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MANUFACTURE OF DETERGENTS AND RELATED COMPOSITIONS

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This invention relates to improvements in the manufacture of detergents and related compositions comprising mixtures of sulfonated higher alkyl derivatives of benzene hydrocarbons in which the alkyl groups are derived from complex hydrocarbon mixtures of mineral origin as, for example, crude petroleum and preferably petroleum fractions comprising not more than 20 per cent of aromatic compounds, the term "alkyl" referring to non-aromatic radicals and including aliphatic, cycloaliphatic and aralkyl radicals. It relates more particularly to improvements in the process of producing such higher alkyl aryl sulfonates which involves condensing a kerosene fraction of a petroleum distillate with a benzene hydrocarbon, such as benzene, toluene, etc., and sulfonating resulting mixed alkyl benzene compounds. It relates especially to a method of preparing the mixed alkyl benzene compounds for sulfonation so that upon sulfonation, followed by conversion of the sulfonation product to salts and drying, mixed alkyl benzene sulfonates are obtained which have improved detergent action and other improved properties.

An object of the present invention is to provide improvements in the manufacture of mixed higher alkyl benzene sulfonates from complex hydrocarbon mixtures of mineral origin, whereby products having improved detergency are obtained.

Another object of the present invention is to provide improvements in the method of producing higher alkyl benzene sulfonates from chlorinated kerosene fractions of petroleum distillates and benzene hydrocarbons by condensation with the aid of aluminum chloride as a condensation catalyst, followed by sulfonation, whereby sulfonated products are obtained having improved properties, particularly with respect to detergency, color and odor.

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

Mixtures of sulfonated higher alkyl derivatives of benzene hydrocarbons in which the alkyl groups are derived from complex hydrocarbon mixtures of mineral origin represent a desirable class of products, particularly in the form of their alkali metal and organic amine salts, for use as substitutes for soaps and as surface active agents in view of certain of their advantageous properties; as, for example, resistance to acid and hard water, washing and lathering ability in hard water and sea water, and freedom from hydrolysis. For most purposes, particularly for use as a general detergent, products derived from petroleum distillates within the kerosene range are preferable; that is, petroleum distillates which boil within the range 180° to 320° C. Those which boil for the most part (i. e., at least 80 per cent thereof) within the range of 210° to 320° C. are preferred, especially when composed predominantly of aliphatic and/or alicyclic hydrocarbons which boil within the range 210° to 290° C. They offer several important advantages over other available synthetic detergents. First, because of the relatively inexpensive raw materials used in their manufacture, they may be produced economically. Also, due to the fact that they consist of not one compound but of a mixture of compounds having varying properties, they are capable of a wider variety of uses than many other synthetic detergents which are usually relatively specific in their action.

In general, the manufacture of the compositions in question involves forming a benzene hydrocarbon-condensation product of a poly-component non-aromatic hydrocarbon mixture of mineral origin by condensing a benzene hydrocarbon with a halogenated petroleum fraction, or a corresponding olefinic product, for example, one obtained by removing hydrogen halide from the halogenated fraction, and sulfonating the mixture of higher alkyl benzene compounds thus produced. The alkyl groups introduced into the aromatic nucleus are principally hydrocarbon groups, and the mixtures may comprise isomeric and homologous hydrocarbon groups. In addition to straight chain and branched chain alkyl groups, aralkyl and cyclo-alkyl groups may be present, all of which are included herein in the term "alkyl" groups. Thus one method of producing an alkyl benzene sulfonate product for use as a detergent comprises chlorinating a petroleum distillate, condensing the resulting mixture of alkyl chlorides with benzene in the presence of anhydrous aluminum chloride or other catalyst or condensing agent of the Friedel and Crafts type, sulfonating the resulting mixture of alkyl benzenes, neutralizing the alkyl benzene sulfonic acid mixture with aqueous sodium hydroxide solution, and recovering the resulting mixture of sodium alkyl benzene sulfonates.

The nature of the complex hydrocarbon mixtures of mineral origin is such, however, as to decrease their usefulness for the production of higher alkyl benzene sulfonates. For example, in the preparation of higher alkyl benzene sulfonates from petroleum distillates which are chiefly non-aromatic hydrocarbons with at least

10 carbon atoms per hydrocarbon molecule, and particularly 10 to 20 carbon atoms per molecule, by processes involving halogenation of the petroleum distillate, the reactivity of the various hydrocarbons present in a given distillate to the halogenating agent is different, with the result that the halogenated product contains a mixture of various halogenated bodies in which the degree of halogenation is non-uniform, together with unhalogenated hydrocarbons. When such a mixture is employed for condensation with a benzene hydrocarbon and the resulting condensation product is sulfonated, the presence of the various constituents in the chlorination product leads to a wide variety of impurities and by-products in the sulfonation product. For example, colored impurities are formed which contaminate the sulfonate mixture. Not only are the resulting detergents visually unattractive but goods washed with such detergents may be stained or discolored thereby. Even slight staining of washed goods is obviously objectionable. In addition, the dry sulfonate products have an unpleasant odor or develop a rancid odor on being stored.

According to the present invention, higher alkyl benzene sulfonates of improved quality, and of increased detergent and surface active action, are obtained from non-aromatic hydrocarbon materials of the type herein described, by incorporating into the process of producing the higher alkyl benzene sulfonates the improvements hereinafter disclosed.

