

UNITED STATES PATENT OFFICE

2,267,725

METHOD OF PRODUCING ALKYL AROMATIC COMPOUNDS

Lawrence H. Flett, Hamburg, N. Y., assignor to
National Aniline & Chemical Company, Inc.,
New York, N. Y., a corporation of New York

No Drawing. Application February 21, 1939,
Serial No. 257,720

15 Claims. (Cl. 260—505)

This invention relates to improvements in the method of producing alkyl aromatic compounds which includes condensing halogenated non-aromatic hydrocarbons with an aromatic hydrocarbon or derivative capable of undergoing condensation with an alkyl halide. (The term "non-aromatic hydrocarbons" is employed herein in the generic sense, including acyclic aliphatic hydrocarbons and cyclic aliphatic hydrocarbons.) It relates more particularly to improvements in the method of producing alkyl aromatic compounds which includes chlorinating a non-aromatic hydrocarbon mixture and condensing a resulting mixture of alkyl chlorides with an aromatic hydrocarbon or derivative capable of undergoing condensation with an alkyl chloride. It relates especially to improvements in the method of producing mixtures of alkyl aromatic compounds which are adapted to form sulfonated derivatives that are useful as detergents which method includes the steps of chlorinating non-aromatic petroleum hydrocarbons and condensing a resulting mixture of alkyl chlorides with an aromatic compound of the benzene series in the presence of a metal halide condensing agent.

An object of the present invention is to provide improvements in the above methods whereby improved yields are obtained of the alkyl aromatic compounds.

Another object of the invention is to provide improvements in the above methods whereby improvements in the yield and quality of sulfonated alkyl aromatic compounds are obtained upon sulfonation of the alkyl aromatic compounds.

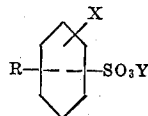
An additional object of the invention is to provide improvements in the method of producing sulfonated alkyl aromatic compounds of the benzene series, particularly adapted for use as detergents and surface active agents which includes the steps of chlorinating a non-aromatic petroleum hydrocarbon mixture, condensing the resulting chlorinated hydrocarbon mixture with an aromatic hydrocarbon or phenol of the benzene series in the presence of a metal halide condensing agent, and sulfonating a resulting mixture of alkyl aromatic compounds, whereby improvements are obtained in the yield and quality of the alkyl aromatic sulfonates.

A further object of the invention is to provide improvements in the method of producing alkyl

aromatic hydrocarbons and derivatives, particularly adapted for the production of detergents by sulfonation, by condensation of benzene or its derivatives capable of undergoing condensation, in the presence of a metal halide condensing agent of the Friedel and Crafts type, with a mixture of alkyl chlorides resulting from the chlorination of petroleum hydrocarbon mixtures of the kerosene type, whereby improvements are obtained in the yield of said alkyl aromatic hydrocarbons and derivatives.

Other objects of the invention in part will be obvious and in part will appear hereinafter.

It has heretofore been proposed to produce sulfonated higher alkylated aromatic compounds which are of particular value for use as detergents in aqueous media, as well as wetting agents, penetrating agents, emulsifying agents, and surface active agents in general, by chlorinating a non-aromatic hydrocarbon mixture of the type of kerosene, "white oil," and the like, condensing a resulting mixture of alkyl chlorides with benzene, toluene, xylene, naphthalene, phenol, cresol, resorcinol, naphthol, anisole, phenetole, chlorobenzene, benzyl benzene, diphenyl, hydroxy diphenyl, benzoic acid, diphenyl oxide and related unsulfonated aromatic compounds, with the aid of aluminum chloride or other condensing agent of the Friedel and Crafts type, and sulfonating the resulting alkyl aromatic compound. Thus, it has heretofore been proposed to produce in this way compounds of the type represented by the general formula



wherein R represents an alkyl, cycloalkyl, aralkyl, alkaryl or similar group derivable from a petroleum fraction and containing at least 7 carbon atoms; X represents a replaceable hydrogen atom or an equivalent thereof, such as halogen, hydroxyl, alkoxy, phenyl, hydroxyphenyl, phenoxy; and Y represents hydrogen or a salt-forming metal or radical, such as sodium, potassium, ammonium, alkyl ammonium, hydroxyalkyl ammonium, and the like. In my application Serial No. 737,777, filed July 31, 1934, products of this type derived from phenols are disclosed. In my ap-

plication Serial No. 93,521, filed July 30, 1936, products of this type derived from various other aromatic compounds are disclosed.

