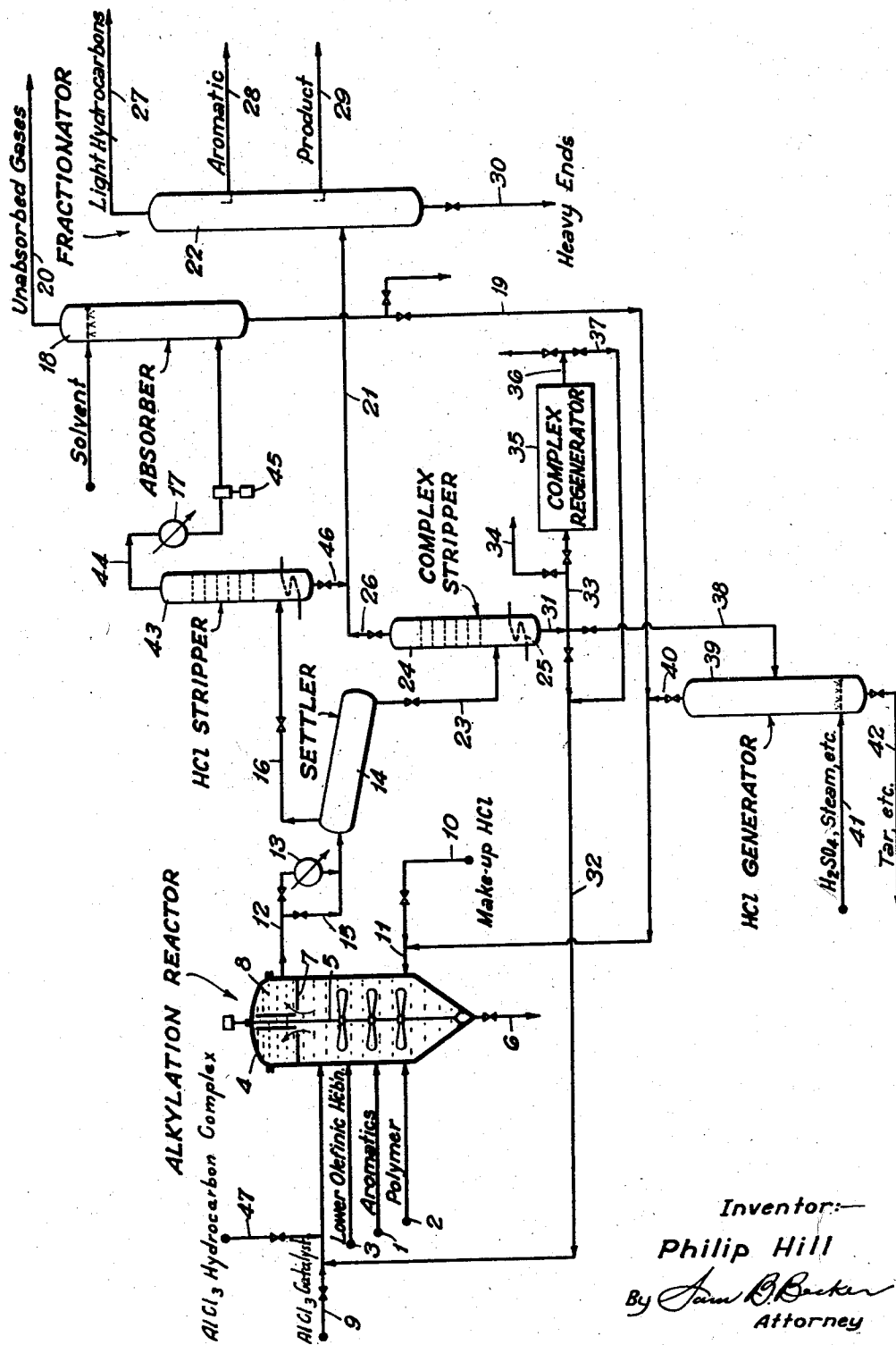
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CATALYTIC ALKYLATION OF AROMATIC HYDROCARBONS BY LONG CHAIN OLEFINS

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CATALYTIC ALKYLATION OF AROMATIC
HYDROCARBONS BY LONG CHAIN OLE-
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This invention relates to the alkylation of aromatic hydrocarbons. More particularly it relates to the alkylation of aromatic hydrocarbons with olefinic hydrocarbons of high molecular weight to yield alkylates whose sulfonates are preferentially soluble in hydrocarbon oils.