The present invention is of value in the treatment of various mixtures of higher alkyl aromatic compounds derived from poly-component hydrocarbon mixtures of mineral origin, such as a petroleum distillate or an otherwise refined petroleum fraction, which contain straight and/or branched-chain alkanes, and preferably consist predominantly of open chain alkanes, and which may also contain cycloalkanes and aryl hydrocarbons, but do not contain more than 20 per cent of aryl hydrocarbons. Preferably the mixtures of higher alkyl aromatic compounds are derived from such hydrocarbon mixtures of mineral origin which contain less than 10 per cent of aryl hydrocarbons. The present invention is of particular value in the treatment of mixtures of higher alkyl aromatic compounds derived from kerosene fractions, especially commercial or treated kerosene fractions of a Pennsylvania grade crude, as described for example in my applications Serial No. 93,521, filed July 30, 1936, and Serial No. 195,414, filed March 11, 1938, and the invention hereof will be described particularly with reference to treatment of this type of product. The present application is in part a continuation of said applications Serial Nos. 93,521 and 195,415.

In the practice of the present invention in accordance with a preferred method of procedure, a selected distillate fraction of a poly-component non-aromatic hydrocarbon mixture of mineral origin, for example, a kerosene fraction of Pennsylvania or similar petroleum, is chlorinated to obtain a mixture which comprises chlorinated hydrocarbons, and the mixture of chlorinated hydrocarbons is condensed with a benzene hydrocarbon in the presence of aluminum chloride as a catalyst or condensing agent (or other Friedel and Crafts condensing agent). The resulting condensation reaction mixture is then subjected to a mechanical separation treatment to separate a crude mixture of higher alkyl benzene compounds from a tarry sludge containing the residual and/or exhausted condensing agent. The separation treatment preferably involves permitting the condensation reaction mixture to stand undisturbed so as to stratify into an upper oily layer containing the crude higher alkyl benzene condensation product and a lower layer of sludge, followed by separation of the layers, as by decantation. The upper oily layer is then subjected to a distillation treatment to remove as distillate higher monoalkyl benzene compounds from by-products and residual products of the previous treatments having higher boiling points. The resulting mixture of higher monoalkyl benzene compounds is then subjected to sulfonation, which if desired, is followed by conversion of resulting sulfonic acids to their corresponding salts.

I have found in accordance with one feature of the present invention that, by mechanically separating from the condensation reaction mixture the crude higher alkyl benzene compounds, the sulfonated products obtained therefrom have improved properties with respect to color, detergency, odor and development of odor, as compared with sulfonated products obtained by treatment of the condensation reaction mixture in the manner usually employed for isolating the condensation products from Friedel and Crafts condensation reaction mixtures.

For the purpose of securing a maximum yield of higher alkyl benzene sulfonates, in accordance with prior practice, the Friedel and Crafts reaction mixture resulting from the condensation reaction was treated with water or dilute acid to convert the residual and/or exhausted catalyst or condensing agent to an aqueous solution, the mixture was allowed to stratify, and the water-insoluble oily material comprising the desired higher alkyl benzene condensation product was separated from the aqueous layer. The present invention is based on the discovery that the catalyst or condensing agent has an attraction for constituents of the condensation reaction mixture that cause undesirable properties of the final sulfonated product. Thus it has been found, that superior sulfonated products can be obtained by causing the Friedel and Crafts condensation reaction mixture to separate into two phases, e. g., by allowing it to stand or by the use of centrifugal force, and removing the lighter, oily phase from the heavier dark colored sludge-like phase containing the residual and/or exhausted catalyst or condensing agent.

The mechanical separation of the sludge-like catalyst phase in accordance with the present invention removes impurities which otherwise exert a degrading effect on mixed higher alkyl benzene compounds and give rise to highly colored and odorous impurities in the higher alkyl benzene sulfonates made from them. Thus, this improving step enables the preparation of detergent mixtures of higher alkyl benzene sulfonates which are characterized by greatly improved color and general appearance. Apparently, the condensing agent enters into some sort of loose combination with impurities and by-products which are present in the crude higher alkyl benzene condensation product and which, if not removed, form compounds which are deleterious to the quality of the detergent mixtures, although they may have no effect, or a relatively small effect, on the unsulfonated alkyl benzene compounds. It was not to have been foreseen that the condensing agent would exert this refining influence, and that mechanical separation of that portion of the

crude condensation reaction mixture which contains the residual and/or exhausted condensing agent would be effective in bringing about the observed improvements in quality of the final detergent mixtures of higher alkyl benzene sulfonates.

In addition to the desired higher monoalkyl benzene compounds, the crude kerosene benzene condensation product includes unreacted benzene, unchlorinated and chlorinated petroleum hydrocarbons, and other condensation products of various types. Even when the condensation reaction mixture is subjected to the preliminary treatment involving stratification of the crude condensation reaction mixture and separation of the upper oily layer containing the higher monoalkyl benzene compounds from the lower tarry layer (or equivalent mechanical separation), the oily layer contains other condensation products and/or other higher-boiling substances which have been found to interfere with the usefulness of the final sulfonated product as a detergent, particularly if the amount of aluminum chloride used in the condensation is less than 9 per cent, and more particularly if it is less than 5 per cent of the weight of the mixture of chlorinated hydrocarbons used in the condensation.

It has heretofore been proposed to subject a crude higher alkyl benzene condensation product, resulting from the condensation of a benzene hydrocarbon with chlorinated kerosene, to distillation to remove unreacted benzene hydrocarbon and petroleum hydrocarbons and chlorinated hydrocarbons. In such a process, however, distillation was used to remove a lower boiling distillate which was composed substantially of the lower boiling benzene hydrocarbons, petroleum hydrocarbons and chlorinated hydrocarbons, and to leave the portion of the distilland which was substantially the higher alkyl benzene condensation product. The resulting higher alkyl benzene condensation product was subjected to sulfonation without further treatment. Prior to my invention, it was not known that the detergency as well as other properties of the sulfonated product can be improved by subjecting said higher alkyl benzene condensation product itself to a distillation treatment. Such an improvement is unexpected and surprising inasmuch as the higher alkyl benzene condensation product is, to a large extent, converted to sulfonic acid derivatives upon sulfonation.