As is well known in the art, petroleum distillates are mainly mixtures of non-aromatic hydrocarbons, including both saturated acyclic aliphatic hydrocarbons (containing straight or branched carbon chains) and cyclic aliphatic hydrocarbons, as well as some unsaturated aliphatic hydrocarbons, depending upon the source of the petroleum and the method of distillation and/or purification. When the petroleum distillates are halogenated in the preparation of alkyl aromatic sulfonates, mixtures of various halogenated derivatives of the said aliphatic hydrocarbons are produced (which are generically referred to herein as "alkyl halides"), and the said mixtures of alkyl halides, when condensed with aromatic compounds, produce mixtures of alkyl aromatic compounds in which the alkyl groups correspond with aliphatic hydrocarbons of the petroleum distillate from which they were produced. Accordingly, when the mixtures of alkyl aromatic compounds are sulfonated, compositions are produced which contain mixtures of sulfonated alkyl aromatic compounds differing from each other in the alkyl groups, which groups correspond with the aliphatic hydrocarbons of the mixture employed.

Owing to the diverse nature of the non-aromatic hydrocarbons in petroleum distillates and their different degrees of reactivity to chlorine, mixtures of various chlorinated non-aromatic hydrocarbons are obtained as a result of their reaction with chlorine, and when the mixtures of chlorinated hydrocarbons are reacted with an aromatic compound, such as benzene or phenol or the like, in the presence of a condensing agent of the Friedel and Crafts type, for the production of alkyl benzenes or alkyl phenols or the like, the resulting condensation products are mixtures of compounds not all of which, when subjected to sulfonation (for example, with 100 per cent sulfuric acid or oleum), result in sulfonated alkyl aromatic compounds useful as detergents and surface active agents in aqueous media.

According to the present invention, the condensation of the aromatic compound with the mixture of chlorinated non-aromatic hydrocarbons is carried out with a weight of the aromatic compound in excess of the weight of the mixture of chlorinated non-aromatic hydrocarbons, more particularly with a weight of the aromatic compound at least one and one-fourth times the weight of the mixture of chlorinated non-aromatic hydrocarbons, and preferably with a weight of the aromatic compound which is one and one-half to two times the weight of the chlorinated non-aromatic hydrocarbon mixture.

The present invention is based on the discovery that markedly higher yields are obtained of alkyl aromatic compounds which are adapted on sulfonation to produce valuable marketable agents in the form of mixtures of alkyl aromatic sulfonates of the type hereinbefore defined, and which are derivable from any specific type of non-aromatic hydrocarbon mixture (for example, a kerosene or a kerosene distillate) by chlorinating the hydrocarbon mixture, admixing the chlorinated hydrocarbon mixture with the aromatic compound, and heating the admixture at a condensation temperature in the presence of a metal halide condensing agent, when the amount by weight of the aromatic compound

employed is greater than the amount by weight of the chlorinated hydrocarbon mixture.

Thus I have found, in accordance with the present invention, when the chlorination reaction mixture resulting from the chlorination of a petroleum distillate such as kerosene or a kerosene distillate is heated with at least one and one-fourth times its weight of benzene, phenol, or other aromatic compound of the type above referred to, in the presence of aluminum chloride, zinc chloride or other metal halide condensing agent of the Friedel and Crafts type, a product is obtained which contains a considerably higher yield of desirable alkyl aromatic compounds, as is evident in the higher amount of alkyl aromatic sulfonates obtained finally from such condensation products, as compared with the condensation products resulting from the use of an amount by weight of the aromatic compound less than the weight of the chlorination reaction mixture.

This result is surprising inasmuch as according to British Patent No. 364,537 the wetting and dispersing properties of products obtained by treating aromatic hydrocarbons or their derivatives with aliphatic alcohols containing at least three carbon atoms in such proportion that, for each molecule of the hydrocarbon, more than 2.2 mols of the alcohols come into operation are superior as compared with the properties of the products made with a lesser amount of the alcohol. The weights of alkyl chlorides employed in accordance with the present invention represent only a fraction of 1 mol per mol of aromatic compound.