As used in this specification and the appended claims, the term "alkylation" is intended to designate the reaction between an aromatic hydrocarbon and an olefin wherein the net effect of the reaction is the replacement of a hydrogen atom on a nuclear carbon atom of the aromatic hydrocarbon by an alkyl group having the same number of carbon atoms as the olefin.

The present invention finds its preferred application in the alkylation of aromatic hydrocarbons, particularly monocyclic aromatic hydrocarbons, with aluminum chloride and a minor proportion of hydrogen chloride. In this type of alkylation reaction, olefinic hydrocarbons having less than about 15 carbon atoms in the molecule react quite smoothly, rapidly, and in good yields, and require the employment of a relatively small proportion of an aluminum chloride catalyst, e. g., in the range of about 0.5 to about 5 percent by weight based on olefinic hydrocarbons. However, higher olefinic hydrocarbons, by which I mean olefinic hydrocarbons having at least 15 carbon atoms, especially 20 or more carbon atoms, e. g., 25, 30, 40, or 50 carbon atoms in the molecule, do not alkylate well, that is to say, they require relatively gross amounts of aluminum chloride catalyst, long reaction periods and afford relatively poor yields. Attempts to overcome the sluggish behavior of higher olefinic hydrocarbons in these alkylation reactions by the employment of more severe operating conditions, such as high alkylation temperatures, high proportions of catalysts, or long reaction periods are unsuccessful. Failure to improve the alkylation reaction by the selection of relatively severe operating conditions may be attributed primarily to the fact that these conditions induce decomposition of the higher olefinic hydrocarbon to produce products having both more and less carbon atoms in the molecule than the olefinic feed stock, and these degradation products may then alkylate the aromatic hydrocarbon to produce nondescript alkylates of wide boiling range containing a greatly reduced proportion of the desired alkylation product. Also, severe operating conditions tend to destroy the alkylate produced from the feed stocks.

This invention is concerned primarily with the production of alkyl aromatic hydrocarbons, particularly monocyclic aromatic hydrocarbons, having one or more side chains containing at least 15 carbon atoms. Alkyl aromatic hydrocarbons of this description are eminently suitable

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for sulfonation to yield sulfonic acids whose salts, i. e., soaps, are either preferentially soluble in hydrocarbon oils or highly soluble in hydrocarbon oils and quite insoluble in water at ordinary temperatures. Soaps of this type may be regarded as "synthetic" mahogany soaps. These soaps are capable of specialized applications which necessitate the placement of rigid specifications on the soaps, one of the specifications being the absence of preferentially water soluble soaps. Preferentially water soluble soaps result from the sulfonation and neutralization of alkyl aromatic hydrocarbons having less than 15 carbon atoms in the alkyl group. Therefore it is essential, in the preparation of a preferentially oil soluble alkyl aromatic hydrocarbon sulfonate, to employ alkyl aromatic hydrocarbons containing no substantial proportion of constituents having less than 15 carbon atoms in the alkyl group.

In a preferred embodiment, this invention relates to the alkylation of an aromatic hydrocarbon with a selected olefinic hydrocarbon or a mixture of olefinic hydrocarbons of relatively narrow boiling range and restricted variation in the number of carbon atoms in the molecule, to produce alkylates of relatively narrow boiling range and restricted variation in the number of carbon atoms in the molecule. More particularly, the invention relates to the alkylation of benzene or similar hydrocarbons with olefins having at least 15 carbon atoms in the molecule and of restricted molecular weight range, i. e., olefin fractions having about 15 to 21 carbon atoms in the molecule or about 20 to 30 carbon atoms in the molecule, without substantial concomitant production of alkyl benzenes having less than about 15 alkyl carbon atoms in the molecule. In my invention, no substantial proportion, e. g., not more than about 5%, of olefinic hydrocarbons having a molecular weight between about 130 and 210 is included in the feed stock.