It has been found as another feature of the present invention that even though many of the other higher condensation products present in the crude kerosene benzene condensation product are converted to sulfonation derivatives along with the desired higher monoalkyl benzene compounds by the sulfonation treatment, the sulfonation derivatives of such other higher condensation products interfere with the detergent action of the higher monoalkyl benzene sulfonates.

Accordingly, in the practice of the present invention, the crude kerosene benzene condensation product is subjected to vacuum distillation and a fraction of the distillate comprising essentially higher monoalkyl benzene compounds is collected separately. Ordinarily the distillation is carried out in such a manner that residual benzene hydrocarbon and other low boiling constituents of the crude condensation product (e. g., low boiling petroleum hydrocarbons and chlorinated hydrocarbons) are first distilled off, and collected as a separate fraction, as in the prior practice; and then the remainder of the distilland, composed substantially of the refined condensation product is subjected to vacuum distillation, preferably under high vacuum conditions, which do not exceed an absolute pressure of 30 mm. mercury, and the distillate which is to be used for further treatment in the production of sulfonated products for use as detergents is collected separately until the undistilled residue remaining in the still amounts to at least 10 per cent of the refined condensation product subjected to the distillation treatment of the present invention: that is, of the portion of the condensation product from which uncondensed benzene hydrocarbons and other low boiling constituents have been removed by preliminary distillation. The amount of residue remaining in the still will vary with the degree of chlorination employed in the preparation of the chlorinated kerosene, an increase in the degree of chlorination increasing the amount of still residue.

If desired, the still residue may itself be subjected to a distillation treatment and in general distills for the most part at temperatures below 300° C. at an absolute pressure of 4 mm. of mercury. The resulting distillate is a light colored oil. It comprises polyalkyl benzene condensation products and polyaryl alkyl condensation products. It can be sulfonated to produce sulfonated products, but the resulting sulfonated products are of inferior detergent action and if added to the sulfonated products derived from the distilled higher monoalkyl benzene compounds have a deleterious effect upon their detergent properties. If desired, it may be employed for other purposes, however; for example, as a lubricant, or for addition as a modifying agent to other lubricants.

In the preferred practice of the present invention, the vacuum distillation of the kerosene benzene condensation product is employed in conjunction with the mechanical separation of the kerosene benzene condensation product from the Friedel and Crafts condensation reaction mixture. A process embodying both of said features of the present invention is of especial value in connection with the treatment of kerosene benzene condensation products obtained by condensing benzene with a kerosene fraction of petroleum distillate which has been chlorinated to an extent corresponding with from 75 to 200 per cent chlorination (that is, chlorination to an extent such that the resulting chlorinated kerosene contains three-fourths to two atoms of combined chlorine for each molecule of hydrocarbon present in the original kerosene) with the aid of an amount of anhydrous aluminum chloride which is less than 9 per cent of the weight of the chlorinated kerosene, particularly when the amount of benzene employed in the condensation is in excess, and especially when the kerosene employed as starting material boils mainly over a maximum range less than 100° C. in extent.

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

10,620 lbs. Pennsylvania kerosene (having a specific gravity of 0.788 at 24° and boiling range from 185° to 275°) were charged 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 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°. The amount of chlorine required for the purpose was about 4825 lbs. The final chlorinated kerosene mixture weighed 12,834 lbs.

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, and the mixture was allowed to stand undisturbed for about 2 hours, whereupon the mixture separated into an upper oily layer and a lower tarry layer. The lower tarry layer, comprising the aluminum chloride residue resulting from the condensation and by-products, was withdrawn. The upper oily layer, comprising the desired kerosene-benzene condensation product (herein referred to as mixed higher monoalkyl benzenes), together with unreacted benzene, unchlorinated and chlorinated petroleum hydrocarbons and by-products of the chlorination and/or condensation, was transferred to a stripping kettle where the oil was stripped of low-boiling compounds, chiefly benzene, by boiling the oil until its temperature reached 150°, at atmospheric pressure, then reducing the pressure in the distilling system to an absolute pressure of 3 to 4 inches of mercury, 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. Between 200° and 250°, only a relatively small amount of material was distilled. The separately collected distillate amounted to about 9800 pounds. For convenience it is called "keryl benzene." There remained in the still at this point about 1300 pounds of residue.

The keryl benzene was given a purifying treatment by mixing it with about 15 per cent of its weight of 100 per cent sulfuric acid and agitating the mixture for about 1 hour at about 40° in an enamel-lined kettle. The mixture was allowed to stand for about a half hour to permit separation of a lower layer of acid and impurities, which was withdrawn and discarded.

The upper, acid-treated layer of keryl benzene was then sulfonated by mixing it with about 1¼ times its weight of 100 per cent sulfuric acid at a temperature between 30° and 35° in an enamel-lined kettle, warming the mixture to 55° and agitating it at that temperature for 1 hour, and then allowing it 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 keryl benzene; 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 sufficient sodium sulfate was added to adjust the inorganic salt content in the mixture to 60 per cent of the total solute in the solution. The resulting slurry was mixed thoroughly and dried on a rotary double drum drier internally heated with steam. The resulting dried flaky product was substantially white in color and dissolved in water to form substantially colorless solutions having high detergent powers.

Example 2

To 12,000 grams of Pennsylvania kerosene (boiling range about 189° to 261°) were added 1320 cc. of 100 per cent sulfuric acid, and the mixture was agitated for 1 hour at 50 to 55°. The acid was then separated, leaving 11,020 grams of kerosene. This kerosene was then agitated with 1200 cc. of 100 per cent sulfuric acid for 1 hour at room temperature. The acid was separated leaving 10,536 grams of kerosene. This kerosene was agitated for 30 minutes with 160 grams of an activated clay of the grade known commercially as "Tonsil." The mixture was filtered, yielding 10,324 grams of kerosene.