The fact that the use of the preferred amounts of aromatic compound in the condensation of chlorinated kerosenes and related chlorinated hydrocarbon mixtures with benzene and related aromatic compounds, in accordance with the present invention, leads to increased yields of sulfonatable products is of special importance in connection with the production of detergents from the alkyl benzenes and other alkyl aromatic compounds by sulfonation. The preparation of detergents such as keryl benzene sulfonates from chlorinated kerosene fractions involves the difficulty of excluding much unreacted kerosene-like (unsulfonated) products from the keryl benzene sulfonate. The chlorinated kerosene mixture always contains unchlorinated hydrocarbon which cannot be separated profitably from the chlorinated hydrocarbons. When the crude chlorinated kerosene mixture is condensed with the aromatic compound, for example, benzene, to form the keryl-aryl mixture, the unchlorinated kerosene portion remains unreacted, and is not removable by simple stripping and/or distillation, without excessive losses, because the said kerosene boils over a range which overlaps that of the keryl aryl mixture. It is therefore present after the sulfonating step, through which it passes apparently unchanged. Accordingly, as the yield of keryl benzene sulfonate from a given amount of crude chlorinated kerosene is increased (all conditions of preparation being constant) the proportion of residual unsulfonatable material remaining associated with the keryl aryl sulfonate is proportionately decreased, and the amount which must be removed if the keryl aryl sulfonate is to function as a detergent is also proportionately decreased. Thus I have found, in accordance with the present invention, a greatly increased yield is obtained of alkyl benzene sulfonates which, in the form of their

sodium salts, are excellent detergents and surface active agents in aqueous media, when a petroleum distillate of the kerosene type is chlorinated, the resulting chlorinated hydrocarbon mixture is reacted with at least one and one-fourth times its weight of benzene in the presence of a small amount of anhydrous aluminum chloride as a condensing agent, the resulting condensation product is distilled to separate from lower boiling and higher boiling unreacted constituents and by-products, a middle fraction comprising chiefly the desired alkyl benzenes and the mixture of alkyl benzenes is sulfonated, as compared with the yield obtained when a weight of benzene less than the weight of the chlorinated hydrocarbon mixture is employed under the same conditions.

The invention will be illustrated by the following examples. It will be realized by those skilled in the art that the invention is not limited thereto except as indicated in the appended patent claims. The parts are by weight, the temperatures are in degrees centigrade and the pressure is atmospheric, unless otherwise indicated.

EXAMPLE 1.—1000 parts of a kerosene fraction of Pennsylvania petroleum boiling over the range 186° to 291°, with 80 per cent of the distillate boiling between 200° and about 265°, were filtered into a closed nickel-clad vessel fitted with a nickel agitator. 0.4 part of iodine was dissolved in the agitated kerosene fraction. Chlorine gas, filtered through a porous earthenware plate, was run at the rate of about 3 parts per minute into the liquid charge at a temperature of 55° to 60° until the specific gravity of the kerosene had increased from about 0.790 to 0.920. This chlorination period was about 2 hours.

1000 parts of benzene and 25 parts of anhydrous aluminum chloride were charged into a glass flask fitted with a glass agitator. 500 parts of the chlorinated kerosene were then run in with agitation during the course of 20 minutes, the temperature being about 30°. The agitated mixture in the flask was heated to 45° and maintained at that temperature for about 1½ hours. The reaction mass was transferred to a separatory funnel and tar was allowed to separate from the crude alkyl benzene for at least two hours. The lower, tar layer was withdrawn and discarded.

The crude alkyl benzene contained considerable free benzene, which was removed by stripping the crude alkyl benzene first to 100°–105° at atmospheric pressure and then in vacuo to 85° at 30–40 mm. absolute pressure. The residual material weighing about 450 parts was distilled at 4 mm. pressure. The first distillate from about 7 per cent of the distilland was removed and consisted mainly of kerosene. The distillation was then continued and the distillate obtained from that point until the boiling point of the distilland was 234° at 4 mm. was collected as alkyl benzene.

100 parts of the resulting alkyl benzene distillate were agitated for 45 minutes with 19 parts of 100 per cent sulfuric acid; the mix was allowed to settle for 15 minutes and the acid layer was withdrawn.

The acid treated alkyl benzene was then treated with 120 parts of 100 per cent sulfuric acid in a glass vessel. After agitating without warming for 15 minutes, the temperature of the mixture was raised to 55 to 60° and held there with continued agitation for 1 hour. The sulfonation mixture was allowed to settle for 1 hour. Three distinct layers were formed. The middle, sul-

fonic acid layer was separated from the other layers and drowned in 500 parts of water containing 100 parts of cracked ice, the drowned mass was neutralized with 50 per cent aqueous caustic soda, and dried on a rotary drum drier.