It is an object of my invention to provide an improved process for the alkylation of aromatic hydrocarbons with olefinic hydrocarbons having at least 15 carbon atoms in the molecule in the presence of a catalyst of the type of aluminum chloride and a minor proportion of hydrogen chloride. Another object of my invention is to provide a process for the alkylation of monocyclic aromatic hydrocarbons with olefinic hydrocarbons having at least 15 carbon atoms in the molecule to produce alkyl aromatic hydrocarbons whose alkyl groups contain at least 15 carbon atoms without substantial production of alkyl aromatic hydrocarbons whose alkyl groups contain less than 15 carbon atoms. An additional object of my invention is to provide a process for the alkylation of aromatic hydrocarbons such as benzene with olefinic hydrocarbons contain-

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ing at least 15 carbon atoms in the molecule in the presence of a catalyst of the type of aluminum chloride promoted by a minor proportion of hydrogen chloride, which process is characterized by improved yields of desired alkylate, lower catalyst requirements and consumption, lower reaction temperatures, and shorter reaction periods for a given yield.

Briefly, this invention relates to the employment of a minor proportion, less than about 10%, of a lower olefinic hydrocarbon having a molecular weight below about 130 to facilitate the alkylation of an aromatic hydrocarbon, particularly a monocyclic aromatic hydrocarbon, by an olefinic hydrocarbon or a mixture of olefinic hydrocarbons having at least 15 carbon atoms in the molecule in the presence of a catalyst such as aluminum chloride promoted by a minor proportion of hydrogen chloride. Suitable lower olefinic hydrocarbons which may serve as promoters in the alkylation of aromatic hydrocarbons such as benzene and the like with higher olefinic hydrocarbons include various octenes, heptenes, hexenes, pentenes, butenes, etc. I may also employ lower molecular weight cyclo-olefins such as cyclohexene, methylcyclohexene, cyclopentene, and methylcyclopentene. Although I prefer to employ aliphatic olefinic hydrocarbons, I may employ other olefinic materials such as styrene, vinylfuran, vinylacetylene, vinylpyridines, methyl vinyl ketone, vinyl acetate, and the like. It will be understood that the lower molecular weight olefinic hydrocarbon need not be employed in the pure form. Thus the olefinic hydrocarbon may contain non-reactive, non-deleterious materials such as normal paraffins and the like. Also, it is possible to employ a mixture of two or more lower olefinic materials.

I have found that the addition of a minor proportion of a lower olefinic hydrocarbon having a molecular weight below about 130 to an alkylation zone wherein benzene is being alkylated with a higher olefinic hydrocarbon having at least 15 carbon atoms in the molecule in the presence of a catalyst of the type of aluminum chloride promoted by a minor proportion of hydrogen chloride exerts a promoting effect upon the alkylation reaction, rendering possible the use of much shorter reaction periods, proportions of catalyst, and temperatures than would be possible in the absence of said lower olefinic hydrocarbon. Furthermore, the presence of the lower olefinic hydrocarbon results in increased yields of desired alkylate and inhibits or prevents the cracking or degradation of the higher molecular weight olefinic feed stock and the production of undesired alkylates of lower and higher molecular weight than that which would be produced by the chemical union of the aromatic hydrocarbon and higher molecular weight olefin feed stocks.

Particularly suitable aromatic feed stocks are monocyclic aromatics, especially benzene and the like. The process of my invention may also be applied to alkyl substituted benzenes such as toluene, xylene, cumene, n-propyl benzene, trimethylbenzenes, triethylbenzenes, and the like. My invention may also be applicable to the alkylation of monocyclic aromatics containing one or more non-hydrocarbon nuclear substituents, e. g., amino, N-substituted amino, amido, nitro, halogen, or O-R groups wherein "R" is a hydrocarbon radical, carbonyl, carboxyl groups, and the like.