To 2500 grams of this acid-treated kerosene, 1.0 gram of iodine was added, and chlorine was passed into the resulting mixture at 60 to 62° with vigorous agitation, until the weight of the mixture was increased by 545 grams, the specific gravity increase was 0.131 at 24°. This amounts to about 119 per cent chlorination on a molar basis.

From the resulting chlorinated kerosene, duplicate condensations with benzene were made as follows:

To a mixture of 608 grams of benzene and 15.2 grams of anhydrous aluminum chloride, 304 grams of the chlorinated kerosene were added at room temperature during the course of 20 minutes with good agitation. The temperature of the reaction mixture was then raised to 45° in 5 minutes, and agitation at 44° to 46° was continued for 90 minutes.

One of the resulting duplicate condensation reaction mixtures was cooled to 30° and poured slowly onto 1 kg. of ice with agitation. 500 cc. of concentrated hydrochloric acid were added to facilitate separation of the oily condensation product from the mixture, and the mixture was permitted to stand and stratify. Two layers formed. The aqueous layer was removed, and the oily layer washed once with 500 cc. of water. The washed oil was distilled in vacuo. The fraction of distillate whose boiling point was 80° to 234° at 4 mm. (250 g.) was collected separately and designated as distillate B. The residue remaining from the distillation weighed 29 grams.

The other of said duplicate condensation reaction mixtures was allowed to stand in a separatory funnel at room temperature over night. Two layers formed. The bottom layer, consisting of 63 grams of tar, was separated from the upper oily layer, which was then distilled in vacuo. The fraction of distillate whose boiling point was 80° to 234° at 4 mm. (234 g.) was collected separately and designated as distillate A. The residue remaining from the distillation weighed 26 grams.

Both distillates A and B were separately sulfonated in the following way: A 100 gram sample of the distillate was agitated for 45 minutes with 10 cc. of 100 per cent sulfuric acid and then allowed to stand for 30 minutes. Two layers formed; an acid layer and an oil layer. The acid layer was removed. To the oil there were added

during 10 minutes 100 cc. of 100 per cent sulfuric acid, using good agitation. The reaction mixture was warmed to 55° to 60°, held at that temperature for 60 minutes, and then allowed to stand 60 minutes. Separation into three layers took place. The middle, higher alkyl benzene sulfonate layer, was drowned in ice and neutralized with aqueous caustic soda, keeping the temperature below 35°. The salt content of the resulting product was adjusted by adding sodium sulfate in such amount that the per cent of higher alkyl benzene sodium sulfonate in the product after drying was 42 per cent. The resulting solution was drum dried.

A comparison of the resulting products showed the following results:

Table I

Product	Yield of alkyl benzene sodium sulfonate per kg. of kerosene	Solution color [1]	Wetting time [2]
A	845 grams	39% of B	0.60 min.
B	885 grams	255% of A	0.67 min.

[1] The method of comparing colors of solutions was as follows: 100 cc. of a 5 per cent solution of the product were placed in a rectangular 4-ounce clear glass bottle. The solution was compared with a standard light-colored solution of the same concentration by reflected light from a white background. The solution of the sample undergoing examination was diluted with water until the color of the diluted solution was substantially equal to that of the standard solution. Color is expressed in terms of this dilution.

[2] Wetting power was measured by determining the length of time necessary to wet out a sample of standard fabric of standard size with a solution of the product under definite temperature and concentration conditions. 500 cc. of a 0.2 per cent solution of the product to be tested were placed in a 600 cc. beaker and maintained at 50° C. A #10 canvas disc, 1 inch in diameter, was placed on the surface of the solution and immediately cupped in an inverted, long-stem funnel and forced below the liquid level to a depth of 5 to 6 centimeters. The time from cupping until the disc commenced to fall out of the funnel was measured and is given as the wetting time in the table.

EXAMPLE 3

A Pennsylvania petroleum distillate (kerosene) which distills from about 200° to about 266°, and of which about 80 per cent distills over the range of about 220° to 260°, and which comprises substantially a mixture of hydrocarbons which are chiefly aliphatic and saturated, is chlorinated at about 50° by passing through it a stream of chlorine gas until the chlorinated mixture has increased in weight by about 20 per cent because of organically-combined chlorine therein. The resulting mixture of unchlorinated and chlorinated hydrocarons is aerated to remove practically all dissolved hydrogen chloride.

To an agitated mixture of 300 parts of the resulting chlorination product and 200 parts of benzol, 30 parts of anhydrous aluminum chloride are added slowly. The mixture is cooled externally until the vigorous evolution of hydrogen chloride gases from the mixture has abated. It is then heated and maintained at its refluxing temperature for about one hour, or until the evolution of hydrogen chloride has ceased. The reaction mass is cooled and drowned with a mixture of about 400 parts of crushed ice, 200 parts of water and 50 parts of commercial muriatic acid. The mixture is allowed to stratify, the organic oily layer above the aqueous solution is separated, washed with a small amount of water, and distilled. The portion which distills from about 160° to about 210° at 4 mm. of mercury pressure is collected and consists of a mixture of alkylated benzenes. The resulting mixture is a light amber-colored, somewhat oily, but not viscous, liquid which is insoluble in water, but soluble in the common organic solvents.

100 parts of the resulting distilled oil are mixed with 130 parts of 20 per cent oleum at a temperature of approximately 10°. The mixture is allowed to warm to 25° to 30° and is stirred at this temperature for 1½ to 3 hours or until one part of a test portion, after neutralizing with sodium hydroxide, is soluble in 20 parts of water. The mixture is then poured into approximately 600 parts of an ice-water mixture, and the resulting solution is made neutral to Brilliant Yellow and Congo Red papers with caustic alkali (e. g., sodium hydroxide). The neutralized solution is evaporated to dryness on a rotary drum drier. The product obtained is in the form of light-buff to white flakes. It comprises chiefly a mixture of alkyl benzene sulfonates and alkali metal sulfate. Aqueous solutions of the product have excellent washing properties.