EXAMPLE 2.—10,620 lbs. Pennsylvania kerosene (having a specific gravity of 0.788 at 24° and boiling range 185° to 275°) were filtered through porous stoneware into a lead-lined kettle fitted with lead-covered agitator, thermometer well and other accessories. 4.4 pounds of iodine were dissolved in the agitated kerosene charge which was then warmed to about 60° and maintained between 60° and 70° while chlorine gas, also filtered through porous stoneware, was passed into the liquid at an average rate of about 300 pounds per hour, until the specific gravity of the chlorinated kerosene was 0.918 at 24°, corresponding with 115 per cent monochlorination of the kerosene. The amount of chlorine required for the purpose was about 4825 lbs. The final chlorinated kerosene mixture weighed 12,834 lbs. The chlorinated hydrocarbon thus obtained was condensed in portions with benzene as follows:

A mixture of 13,272 lbs. of benzene and 332 lbs. of anhydrous aluminum chloride was agitated and 6636 lbs. of the chlorinated kerosene mixture were added thereto over a period of three hours, during which the temperature of the mass rose to about 35°. The mixture was then heated to 45° and held there for about 1½ hours. Agitation was then stopped, the mixture was allowed to stand for about 2 hours; thereafter the lower tarry layer was withdrawn. The upper layer was conveyed to a stripping kettle in which the liquid was stripped of low-boiling hydrocarbons, chiefly benzene, by boiling the liquid until its temperature reached 150° at atmospheric pressure, then reducing the pressure in the distilling system to a pressure of 3 to 4 inches of mercury absolute pressure and continuing the boiling without further supply of heat for about one hour, until the temperature of the distilland was about 120°. The material left after this stripping was distilled in vacuo until about 7 per cent of the charge in the still had been removed as distillate. The remaining distilland was distilled, and distillate therefrom was collected separately until the boiling point of the distilland was 250° at 14 mm. mercury pressure. This last distillate was chiefly the condensation product of the chlorinated hydrocarbons of the kerosene fraction and the benzene; and for convenience it is called "kerylbenzene."

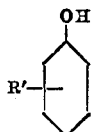
The kerylbenzene was treated with 100 per cent sulfuric acid by mixing it with about 15 per cent of its weight of the acid and agitating the mixture for about 1 hour at about 40°. The mixture was allowed to stand about ½ hour to permit separation of the acid, which constituted the lower layer and was withdrawn.

The upper acid-treated layer of kerylbenzene was mixed with about 1.25 times its weight of 100 per cent sulfuric acid at a temperature between 30° and 35°. The mixture was then warmed to 55° and agitated at that temperature for 1 hour. It was then allowed to stand for 2 hours during which time three layers of material separated. The top layer was chiefly unsulfonated material; the middle layer was chiefly sulfonated kerylbenzene; and the bottom layer was spent sulfuric acid. The middle layer was separated from the others; drowned in ice water; neutralized with caustic soda (aqueous solution), and dried on a rotary drum drier.

EXAMPLE 3.—Part 1.—Chlorine is passed into

4C) parts of a kerosene boiling from about 195° to about 300° (and boiling for the most part from about 225° to 275°), having a specific gravity of 0.799 at 24°, containing about 5.6 per cent of unsaturated hydrocarbons, and having a probable carbon content ranging from 11 to 18 carbon atoms and a probable average content of about 13.4 carbon atoms, at 50° in diffused light until there is an increase of weight of 111 parts, 2 parts of which are due to dissolved hydrogen chloride. The resulting product comprises unchlorinated hydrocarbon in admixture with mono-, di- and polychlorinated hydrocarbons, the average chlorine content of the mixture being equivalent to about one and one-half atoms of chlorine per molecule of hydrocarbon having the stated carbon content.

Part 2.—150 parts of the chlorinated mixture produced in Part 1 of this example are slowly added to an agitated mixture of 200 parts of phenol and 5 parts of anhydrous zinc chloride at 75°, and the temperature is maintained at 75° for about 30 minutes after all the chlorinated mixture has been added. The temperature of the mixture is then raised and maintained at 135° for 2.5 hours. 5 parts of zinc dust are then added, and after one hour another 5 parts of zinc dust are added, the temperature being maintained during this addition, and for about 3 hours afterward, at 135°. The reaction mixture is cooled, treated with water, and the oil is separated from the water and residual zinc dust and fractionally distilled. The fraction boiling from 140° to 250° at 4 mm. pressure is separately collected. The product, which is an oil showing fluorescence under ultra-violet light, insoluble in water, soluble in alcohol, gasoline, and other organic solvents, is comprised mainly of a mixture of alkyl phenols which may be represented by the general formula:



in which R' is a primary, secondary or tertiary alkyl group which for the most part is probably in the para-position to the hydroxyl group.

EXAMPLE 4.—Part 1.—A crude chlorinated hydrocarbon mixture is prepared by chlorinating at 50°, in a lead-lined vessel, a kerosene of the type employed in Example 3, until the reaction mixture reaches a specific gravity of 0.91.