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Suitable aromatic hydrocarbons may be derived from fractionation or other purification procedures applied to coal, coal tars, or hydrocarbon oil mixtures, produced by conversion and/or solvent extraction, e. g., hydroforming of naphthas, hydrogenation of oils, dehydrogenation of naphthenes such as cyclohexane, methylcyclohexane and the like, coking of hydrocarbon oils, thermal or catalytic cracking of hydrocarbon oils, coal hydrogenation, etc.

A wide variety of higher olefinic hydrocarbons having at least 15 carbon atoms in the molecule may be used as alkylating agents for the purposes of this invention. I may use either pure or mixed olefinic hydrocarbons. Normally I prefer to use a mixture of olefinic hydrocarbons having a relatively restricted molecular weight range. Suitable higher olefinic hydrocarbon feed stocks may be prepared by polymerizing lower molecular weight olefins, especially in the presence of a catalyst, e. g., an aluminum chloride-hydrocarbon complex and hydrogen chloride as described in U. S. patent applications S. N. 510,112 filed by B. L. Evering et al., on November 13, 1943, now U. S. Patent 2,407,873, issued September 17, 1946, and S. N. 466,286, filed by D. E. Burney et al., on November 20, 1942, now U. S. Patent 2,397,945, issued April 9, 1946. Olefinic feed stocks may also be prepared by dehydrating higher molecular weight alcohols having the same number of carbon atoms as that desired in the olefinic hydrocarbon, e. g., myristyl, palmityl, stearyl alcohols and the like, using a variety of catalysts, e. g., alumina, phosphoric acid and acid-acting metal salts, such as NiCl_2 , MgCl_2 , etc. A desirable source of high molecular weight olefins is paraffin wax which may be catalytically dehydrogenated over sixth group metal oxides or cracked in the vapor phase at high temperatures to yield the desired olefins. Numerous other methods of preparing olefins are known and need not be detailed here. Higher olefinic hydrocarbons are applicable in my process regardless of their source or method of manufacture.

I prefer particularly to employ higher olefinic hydrocarbons of straight chain or slightly branched chain structure, e. g., olefins produced by polymerization of a normal olefin hydrocarbon such as ethylene, propylene, butene-1, butene-2, and the like. For purposes of illustration, Table I is included to depict representative fractions of a polymer prepared by polymerizing propylene with an aluminum chloride catalyst.

Table I.—Properties of propylene polymer fractions

Fraction	Boiling Range (5 mm.)	N_D^{20}	Molar Wt. (Calculated From Bromine Number)	Carbon Atoms in the Molecule
	°F.			
1	180-205	1.4457	213	15.2
2	205-230	1.4484	240	17.1
3	230-250	1.4511	261	18.6
4	250-270	1.4520	267	19.1
5	270-290	1.4541	291	20.8
6	290-310	1.4562	302	21.6
7	310-330	1.4578	320	22.8
8	330-350	1.4590	328	23.4
9	350-370	1.4610	348	24.8
10	370-390	1.4623	372	26.6
11	390-410	1.4634	400	28.6

I may use any one or a composite of two or more of the fractions shown in Table I for the alkylation of an aromatic hydrocarbon such as

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benzene to produce alkylates suitable for the manufacture of preferentially oil soluble alkyl aromatic hydrocarbon sulfonates.

In my alkylation process I may feed aromatic hydrocarbons and the higher olefinic hydrocarbon into the alkylation reactor in mol ratios of at least one but preferably two or more, e. g., five or even ten. When the aromatic hydrocarbon is benzene, I prefer to feed it into the alkylation reactor in a mol ratio between about 2 and about 5 with respect to the higher olefinic hydrocarbon.

My preferred catalyst is aluminum chloride and a minor proportion of a hydrogen halide, particularly hydrogen chloride. Ordinarily I use about 0.5 to about 5% by weight of aluminum chloride based on olefin hydrocarbon, preferably about 2 to about 3 weight percent. The hydrogen halide may be used in proportions of about 5 to about 30 weight percent based on $AlCl_3$. My invention may also be effected with other Friedel-Crafts catalysts of the type of aluminum chloride, e. g., BF_3 , HF , and halides, e. g., chlorides, of Fe, Sn, Zn, Be, Cb, Ge, Ti, Zr, and Hf.