EXAMPLE 4

Part 1.—A kerosene fraction of Pennsylvania petroleum boiling from 185° to 280° is fractionated and a fraction is collected between 91° at 13 mm. pressure and 109° at 12 mm. pressure. The collected fraction boils from 200° to 235° at atmospheric pressure and 90 per cent of it boils between 212.5° and 231°. Chlorine is passed into 340 parts of the resulting fraction maintained below 60°, in the presence of light, until there is an increase in weight of 88 parts.

Part 2.—150 parts of the mixture produced in Part 1 of this example are added with agitation, to a mixture of 80 parts of benzene and 4 parts of anhydrous aluminum chloride at ordinary temperature. The addition is made as rapidly as possible. The mixture is agitated for one hour and then allowed to separate. The resulting condensation product is decanted from the aluminum chloride sludge and washed with water. The washed material is stripped of unreacted materials by distilling off the portion boiling up to 118° at 10 mm. which contains residual benzene. The remainder comprises a mixture of alkyl benzene and residual kerosene.

Part 3.—75 parts of the alkyl benzene product of Part 1 of this example is sulfonated with 1¼ times its weight of 26 per cent oleum. The oleum is added thereto at 10 to 15°, and the mixture is then agitated at room temperature for about 2 hours. The sulfonation mixture is diluted with four times its weight of an ice-water mixture and neutralized with caustic alkali (e. g., sodium hydroxide) to a pH of 7.0 to 8.0. The neutral solution is evaporated to dryness on an atmospheric double drum drier.

EXAMPLE 5

A kerosene fraction of Pennsylvania petroleum distillate, substantially all of which boiled between 180° and 300°, having a specific gravity of 0.79 at about 25°, and consisting principally of saturated aliphatic hydrocarbons which, on the basis of the source and properties of the distillate, were considered to be hydrocarbons (mainly open chain aliphatic hydrocarbons) having an average molecular carbon content of 13 to 14 carbon atoms and a range from 10 to 17 carbon atoms per molecule, was chlorinated by passing into it a stream of chlorine gas in the presence of a small amount of iodine as a catalyst while maintaining the temperature of the mixture around 55° to 60°, until the specific gravity of the liquid had increased by 0.125. At this stage, about 1¼ times the amount of chlorine theoretically necessary to yield the monochlor substitu-

tion products of all of the hydrocarbons in the mixture had been absorbed. The resulting chlorination product consisted of a mixture of monochlor hydrocarbons together with more highly chlorinated hydrocarbons and unchlorinated hydrocarbons.

10 parts of the resulting chlorination product were reacted with 6 parts of benzene in the presence of 0.8 part of anhydrous aluminum chloride, for about 45 minutes with vigorous agitation at 42° to 45°. The reaction mixture was then allowed to stand for about 2 hours. It separated into two layers. The upper oily layer was decanted. It contained a mixture of higher alkyl benzenes resulting from the condensation, together with unreacted benzene, unreacted petroleum hydrocarbons and chlorinated petroleum hydrocarbons, and by-products of the reaction. The oil was heated in a still until the liquid temperature reached 150°. After cooling slightly, vacuum was applied and heating and distillation were continued until the vapor temperature reached 115° at an absolute pressure corresponding to 40 to 45 mm. mercury pressure, to remove a distillate comprising chiefly unreacted benzene, with some other low-boiling hydrocarbons. The receiver was then changed and distillation was continued until the vapor temperature reached 240° at 20 mm. mercury pressure, whereby a distillate was obtained comprising a mixture of the higher alkyl benzenes, together with other high-boiling constituents and by-products of the foregoing procedure.

7.5 parts of the resulting distillate were agitated at 30° to 40° with 1 part of 100 per cent sulfuric acid for about 45 minutes. After standing quiescent for 1 to 2 hours, two layers were formed. The lower layer of spent acid was withdrawn. The remaining acid-washed oil was agitated with 6.5 parts of 100 per cent sulfuric acid at 60° for about 1 hour. The reaction mixture was then allowed to stand quiescent until it separated into three layers (about 1 hour). The upper layer, consisting of oily material and containing substantially all of the residual petroleum hydrocarbons and chlor hydrocarbons as well as the greater portion of the water-insoluble by-products formed in the condensation and sulfonation operations, was removed by decantation. The bottom sulfuric acid layer, containing principally spent sulfuric acid, was removed and discarded. The original middle layer, containing the alkyl benzene sulfonic acids and some sulfuric acid, was drowned in about 32 parts of cold water and neutralized with aqueous sodium hydroxide; for example, by treatment with a 50 per cent aqueous solution of caustic soda in an amount sufficient to render the resulting solution neutral to Brilliant Yellow and Congo Red. The neutralized solution, when evaporated to dryness on a rotary drum drier, resulted in a white flaked solid, which was readily soluble in water to form solutions which were clear and which possessed excellent wetting and washing properties. The resulting product contained chiefly the sodium salts of alkyl benzene sulfonic acids, in which the alkyl groups averaged about 13 to about 14 carbon atoms, and sodium sulfate.

It will be evident to those skilled in the art that the invention is not limited to the details of the foregoing illustrative examples and that changes can be made without departing from the scope of the invention. A number of such changes are disclosed in my copending applications Serial Nos. 93,521 and 195,414, referred to above.

Thus the nature of the poly-component non-aromatic hydrocarbon mixture of mineral origin employed, the manner and degree of chlorination or other treatment to which it is subjected prior to condensation with the benzene hydrocarbon, and the conditions of condensation may be varied. Further, the proportion of benzene hydrocarbon compound employed can be varied. Generally, the amount of benzene hydrocarbon to be employed is dependent upon the amount of combined chlorine contained in the chlorinated hydrocarbon mixture. In order to obtain complete reaction, one mol of benzene hydrocarbon should be used for each atom of combined chlorine in the chlorinated hydrocarbon mixture. Preferably, an excess of the benzene hydrocarbon is used as this favors complete reaction of the chlorinated hydrocarbons.