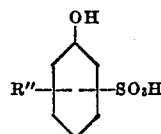
Part 2.—150 parts of the product of Part 1 of this example is reacted with 200 parts of phenol as described in Example 3. The crude alkyl phenol product is washed with water and distilled in vacuo. The fraction distilling from 140° to 240° at 3 mm. pressure is separately collected. It comprises a mixture of alkyl phenols in which the alkyl groups correspond with the hydrocarbons of the kerosene, being probably for the main part saturated alkyl hydrocarbon groups.

Part 3.—The crude oil obtained in Part 2 of this example is fractionally distilled in vacuo and the distillate boiling from 175° to 225° at 4 mm. pressure is separately collected. To 25 parts of this distillate, under agitation and maintained at a temperature of 30°, there is slowly added 11.6 parts of chlorsulfonic acid. The mixture is agitated for 15 minutes after all of the chlorsulfonic acid has been added. The tem-

perature of the mixture is then raised and held at 70° for 15 minutes. The mixture is then drowned in 250 parts of water, the solution is made neutral to Brilliant Yellow and Congo Red papers by addition of caustic soda thereto, and evaporated to dryness on a double drum drier. The resulting product comprises the sodium salts of a mixture of alkyl phenol sulfonic acids in which the alkyl groups are mainly saturated aliphatic hydrocarbons. It is a light colored to white powder substantially free (less than 4 per cent) of inorganic salts.

EXAMPLE 5.—10 parts of the alkyl phenol mixture obtained in Example 4, Part 2, are stirred and thereto 10 parts of sulfuric acid monohydrate (100 per cent sulfuric acid) are added slowly so that the temperature of the reaction mixture does not exceed about 30° to 35°. The sulfonation mixture is then warmed to 40° and held at that temperature until a sample is completely soluble in neutral, acid and alkaline water, and/or does not precipitate calcium salts from a calcium chloride solution containing the equivalent of 0.224 gram calcium oxide per liter (30 to 90 minutes). The solution is sometimes slightly turbid due to the presence of insoluble impurities. The sulfonation mass is then diluted with water to about 100 parts by weight and neutralized with sodium or potassium hydroxide, or their equivalents. The neutral solution of sulfonates is filtered and evaporated to dryness.

The final product is a mixture of sodium (or potassium, etc.) salts of alkyl phenol sulfonic acids which in the free state correspond with the general formula



in which R'' is a primary, secondary or tertiary alkyl group. The alkyl group is probably para, and the sulfonic acid group is probably ortho to the hydroxyl group.

The following tables set out representative comparative results obtained in accordance with the procedure set out in above Example 2. Each series was made from a separate composite mixture of several lots of uniformly chlorinated kerosene. In each preparation the chlorinated kerosene was condensed with benzene by means of aluminum chloride, the condensation mass was stripped of excess benzene and low boiling material, the distilled product was sulfonated with sulfuric acid, neutralized, and evaporated to dryness. The amount of keryl benzene sulfonate in the final product was ascertained by extracting the dry product with alcohol and evaporating off the alcohol from the extract. All of the experiments set out in one table were conducted under the same conditions and with the same amounts of reagents, except as indicated in the table. All amounts in the tables are on the basis of 100 parts by weight of the chlorkerosene. As noted from the above examples, the chlorkerosene contained unchlorinated, monochlorinated and polychlorinated hydrocarbons. In carrying out the sulfonations set out in Tables I and II, the amount of sulfuric acid employed for the two sets of experiments was somewhat different (being based on the amount of sulfonatable products found by analysis to be present in the keryl benzene product). As above

noted, however, the same amount of sulfuric acid was employed for all experiments of one table.

Table I

Parts benzene in condensation	Yield, parts of distillate of keryl benzene	Yield, parts of pure sodium keryl benzene sulfonate
75.....	69.2	43.8
100.....	69.8	44.6
125.....	72.7	50.1
150.....	74.5	50.8
175.....	73.2	54.0
200.....	74.7	54.6
300.....	76.8	57.4
400.....	78.9	59.3
500.....	78.6	60.7

Table II

Parts benzene in condensation	Yield, parts of distillate of keryl benzene	Yield, parts of sodium keryl benzene sulfonate
75.....	63.6	47.4
100.....	65.3	49.5
125.....	73.1	59.8
175.....	71.5	59.7
200.....	73.7	60.7
300.....	76.7	67.3
400.....	74.5	68.7
500.....	73.1	67.9

Table III

Parts of benzene in condensation	Yield, parts of distillate of keryl benzene	Parts of 100% sulfuric acid used for sulfonation	Yield, parts of sodium keryl benzene sulfonate
100.....	79.4	126	45.7
150.....	81.4	139	52.4
200.....	82	150	56.8

It will be realized by those skilled in the art that changes may be made in the processes hereinbefore described without departing from the scope of the invention.