Alkylation of aromatics with the higher olefinic hydrocarbons can usually be effected at temperatures in the range of about 0 to about 150° F. The alkylation of benzene can usually be effected at temperatures in the range of about 0 to about 100° F., preferably about 30 to about 90° F. The hydrocarbon reactants are maintained in the liquid phase throughout the reaction. Alkylation may often be effected at atmospheric pressure but higher pressures, e. g., about 50 to 500 p. s. i., may sometimes be necessary or convenient.

The accompanying figure illustrates one embodiment of the process of my invention. As shown, the aromatic hydrocarbon, e. g., benzene, and higher olefinic feed stocks are charged via lines 1 and 2 into an alkylation reactor 4. The lower olefinic hydrocarbon is charged into reactor 4 by line 3. The alkylation reactor is provided with an agitator 5 which may be of conventional design, a valved outlet line 6, a baffle plate 7, and a quiescent zone 8 from which the reaction mixture is led out of the reactor. The aluminum chloride catalyst is introduced into the reactor via valved line 9, e. g., as a slurry in a non-reactive liquid, e. g., a straight chain paraffin hydrocarbon, or the aluminum chloride may be dissolved in an aluminum chloride-hydrocarbon complex produced in the alkylation reaction or in some other reaction and passed into line 9 via line 32. An aluminum chloride-hydrocarbon complex may be produced by agitating granular aluminum chloride with a portion of the lower olefinic hydrocarbon and a minor proportion of HCl at temperatures in the range of about 30 to about 90° F. and the resulting complex may be passed into reactor 4 via lines 47 and 9. The use of a pre-formed aluminum chloride complex with the lower olefinic hydrocarbon tends to reduce the amounts of lower olefinic hydrocarbon which it is necessary to add to the reaction mixture in the alkylation reactor. Hydrogen chloride is passed into the reactor by lines 10 and 11. In the reactor, the catalysts and feed stocks are thoroughly agitated and thereafter are passed through an opening in baffle 7 into the upper quiescent zone 8. Suitable operating conditions in the alkylation reactor are a temperature in the range of about 30 to about 90° F., a pressure in the range of about 0 to about 50 p. s. i. g. and a reaction time between about 5 and about 30 minutes, preferably between about 10 and about 15 minutes.

Products are withdrawn from the reactor by

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valved line 12 and may be passed through a heat exchanger, e. g., cooler 13, to a settler 14. Part or all of the products may by-pass the cooler by employment of valved line 15. The settler is preferably maintained at about the same temperature and pressure as the reactor. Two liquid phases are formed in settler 14; the upper phase contains principally alkylation products and unreacted feed stock, and absorbed hydrogen chloride. The upper liquid phase is removed from settler 14 by valved line 16 into HCl stripper 43.

The lower liquid phase in settler 14 comprises principally a complex of aluminum chloride with hydrocarbons, diluted more or less by absorbed hydrocarbons and possibly containing some dissolved aluminum chloride. This lower liquid phase is removed from the settler through line 23 and is passed into the lower portion of a complex stripper 24. Stripper 24 may be provided with gas-liquid contact devices such as foraminous plates, bubble cap trays, screens, ceramic bodies, and the like. In the stripper, heat is applied to the contents by means of a heating coil 25; alternatively or in addition, the stripper may be heated by the injection of hot inert gas, e. g., methane, ethane, propane, flue gases, or the like. Occluded or absorbed hydrocarbons are vaporized and fractionated in stripper 24 and pass overhead through valved line 26 to line 21 to join the stream of products passing to fractionator 22.