As above pointed out, the preferred practice of the invention involves the use of both features of the present invention. It is not essential to the obtainment of improved detergent mixtures of higher monoalkyl benzene sulfonates to employ both features of the present invention, but either may be employed without the other. Thus, a vacuum distillation of the kerosene benzene condensation product recovered from the condensation reaction mixture in other ways than the mechanical separation of the preferred procedure of the present invention effects improvements in the detergency as well as other properties of the sulfonated products obtained therefrom.

The conditions of the vacuum distillation of the kerosene condensation product also may be varied.

When a chlorinated mineral oil distillate, such as is used in the foregoing examples, is condensed with a benzene hydrocarbon to form a kerosene benzene compound, a mixture of products results, as becomes evident when the crude kerosene benzene condensation product is distilled. The unreacted excess of the benzene hydrocarbon is the first product to distill, and distillation takes place within a fairly close range of temperatures, which is below the temperature at which the higher monoalkyl benzene compounds distill. Likewise, unreacted hydrocarbons from the mineral oil distillate start to distill at a temperature below that at which the higher monoalkyl benzene compounds begin to distill. As the distillation continues, preferably under vacuum conditions, the higher monoalkyl benzene compounds begin to distill. There is little or no evidence of any break in the distillation, and as the mixture of higher alkyl benzene compounds and residual mineral oil hydrocarbons is distilled, the vapor temperature slowly rises without distinct evidence of the fact that mixtures of two different types of compounds are being distilled. In the case of products derived from benzene and kerosene, the mixture of higher monoalkyl benzene compounds and residual kerosene hydrocarbons distills from about 80° C. at 4 mm. to about 200° C. at 4 mm. After 200° C. at 4 mm. is reached, the temperature rises rather rapidly and a relatively small amount of an inferior grade of higher alkyl benzene compounds distills over, leaving a residue amounting to about 10 per cent of the kerosene benzene condensation product remaining after removal of the unreacted benzene hydrocarbon. The point at which the distillation of the higher monoalkyl benzene compounds is stopped will vary, depending upon the nature

and boiling range of the mineral oil distillate employed as starting material, and the conditions employed in the preceding steps of the complete process. In cases where a mineral oil distillate with a narrow boiling range (a boiling range of 50° to 100 C.) is used, there is a distinct break in the distillation when the higher monoalkyl benzenes have been distilled, at which point the temperature rises rapidly and only relatively small amounts of material distill over. This break serves as a guide in cutting the distillation. From the standpoint of quality, the cut should be made in the early period of the rapid temperature rise; from the standpoint of economy a portion of this higher boiling distillate may be collected without serious decrease in the quality of the resulting detergent. In cases where the mineral oil distillate has a wider boiling range, the break will be less evident or not evident at all. In such a case, an arbitrary amount of material is left in the still when the cut is made. While the removal of any of the high boiling material is beneficial, it is preferable to leave at least 10 per cent of residue, based on the weight of stripped kerosene benzene condensation product.

The distillation of the kerosene benzene condensation product is preferably carried out at an absolute pressure not exceeding 15 mms. of mercury, and especially at an absolute pressure not exceeding 7 mms. of mercury.

The subsequent treatment of the higher monoalkyl benzene compounds obtained from the vacuum distillation, for conversion to sulfonated products useful as detergents also can be varied. Thus, sulfuric acids of various strengths such as 66° Bé. sulfuric acid, 100 per cent sulfuric acid, 26 per cent oleum and 65 per cent oleum, and chlorsulfonic acid may be used as sulfonating agents. The sulfonation may be carried out in the presence of inert solvents or diluents, and sulfonation assistants as, for example, the lower fatty acids and their anhydrides, such as acetic acid and acetic anhydride, or the alkali metal sulfates, such as sodium or potassium sulfate, may be employed. Also, the temperature at which the sulfonation is carried out may vary within wide limits. For example, temperatures as low as about 0° C. and as high as about 140° C. may be employed. In general the more vigorous the sulfonating agent the lower is the preferred temperature. In most cases the sulfonation is carried out most efficiently at temperatures between 5° and 90° C. For complete sulfonation the sulfonating agent in terms of 100 per cent sulfuric acid may be employed in amounts which range from 0.3 to 5 times or more the weight of the condensation product to be sulfonated. Ordinarily, the extent to which the sulfonation is carried out will vary with the individual material being sulfonated, the duration of the sulfonation, and the use to be made of the sulfonated product.

By the term "a poly-component non-aromatic hydrocarbon mixture of mineral origin" as employed in some of the following claims, I mean a hydrocarbon mixture, such as petroleum and petroleum distillates or otherwise refined petroleum fractions, containing straight and/or branched chain alkanes and which may also contain cycloalkanes and aryl hydrocarbons but does not contain more than 20 per cent of aryl hydrocarbons.

I claim:

1. In the process of producing a detergent mixture of higher alkyl benzene sulfonates by forming a benzene hydrocarbon condensation product of a poly-component non-aromatic hydrocarbon mixture of mineral origin and sulfonating the condensation product, the improvement which comprises distilling the benzene hydrocarbon condensation product, collecting a fraction of the distillate containing higher monoalkyl benzene compounds, and sulfonating resulting higher monoalkyl benzene compounds.

2. In the process of producing a detergent mixture of higher alkyl benzene sulfonates by forming a benzene hydrocarbon condensation product of a poly-component non-aromatic hydrocarbon mixture of mineral origin and sulfonating the condensation product, the improvement which comprises condensing a benzene hydrocarbon with a chlorinated kerosene fraction of petroleum distillate in the presence of a Friedel and Crafts condensing agent, to produce a condensation product containing higher monoalkyl benzene compounds, distilling the condensation product at a subatmospheric pressure, collecting a fraction of the distillate containing a purified mixture of higher monoalkyl benzene compounds, and sulfonating the purified mixture of higher monoalkyl benzene compounds.