The non-aromatic hydrocarbon mixtures which are useful in connection with the present invention are the petroleum hydrocarbon mixtures containing hydrocarbons having 7 or more carbon atoms, particularly those having not less than 10 carbon atoms and not more than 30 carbon atoms per molecule; the mixtures which consist of hydrocarbons having not less than 10 and not more than 23 carbon atoms, and especially those consisting of not less than 12 nor more than 16 carbon atoms per molecule are preferred. The preferred non-aromatic hydrocarbon mixtures employed in accordance with the present invention are exemplified by fractions of Pennsylvania and Michigan (Mount Pleasant) petroleum distillates, and especially the kerosene fractions of said distillates. These distillates consist essentially of open chain aliphatic (paraffinic) hydrocarbons of which a large portion have probably relatively long carbon chains rather than more condensed molecules. Such distillates will be referred to as "of the Pennsylvania type", whether derived from natural sources or derived by processing or by purification of less favorable distillates from other sources.

The extent to which the non-aromatic hydrocarbons may be halogenated may vary. In general, halogenation of a petroleum hydrocarbon mixture may be carried out to an extent corresponding with a product containing a ratio of about $\frac{1}{4}$ to $2\frac{1}{2}$ atoms of halogen per molecule

of petroleum hydrocarbon. Preferably the halogenation of the non-aromatic hydrocarbon mixture is carried out to an extent such that the resulting halogenation reaction mixture contains an amount of organically combined halogen substantially corresponding with 75 per cent to 175 per cent complete monohalogenation of the original non-aromatic hydrocarbon mixture.

The halogenation of the non-aromatic hydrocarbon mixtures may be carried out by any well known process. The approximate extent of halogenation may be determined by the increase in the weight of the hydrocarbon material halogenated or by the increase in the specific gravity of the mixture. Instead of chlorine, other halogens may be employed in the processes of the above examples, e. g., bromine, etc.

Various chlorination temperatures may be employed, for example, temperatures within the range 0° to 75° C., and preferably in the neighborhood of 50° to 60° C. The chlorination may be carried out with the aid of chlorine carriers, catalysts or adjuvants; as for example, phosphorus trichloride, iodine, sunlight, etc.

In carrying out the condensation of the mixed alkyl halides with the aromatic compound and the further treatment of the alkyl aromatic compounds for the production of the desired sulfonated products, the reagents, methods and conditions of treatment may be varied. For example, there may be used those described in my copending applications Serial No. 737,777, filed July 31, 1934, and Serial No. 93,521, filed July 30, 1936, of which this application is a continuation-in-part, as well as my copending applications Serial No. 186,231, filed January 21, 1938; Serial No. 186,733, filed January 24, 1938; Serial No. 195,414, filed March 11, 1938; and Serial No. 257,719, filed of even date herewith.

I claim:

1. In the production of an alkyl aromatic compound which is adapted to be converted by sulfonation to an alkyl aromatic sulfonate useful as a detergent, by a process which comprises halogenating a non-aromatic hydrocarbon mixture containing at least 7 carbon atoms per molecule and condensing a resulting mixture of alkyl halides with an aromatic compound to produce a mixture of alkyl aromatic compounds, the improvement which comprises carrying out the condensation with a weight of the aromatic compound in excess of the weight of alkyl halide mixture.

2. In the production of an alkyl aromatic compound which is adapted to be converted by sulfonation to an alkyl aromatic sulfonate useful as a detergent, by a process which comprises chlorinating a petroleum distillate containing at least 10 carbon atoms per molecule of hydrocarbon and condensing a resulting mixture of alkyl chlorides with an aromatic compound in the presence of a metal halide condensing agent to produce a mixture of alkyl aromatic compounds, the improvement which comprises carrying out the condensation with at least one and one-fourth parts of an aromatic compound of the benzene series per part by weight of alkyl chloride mixture.

3. In the production of an alkyl aromatic compound which is adapted to be converted by sulfonation to an alkyl aromatic sulfonate useful as a detergent, by a process which comprises chlorinating a non-aromatic petroleum hydrocarbon mixture containing about 10 to about 30 carbon atoms per molecule, and condensing a resulting mixture of alkyl chlorides with an aromatic com-

pound in the presence of a metal halide condensing agent to produce a mixture of alkyl aromatic compounds, the improvement which comprises carrying out the condensation with one and one-half to two parts of the aromatic compound per part by weight of the alkyl chloride mixture.