The HCl stripper 43 may suitably be operated at a bottoms temperature in the range of about 200 to about 250° F. and a pressure in the range of about 0 to about 50 p. s. i. g. The gases and vapors pass overhead from stripper 43 into line 44, pass through a cooler 17 and are pumped by pump 45 into the lower portion of an absorber 18. The use of a hydrogen chloride absorber is highly desirable to insure low hydrogen chloride consumption. Absorption and recycle of this stripped hydrogen chloride to the reactor maintains optimum alkylation conditions therein. The absorber may be provided with conventional gas-liquid contact means. In the absorber, the gases and vapors introduced are countercurrently contacted with a liquid medium which serves as a solvent for hydrogen chloride. The liquid absorption medium may be an aluminum chloride-hydrocarbon complex produced in the alkylation process of this invention or in other hydrocarbon conversion operations. Other suitable absorption media are hydrocarbon oils, e. g., mineral seal oil or other absorber oils, a portion of the aromatic feed stock, or by-product, high molecular weight alkylates which may be produced in the alkylation process of this invention. It is preferred to use an absorption medium such as a portion of the aromatic feed stock which takes part in the reaction being effected in reactor 4, since it will not be necessary in such case to provide a stripper (not shown), enriched absorption medium being passed directly into reactor 4 by lines 19 and 11. Suitable operating conditions for the absorber are a temperature in the range of about 30 to about 100° F. and a pressure in the range of about 30 to about 300 p. s. i. g. Unabsorbed gases leave absorber 18 by line 20 and may be subjected to a second absorption operation or be discarded from the system.

Liquid products containing some unreacted materials pass from HCl stripper 43 by line 46 into line 21 and thence to fractionator 22. In fractionator 22, alkylation products and unreacted feed stocks are separated. Light hydrocarbons may be discarded from the fractionator by line

27. Unreacted aromatic hydrocarbons and other materials of similar boiling range may be removed from the fractionator by means of line 28, and may be recycled wholly or in part to reactor 4 (by a line not shown). The desired alkylation product is removed from the fractionator by line 29; it constitutes a highly desirable feed stock for sulfonation to form preferentially oil soluble sulfonates such as "synthetic" mahogany soaps. A relatively small proportion of heavy products may be formed and is removed from the fractionator by valved line 30. The heavy ends may be discarded or all or a fraction thereof may be cycled to absorber 18 to serve as an absorption medium.

Stripped aluminum chloride complex leaves stripper 24 by line 31 and all or a fraction thereof may be cycled to the reactor via valved lines 32 and 9. Line 9 may be provided with mixing devices, e. g., baffles, venturis, etc., to assure thorough admixture of recycled aluminum chloride complex and added aluminum chloride. A fraction of the aluminum chloride complex may be cycled to absorber 18 by valved lines 33 and 34 to serve as an absorption medium therein. When a substantial reduction in the reactivity of the aluminum chloride complex occurs, it may be cycled from the complex stripper to a regeneration system indicated schematically by 35 via valved lines 31 and 33. A suitable aluminum chloride-hydrocarbon complex regeneration system may involve catalytic hydrogenation of the complex, as described in U. S. Patent 2,348,408, of James M. Page, Jr. The regenerated complex may be recycled to reactor 4 by means of lines 36, 37, 32, and 9.

All or part of the catalytically inactive complex may also be passed from stripper 24 to a hydrogen chloride generator 39 by means of valved lines 31 and 38. In the hydrogen chloride generator 39, the aluminum chloride bound in the spent complex is hydrolyzed by reaction with water, steam, aqueous sulfuric acid or other hydrolyzing media introduced by line 41, resulting in the generation of hydrogen chloride which is cycled to the reactor 4 by lines 40, 19, and 11. Non-gaseous products formed in the hydrogen chloride generator include alumina and cokey and liquid hydrocarbons which are withdrawn by line 42 for subsequent treatment which may include filtration or settling, decanting liquid hydrocarbons and fractionation of the liquid hydrocarbons.