3. In the process of producing a detergent mixture of higher alkyl benzene sulfonates by forming a benzene hydrocarbon condensation product of a poly-component non-aromatic hydrocarbon mixture of mineral origin and sulfonating the condensation product, the improvement which comprises distilling the condensation product at a subatmospheric pressure, collecting a fraction of the distillate comprising essentially higher monoalkyl benzene compounds, and sulfonating said higher monoalkyl benzene compounds.

4. In the process of producing a detergent mixture of higher alkyl benzene sulfonates by forming a benzene hydrocarbon condensation product of a poly-component non-aromatic hydrocarbon mixture of mineral origin and sulfonating the condensation product, the improvement which comprises condensing a benzene hydrocarbon with a chlorinated kerosene fraction of petroleum distillate in the presence of a Friedel and Crafts condensing agent, to produce a condensation product containing higher monoalkyl benzene compounds, distilling the resulting condensation product at a final absolute pressure not exceeding 30 mm. of mercury, collecting a fraction of the distillate until the undistilled residue is equal to about 10 per cent by weight of the refined condensation product subjected to distillation treatment, and sulfonating said fraction of distillate.

5. A method of producing higher alkyl benzene sulfonates adapted for use as a detergent, which comprises condensing one of the group consisting of a halogenated kerosene fraction of petroleum distillate and olefines derived therefrom with a benzene hydrocarbon in the presence of a Friedel and Crafts condensing agent, mechanically separating a condensation product comprising essentially higher alkyl benzene compounds from other constituents of the resulting condensation reaction mixture, distilling the separated condensation product, collecting a fraction of the distillate containing higher monoalkyl benzene compounds, and sulfonating resulting higher monoalkyl benzene compounds.

6. A method of producing higher alkyl benzene

sulfonates adapted for use as a detergent, which comprises condensing a chlorinated kerosene fraction of petroleum distillate with a benzene hydrocarbon in the presence of a Friedel and Crafts condensing agent, mechanically separating a condensation product comprising essentially higher alkyl benzene compounds from other constituents of the resulting condensation reaction mixture, distilling the separated condensation product at a subatmospheric pressure, collecting a fraction of the distillate containing a purified mixture of higher monoalkyl benzene compounds, and sulfonating the purified mixture of higher monoalkyl benzene compounds.

7. A method of producing higher alkyl benzene sulfonates adapted for use as a detergent, which comprises condensing one of the group consisting of a halogenated kerosene fraction of petroleum distillate and olefines derived therefrom with a benzene hydrocarbon in the presence of a Friedel and Crafts condensing agent, stratifying the resulting condensation reaction mixture into an oily layer comprising higher alkyl benzene compounds and a sludge-like layer containing other constituents, fractionally distilling the oily layer at a subatmospheric pressure, collecting a fraction of the distillate comprising essentially higher monoalkyl benzene compounds, and sulfonating said higher monoalkyl benzene compounds.

8. A method of producing higher alkyl benzene sulfonates adapted for use as a detergent which comprises condensing benzene with one of the group consisting of a halogenated kerosene fraction of petroleum distillate and olefines derived therefrom in the presence of aluminum chloride as a condensing agent, stratifying the resulting condensation reaction mixture into an upper oily layer containing higher alkyl benzene compounds and a lower layer containing the condensing agent and by-products of the condensation, distilling the oily layer at a subatmospheric pressure, separately collecting a distillate comprising essentially purified higher monoalkyl benzene compounds, and sulfonating the higher monoalkyl benzene compounds.

9. A method of producing higher alkyl benzene sulfonates adapted for use as a detergent which comprises condensing benzene with a chlorinated kerosene fraction of petroleum distillate in the presence of aluminum chloride as a condensing agent, stratifying the resulting condensation reaction mixture into an upper oily layer containing higher alkyl benzene compounds and a lower layer containing the condensing agent and by-products of the condensation, distilling the oily layer at a final absolute pressure not exceeding 30 mm. of mercury, collecting a fraction of the distillate until the undistilled residue is equal to about 10 per cent by weight of the refined condensation product subjected to distillation treatment, and sulfonating said fraction of distillate.

10. In the production a detergent mixture of higher alkyl benzene sulfonates by a process which comprises forming a benzene hydrocarbon condensation product of a poly-component non-aromatic hydrocarbon mixture of mineral origin and sulfonating the condensation product, the improvement which comprises condensing a benzene hydrocarbon with a chlorinated kerosene fraction of petroleum distillate in the presence of a Friedel and Crafts condensing agent, mechanically separating a condensation product comprising essentially higher alkyl benzene compounds from other constituents of the resulting condensation reaction mixture, and forming the detergent mixture of higher alkyl benzene sulfonates from the separated condensation product.

11. In the production a detergent mixture of higher alkyl benzene sulfonates by a process which comprises forming a benzene hydrocarbon condensation product of a poly-component non-aromatic hydrocarbon mixture of mineral origin and sulfonating the condensation product, the improvement which comprises condensing a benzene hydrocarbon with a chlorinated kerosene fraction of petroleum distillate in the presence of a Friedel and Crafts condensing agent, stratifying the resulting condensation reaction mixture into an oily layer comprising higher alkyl benzene compounds and a sludge-like layer containing other constituents, and forming the detergent mixture of higher alkyl benzene sulfonates from the oily layer.