4. In the production of an alkyl aromatic compound which is adapted to be converted by sulfonation to an alkyl aromatic sulfonate useful as a detergent, by a process which comprises chlorinating a non-aromatic hydrocarbon mixture and condensing a resulting mixture of alkyl chlorides with an aromatic compound to produce a mixture of alkyl aromatic compounds, the improvement which comprises chlorinating a mixture of non-aromatic hydrocarbons containing at least 7 carbon atoms per molecule, admixing the resulting chlorination reaction mixture with an amount by weight of the aromatic compound in excess of the weight of the resulting chlorination reaction mixture, and heating the admixture at a condensation temperature in the presence of a metal halide condensing agent.

5. In the production of an alkyl aromatic compound which is adapted to be converted by sulfonation to an alkyl aromatic sulfonate useful as a detergent, by a process which comprises chlorinating a non-aromatic hydrocarbon mixture and condensing a resulting mixture of alkyl chlorides with an aromatic compound to produce a mixture of alkyl aromatic compounds, the improvement which comprises chlorinating a petroleum distillate containing at least 10 carbon atoms per molecule of hydrocarbon, admixing the resulting chlorination reaction mixture with an amount by weight of an aromatic compound of the benzene series in excess of the weight of the resulting chlorination reaction mixture, and heating the admixture at a condensation temperature in the presence of a metal halide condensing agent.

6. In the production of an alkyl aromatic sulfonate useful as a detergent, by a process which comprises chlorinating a non-aromatic hydrocarbon mixture and condensing a resulting mixture of alkyl chlorides with an aromatic compound to produce a mixture of alkyl aromatic compounds, the improvement which comprises chlorinating a non-aromatic petroleum hydrocarbon mixture containing about 10 to about 30 carbon atoms per molecule, admixing the resulting chlorination reaction mixture with an amount by weight of the aromatic compound at least one and one-fourth times the weight of the resulting chlorination reaction mixture, and heating the admixture at a condensation temperature in the presence of a metal halide condensing agent.

7. In the production of an alkyl aromatic compound which is adapted to be converted by sulfonation to an alkyl aromatic sulfonate useful as a detergent, by a process which comprises chlorinating a non-aromatic hydrocarbon mixture and condensing a resulting mixture of alkyl chlorides with an aromatic compound to produce a mixture of alkyl aromatic compounds, the improvement which comprises chlorinating a petroleum hydrocarbon mixture containing about 10 to about 30 carbon atoms per molecule, admixing the resulting chlorination reaction mixture with one and one-half to two times its weight of an aromatic compound of the benzene series, and heating the admixture at a condensation temperature in the presence of a metal halide condensing agent.

8. In the production of an alkyl aromatic com-

pound which is adapted to be converted by sulfonation to an alkyl aromatic sulfonate useful as a detergent, by a process which comprises chlorinating a non-aromatic hydrocarbon mixture and condensing a resulting mixture of alkyl chlorides with an aromatic compound to produce a mixture of alkyl aromatic compounds, the improvement which comprises chlorinating a petroleum hydrocarbon distillate of the Pennsylvania type containing 10 to 23 carbon atoms per molecule of hydrocarbon, admixing the resulting chlorination reaction mixture with a benzene hydrocarbon and aluminum chloride, the weight of benzene hydrocarbon being at least one and one-fourth times the weight of the chlorination reaction mixture, and heating the resulting admixture to effect condensation of alkyl chlorides with the benzene hydrocarbon.

9. In the production of an alkyl aromatic compound which is adapted to be converted by sulfonation to an alkyl aromatic sulfonate useful as a detergent, by a process which comprises chlorinating a non-aromatic hydrocarbon mixture and condensing a resulting mixture of alkyl chlorides with an aromatic compound to produce a mixture of alkyl aromatic compounds, the improvement which comprises chlorinating a petroleum hydrocarbon distillate of the Pennsylvania type containing about 12 to about 16 carbon atoms per molecule, admixing the resulting chlorination reaction mixture with an amount by weight of benzene from one and one-half to two times the weight of the resulting chlorination reaction mixture, and heating the admixture at a condensation temperature in the presence of aluminum chloride as a condensing agent.

10. In the production of an alkyl aromatic compound which is adapted to be converted by sulfonation to an alkyl aromatic sulfonate useful as a detergent, by a process which comprises chlorinating a non-aromatic hydrocarbon mixture, condensing a resulting mixture of alkyl chlorides with an aromatic compound to produce a mixture of alkyl aromatic compounds, and separating a mixture of alkyl aromatic compounds from higher-boiling by-products by distillation, the improvement which comprises chlorinating a mixture of non-aromatic hydrocarbons containing at least 7 carbon atoms per molecule to an extent such that the resulting chlorination reaction mixture contains an amount of organically combined chlorine substantially corresponding with 75 per cent to 175 per cent complete monochlorination of the hydrocarbon mixture, admixing the resulting chlorination reaction mixture with an amount by weight of the aromatic compound in excess of the weight of said chlorination reaction mixture, and heating the admixture at a condensation temperature in the presence of a metal halide condensing agent.