The following tabulation sets forth experimental data which are illustrative, but not limitative, of the improved and unexpected results obtainable by my improved alkylation process. The higher olefinic hydrocarbons named as a charging stock in Table II were obtained by polymerizing a petroleum refinery propylene fraction with an aluminum chloride catalyst and had an average molecular weight of about 300 indicating that the average carbon chain length in the polymer was 21.5 carbon atoms; the carbon chain length varied from about 19 to about 23 carbon atoms. A. S. T. M. distillation analysis of the higher olefinic hydrocarbons was as follows:

Percent Distilled	Distillation Temperature, °F.
First drop	530
10	590
50	610
90	640

The maximum distillation temperature of the higher olefinic hydrocarbons was 670° F. The

lower olefinic hydrocarbons set forth as a charging stock in Table II were a light fraction obtained by polymerization of a refinery propylene fraction with aluminum chloride, boiling in the range of about 200 to about 350° F. and containing carbon chains in the range of about C₆ to C₁₂, predominating in C₈ to C₉. The technical amylene set forth as a charging stock in Table II were a mixture of pentenes (Eastman Kodak technical amylenes).

In the experiments reported in Table II, benzene was saturated with HCl gas at room temperature (ca. 80° F.), and powdered AlCl₃ was added with stirring. The polymer was then added to the reaction mixture at such a rate that the reaction temperature could be maintained at 85-90° F. by means of an ice-water bath. Stirring was then continued for the intervals set forth in the table. In experiment 4, the low reaction temperature was maintained with a dry ice-alcohol bath. Addition took a much longer time because of the necessity of maintaining a low temperature.

The courses of the alkylation reactions set forth in Table II were followed by titration of small samples with bromine, samples being taken from the reactor from time to time. The theoretical bromine absorption of the alkylation product is, of course, zero, using bromination conditions which are selective for an olefin double bond.

Table II.—Alkylation of benzene

Experiment	1	2	3	4
Charge				
Volume of higher olefinic hydrocarbons, ml.	250	250	250	250
Weight of higher olefinic hydrocarbons, g.	206	206	206	206
Volume of lower olefinic hydrocarbons, ml.		10		10
Volume of technical amylene, ml.			10	
Volume of benzene (saturated with HCl at room temperature), ml.	200	200	200	200
Weight AlCl ₃ , g.	6	6	6	6
Time for polymer addition, min.	5	8	5	35
Reaction temperature, ° F.	85-90	85-90	85-90	42-45
Unsaturation in alkylation mixture (ml. 0.5 Br/ml. soln.) initial	4.17	4.20	4.23	4.20
After 10 minutes stirring	1.38	0.18	1.10	0.07
After 15 minutes stirring				
After 20 minutes stirring		0.0	1.20	
After 25 minutes stirring	1.02			
After 30 minutes stirring			0.12	
After 40 minutes stirring	0.67		0.04	
After 60 minutes stirring	0.65			

¹ HCl gas bubbled through reaction mixture for about 2 minutes to assure saturation.

It will be observed from the data of Table II that in experiment 1, alkylation was only 84% complete after one hour, while in experiment 2, identical except for the inclusion of 4% of lower olefinic hydrocarbons, 96% alkylation was achieved in 10 minutes and 100% alkylation in less than 20 minutes. Experiment 3 indicates that amylene are satisfactory promoters for the alkylation reaction, provided that care is taken to keep the alkylation reaction mixture saturated with HCl gas. Experiment 4 indicates that the alkylation may be effected satisfactorily at a low temperature and with a short reaction period when a lower olefinic hydrocarbon is employed to promote the reaction. The ability to alkylate satisfactorily at low temperatures is important, since, as previously mentioned, cracking of the higher molecular weight olefin and alkylates is avoided with consequent increase in the yield of desired alkylation product. Reduction in the extent of cracking in the alkylation reaction also reduces the required fractionation capacity of the alkylation plant.

It will be apparent that I have provided a novel and improved process for the alkylation of aromatic hydrocarbons, particularly to produce higher alkyl aromatic hydrocarbons suitable for the sulfonation to form oil soluble or preferentially oil soluble sulfonates.

I claim:

1. In the alkylation of an aromatic hydrocarbon with a higher mono-olefin hydrocarbon having at least 20 carbon atoms in the molecule in the presence of a Friedel-Crafts catalyst, the improvement which comprises effecting said alkylation in the presence of a minor proportion, based on said higher mono-olefin hydrocarbon, of an added lower olefinic hydrocarbon having a molecular weight not in excess of about 130.