12. In the production a detergent mixture of higher alkyl benzene sulfonates by a process which comprises forming a benzene hydrocarbon condensation product of a poly-component non-aromatic hydrocarbon mixture of mineral origin and sulfonating the condensation product, the improvement which comprises condensing a benzene hydrocarbon with a chlorinated kerosene fraction of petroleum distillate in the presence of a Friedel and Crafts condensing agent, to produce a condensation product containing higher monoalkyl benzene compounds, distilling the condensation product at an absolute pressure not exceeding 15 mm. of mercury, collecting a fraction of the distillate containing a purified mixture of higher monoalkyl benzene compounds, and sulfonating the purified mixture of higher monoalkyl benzene compounds.

13. In the production a detergent mixture of higher alkyl benzene sulfonates by a process which comprises forming a benzene hydrocarbon condensation product of a poly-component non-aromatic hydrocarbon mixture of mineral origin and sulfonating the condensation product, the improvement which comprises condensing a benzene hydrocarbon with a chlorinated kerosene fraction of petroleum distillate in the presence of a Friedel and Crafts condensing agent, to produce a condensation product containing higher monoalkyl benzene compounds, distilling the condensation product at an absolute pressure not exceeding 7 mm. of mercury, collecting a fraction of the distillate containing a purified mixture of higher monoalkyl benzene compounds, and sulfonating the purified mixture of higher monoalkyl benzene compounds.

14. In the production a detergent mixture of higher alkyl benzene sulfonates by a process which comprises forming a benzene hydrocarbon condensation product of a poly-component non-aromatic hydrocarbon mixture of mineral origin and sulfonating the condensation product, the improvement which comprises condensing a benzene hydrocarbon with a chlorinated kerosene fraction of petroleum distillate in the presence of an amount of aluminum chloride not exceeding 9 per cent of the weight of the chlorinated kerosene, mechanically separating a condensation product comprising essentially higher alkyl benzene compounds from other constituents of the resulting condensation reaction mixture, and forming the detergent mixture of higher alkyl benzene sulfonates from the separated condensation product.

15. In the production a detergene mixture of higher alkyl benzene sulfonates by a process which comprises forming a benzene hydrocarbon

condensation product of a poly-component non-aromatic hydrocarbon mixture of mineral origin and sulfonating the condensation product, the improvement which comprises condensing a benzene hydrocarbon with a chlorinated kerosene fraction of petroleum distillate in the presence of an amount of aluminum chloride not exceeding 5 per cent of the weight of the chlorinated kerosene, mechanically separating a condensation product comprising essentially higher alkyl benzene compounds from other constituents of the resulting condensation reaction mixture, and forming the detergent mixture of higher alkyl benzene sulfonates from the separated condensation product.

16. A method of producing higher alkyl benzene sulfonates adapted for use as a detergent which comprises reacting a benzene hydrocarbon with a halogenated kerosene fraction of petroleum distillate boiling mainly over a maximum range less than 100° C. in extent, with the aid of anhydrous aluminum chloride in an amount less than 9 per cent of the weight of the chlorinated kerosene, the amount of benzene employed being in excess of that required for the reaction, stratifying the resulting condensation reaction mixture into an oily layer containing higher alkyl benzene compounds and a layer containing the aluminum chloride sludge and by-products of the condensation, separating the layers, removing residual benzene hydrocarbon and other low-boiling constituents from the oily layer by distillation, distilling the resulting refined condensation product at an absolute pressure not exceeding 15 mm. of mercury, collecting a separate fraction of distillate until the distilland residue is equal to about 10 per cent by weight of the refined condensation product, and sulfonating the distillate.

17. A method of producing higher alkyl benzene sulfonates adapted for use as a detergent which comprises reacting benzene with a chlorinated kerosene fraction of a petroleum distillate of the Pennsylvania type boiling mainly over a maximum range less than 100° C. in extent, which has been chlorinated to an extent corresponding with from 75 per cent to 200 per cent chlorination, with the aid of anhydrous aluminum chloride in an amount less than 9 per cent of the weight of the chlorinated kerosene, the amount of benzene employed being in excess of one mol per atom of combined chlorine in the chlorinated kerosene, stratifying the resulting condensation reaction mixture into an upper oily layer containing higher alkyl benzenes and a lower layer containing the aluminum chloride sludge and by-products of the condensation, separating the layers, removing residual benzene and other low-boiling constituents from the oily layer by distillation. distilling the refined condensation product at a final absolute pressure not exceeding 15 mm. of mercury, collecting the resulting distillate while leaving at least 10 per cent by weight of the refined condensation product as residue, and sulfonating the collected distillate.

18. A method of producing higher alkyl benzene sulfonates adapted for use as a detergent which comprises reacting benzene with a chlorinated kerosene fraction of a petroleum distillate of the Pennsylvania type boiling mainly over a maximum range less than 100° C. in extent, which has been chlorinated to an extent corresponding with from 75 per cent to 200 per cent chlorination, with the aid of anhydrous aluminum chloride in an amount less than 5 per cent of the weight of the chlorinated kerosene, the amount of benzene employed being in excess of one mol per atom of combined chlorine in the chlorinated kerosene, stratifying the resulting condensation reaction mixture into an upper oily layer containing higher alkyl benzenes and a lower layer containing the aluminum chloride sludge and by-products of the condensation, separating the layers, removing residual benzene and other low-boiling constituents from the oily layer by distillation, distilling the resulting refined condensation product at an absolute pressure not exceeding 7 mm. of mercury, collecting the resulting distillate until the distillation temperature corresponds with about 200 C. at 4 mm. of mercury, and sulfonating the collected distillate.

LAWRENCE H. FLETT.

CERTIFICATE OF CORRECTION.

Patent No. 2,340,654. February 1, 1944.

LAWRENCE H. FLETT.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, line 60, for the serial number "195,415" read --195,414--; page 7, first column, line 6, for "100 C." read --100° C.--; page 8, second column, line 73, claim 15, for "detergene" read --detergent--; page 9, second column, line 44, for "200 C." read --200° C.--; 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 25th day of April, A. D. 1944.

Leslie Frazer

(Seal) Acting Commissioner of Patents.