11. In the production of an alkyl aromatic sulfonate useful as a detergent, by a process which comprises chlorinating a non-aromatic hydrocarbon mixture and condensing a resulting mixture of alkyl chlorides with an aromatic compound to produce a mixture of alkyl aromatic compounds, the improvement which comprises chlorinating a mixture of non-aromatic hydrocarbons containing at least 10 carbon atoms per molecule to an extent such that the resulting chlorination reaction mixture contains an amount of organically combined chlorine substantially corresponding with 75 per cent to 175

per cent complete monochlorination of the hydrocarbon mixture, admixing the resulting chlorination reaction mixture with an amount by weight of the aromatic compound at least one and one-fourth times the weight of the resulting chlorination reaction mixture, and heating the admixture at a condensation temperature in the presence of a metal halide condensing agent.

12. In the production of an alkyl aromatic compound which is adapted to be converted by sulfonation to an alkyl aromatic sulfonate useful as a detergent, by a process which comprises chlorinating a non-aromatic hydrocarbon mixture and condensing a resulting mixture of alkyl chlorides with an aromatic compound to produce a mixture of alkyl aromatic compounds, the improvement which comprises chlorinating a petroleum hydrocarbon distillate of the Pennsylvania type containing hydrocarbons having not less than 10 nor more than 23 carbon atoms per molecule to an extent such that the resulting chlorination reaction mixture contains an amount of organically combined chlorine substantially corresponding with 75 per cent to 175 per cent complete monochlorination of the hydrocarbon distillate, admixing the resulting chlorination reaction mixture with an aromatic compound of the benzene series and aluminum chloride, the amount of aromatic compound being at least one and one-fourth times the weight of the chlorination reaction mixture, and heating the resulting admixture to effect condensation of alkyl chlorides with the aromatic compound.

13. In the production of an alkyl aromatic compound which is adapted to be converted by sulfonation to an alkyl aromatic sulfonate useful as a detergent, by a process which comprises chlorinating a non-aromatic hydrocarbon mixture, condensing a resulting mixture of alkyl chlorides with an aromatic compound to produce a mixture of alkyl aromatic compounds, and separating a mixture of alkyl aromatic compounds from higher-boiling by-products by distillation, the improvement which comprises chlorinating a petroleum hydrocarbon distillate of the Pennsylvania type containing hydrocarbons having not less than 10 nor more than 23 carbon atoms per molecule to an extent such that the resulting chlorination reaction mixture contains an

amount of organically combined chlorine substantially corresponding with 75 per cent to 175 per cent complete monochlorination of the hydrocarbon distillate, admixing the resulting chlorination reaction mixture with a benzene hydrocarbon and aluminum chloride, the weight of benzene hydrocarbon being at least one and one-fourth times the weight of the chlorination reaction mixture, and heating the resulting admixture to effect condensation of alkyl chlorides with the benzene hydrocarbon.

14. The method of producing higher alkyl aromatic sulfonates which comprises chlorinating a petroleum hydrocarbon distillate containing hydrocarbons having not less than 10 nor more than 23 carbon atoms per molecule to an extent such that the resulting chlorination reaction mixture contains an amount of organically combined chlorine substantially corresponding with 75 per cent to 175 per cent complete monochlorination of the hydrocarbon distillate, admixing the resulting chlorination reaction mixture with an aromatic compound of the benzene series and a metal chloride condensing agent, the amount of aromatic compound being at least one and one-fourth times the weight of the chlorination reaction mixture, heating the resulting admixture to effect condensation of alkyl chlorides with the aromatic compound, and reacting a sulfonating agent with a resulting mixture of higher alkyl aromatic compounds.

15. The method of producing higher alkyl aromatic sulfonates which comprises chlorinating a petroleum hydrocarbon distillate of the Pennsylvania type containing hydrocarbons having not less than 10 nor more than 23 carbon atoms per molecule to an extent such that the resulting chlorination reaction mixture contains an amount of organically combined chlorine substantially corresponding with 75 per cent to 175 per cent complete monochlorination of the hydrocarbon distillate, admixing the resulting chlorination reaction mixture with one and one-half to two times its weight of benzene, heating the admixture at a condensation temperature in the presence of aluminum chloride as a condensing agent, and reacting a resulting mixture of alkyl benzenes with a sulfonating agent.

LAWRENCE H. FLETT.