2. The process of claim 1 wherein the higher mono-olefin hydrocarbon is prepared by polymerization of a normal mono-olefin hydrocarbon.

3. The process of claim 1 wherein the aromatic hydrocarbon is benzene.

4. The process of claim 1 wherein the aromatic hydrocarbon is a monocyclic hydrocarbon and the Friedel-Crafts catalyst is aluminum chloride, promoted by a minor proportion of hydrogen chloride.

5. In the alkylation of benzene with a polymer of a normal mono-olefin hydrocarbon, said polymer having at least 20 carbon atoms in the molecule in the presence of aluminum chloride and a minor proportion of hydrogen chloride, the improvement which comprises effecting said alkylation in the presence of a minor proportion, not in excess of about 10% based on said polymer, of a pentene.

6. In the alkylation of benzene with a polymer of a normal mono-olefin hydrocarbon, said polymer having at least 20 carbon atoms in the molecule in the presence of aluminum chloride and a minor proportion of hydrogen chloride, the improvement which comprises effecting said alkylation in the presence of a minor proportion not in excess of about 10%, based on said polymer, of an added propylene polymer having a molecular weight not in excess of about 130.

7. In the alkylation of a monocyclic aromatic hydrocarbon with a mono-olefin polymer having at least 20 carbon atoms in the molecule in the presence of aluminum chloride and a minor proportion of hydrogen chloride at a temperature in the range of about 0 to about 150° F. under a pressure sufficient at least to maintain the liquid phase, the improvement which comprises effecting said alkylation in the presence of a minor proportion not in excess of about 10% based on said mono-olefin polymer, of an added lower mono-olefin hydrocarbon having a molecular weight not in excess of about 130.

8. In the alkylation of benzene with a propylene polymer having at least 20 carbon atoms in the molecule in the presence of aluminum chloride and a minor proportion of hydrogen chloride at a temperature in the range of about 0 to about 100° F. under a pressure sufficient at least to maintain the liquid phase, the improvement which comprises effecting said alkylation in the presence of a minor proportion not in excess of about 10% based on said propylene polymer, of an added lower propylene polymer having a molecular weight not in excess of about 130.

9. In the alkylation of benzene with a propylene polymer having at least 20 carbon atoms in the molecule in the presence of aluminum chloride and a minor proportion of hydrogen chloride at a temperature in the range of about 0 to about 100° F. under a pressure sufficient at least to maintain the liquid phase, the improvement which comprises effecting said alkylation in the presence of a minor proportion not in excess of about 10%, based on said propylene polymer, of a pentene.

10. In the alkylation of an aromatic hydrocarbon with a propylene polymer having at least 20 carbon atoms in the molecule in the presence of a Friedel-Crafts catalyst, the improvement which comprises effecting said alkylation in the presence of a minor proportion, based on said propylene polymer, of an added lower mono-olefin hydrocarbon having a molecular weight not in excess of about 130.

11. In the alkylation of a monocyclic aromatic hydrocarbon with a polymer of a normal mono-olefin hydrocarbon, said polymer having at least about 20 carbon atoms in the molecule in the presence of a Friedel-Crafts catalyst, the improvement which comprises effecting said alkylation in the presence of a minor proportion, not in excess of about 10 per cent based on said polymer, of an added lower mono-olefin hydrocarbon having a molecular weight not in excess of about 130.

12. The process of claim 11 wherein the Friedel-Crafts catalyst is aluminum chloride promoted by a minor proportion of hydrogen chloride.

PHILIP HILL.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,232,118	Kyrides	Feb. 18, 1941
2,378,733	Sensel	June 19, 1945

Certificate of Correction

Patent No. 2,437,356.

March 9, 1948.

PHILIP HILL

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Column 1, line 5, for the word "who" read *whose*; column 2, line 33, for "i. e." read *e. g.*; column 8, line 45, Table 2, first column thereof, for "(ml. 0.5 Br₂/ml. soln.)" read *(ml. 0.5 N Br₂/ml. soln.)*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 27th day of April, A. D. 1948.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.