Patented Mar. 30, 1943 2,314,929

# UNITED STATES PATENT OFFICE

2,314,929

## METHOD OF PRODUCING HIGHER ALKYL AROMATIC SULPHONATES

Lawrence H. Flett, Hamburg, N. Y., assignor to Allied Chemical & Dye Corporation, a corporation of New York

No Drawing. Application November 20, 1940, Serial No. 366,384

11 Claims. (Cl. 260—505)

This invention relates to improvements in methods of producing higher alkyl aromatic sulphonates useful as surface active agents and for detergent, wetting, penetrating, emulsifying and related purposes. It relates more particularly to improvements in methods of producing higher alkyl aromatic sulphonates from halogenated non-aromatic hydrocarbon mixtures by condensation with aromatic compounds with the aid of aluminum chloride as a condensation catalyst, followed by sulphonation of the condensation product.

An object of the invention is to provide improvements in the method of producing higher alkyl aromatic sulphonates from halogenated non-aromatic hydrocarbons, on the one hand, and aromatic compounds of the class consisting of hydrocarbons, chlorhydrocarbons and alkoxy substituted hydrocarbons of the benzene and naphthalene series, on the other hand, by condensation with the aid of aluminum chloride as a condensation catalyst, followed by sulphonation, whereby sulphonated products are obtained having improved properties.

Another object of the invention is to provide improvements in the method of producing higher alkyl aromatic sulphonates from halogenated non-aromatic hydrocarbons and aromatic compounds of the class referred to above by condensation with the aid of aluminum chloride as a condensation catalyst, followed by sulphonation, whereby sulphonated products are obtained which are sufficiently free from colored by-products to be commercially acceptable.

A further object of the invention is to provide improvements in the method of producing higher alkyl aromatic sulphonates from halogenated non-aromatic hydrocarbons and aromatic compounds of the class referred to above by condensation with the aid of aluminum chloride as a condensation catalyst, followed by sulphonation, whereby sulphonated products are obtained having improved surface active, detergent, wetting and penetrating action.

An additional object of the invention is to provide improvements in the method of producing higher alkyl aromatic sulphonates of the benzene series from chlorinated kerosene fractions of petroleum distillates and aromatic hydrocarbons of the benzene series by condensation with the aid of aluminum chloride as a condensation catalyst, followed by sulphonation, whereby sulphonated products are obtained which are sufficiently free from colored by-products to be commercially acceptable, and which have improved surface active, detergent, wetting and penetrating action.

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

Alkyl aromatic sulphonates in which a higher alkyl group is present as a substituent in the aromatic nucleus represent a desirable class of products, particularly in the form of their alkali metal and organic ammonium salts, for use as substitutes for soaps 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.

One method for producing alkyl aromatic sulphonates involves halogenating a mixture of non-aromatic hydrocarbons, condensing the resulting mixture of halogenated hydrocarbons with the aromatic compound of the type desired in the final product, sulphonating the resulting condensation product, and recovering the sulphonated product, after conversion to a salt when desired. Thus, one method of producing an alkyl benzene sulphonate product comprises chlorinating a petroleum distillate, condensing the resulting mixture of alkyl chlorides with benzene with the aid of a small amount of anhydrous aluminum chloride as a catalyst, separating the resulting mixture of alkyl benzenes from the condensation mass, sulphonating the mixture of alkyl benzenes to produce a mixture of alkyl benzene sulphonates, neutralizing the sulphonation reaction mixture with aqueous sodium hydroxide solution, and recovering the resulting mixture of sodium alkyl benzene sulphonates.

The products obtained by this process have the disadvantages that they are highly colored and have insufficient cleansing ability to be commercially acceptable as substitutes for soap in the usual household and textile uses. In general, soap substitutes which are colored are not acceptable because they stain goods treated with them and leave deposits which later develop stains in the goods. Furthermore, their appearance is unattractive and they dissolve in water to form undesirably colored solutions. While in some cases the color of the products can be improved by treatment with reducing agents, as for example zinc and acetic acid or zinc dust, or with oxidizing agents, such treatments are costly and result in yield losses while the improvement in color which is produced is generally of a temporary nature.

According to the present invention alkyl aromatic sulphonates of commercially acceptable color and of sufficient detergent, wetting and surface active action to be commercially acceptable as soap substitutes are obtained by incorporating into the process of producing the alkyl aromatic sulphonates the improvements hereinafter disclosed and claimed in the appended patent claims.

This application is a continuation-in-part of my application Serial No. 186,231, filed January 21, 1938, now U. S. P. 2,223,364, which is a continuation-in-part of my application Serial No.

93,719, filed July 31, 1936, now U. S. P. 2,195,409.

As disclosed in my application Serial No. 186,231, I have found that higher alkyl benzene sulphonates which in the form of solids are a pale yellow to white color, dissolving in water to form clear, almost colorless solutions which possess excellent washing and wetting properties, are obtained in good yield by chlorinating a kerosene fraction of petroleum distillate to an extent such that the resulting chlorination reaction mixture contains an amount of organically combined chlorine substantially corresponding with 100 to 140 per cent complete monochlorination of the kerosene hydrocarbons, reacting benzene with the resulting chlorkerosene mixture (comprising higher alkyl monochlorides together with some polychlorides and unchlorinated kerosene) in the presence of an amount of anhydrous aluminum chloride equal to 5 per cent to 20 per cent of the weight of the chlorkerosene mixture at temperatures not exceeding 110° C., separating the light-colored oily mixture of alkyl benzenes from the dark-colored sludge produced as a by-product, distilling off excess benzene from the mixture of alkyl benzenes, reacting the mixture of alkyl benzenes with a sulphonating agent, and neutralizing the sulphonated product with sodium hydroxide in aqueous solution. The oily mixture of alkyl benzenes obtained as an intermediate product by this procedure are but faintly colored, and the sulphonated products without further purification are sufficiently free from objectionable colored by-products to be acceptable for commercial sale and use.

In the practice of the present invention in accordance with one preferred method of procedure, a non-aromatic hydrocarbon mixture, more particularly one containing at least 10 carbon atoms, and preferably about 12 to about 30 carbon atoms per molecule, is halogenated 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 resulting mixture of halogenated hydrocarbons (herein generically designated by the term "alkyl halide mixture") is reacted with the aromatic compound to be alkylated, in the presence of an amount of aluminum chloride equal to less than 5 per cent of the weight of the alkyl halide mixture (generally 4 per cent or less of the weight of the alkyl halide mixture) and at a temperature which does not exceed 130° C.; the condensation reaction mass is permitted to stratify into an upper layer containing mainly a mixture of alkyl aromatic compounds and a lower layer of darkly colored sludge; the upper layer is removed from the lower layer and is subjected to further treatment at a temperature not exceeding 130° C. with an additional amount of aluminum chloride, the total amount of aluminum chloride being at least 5 but not more than 20 per cent of the weight of the alkyl halide mixture, the resulting reaction mass is permitted to stratify into an upper layer containing mainly a mixture of alkyl aromatic compounds and a lower layer of darkly colored sludge; the upper layer is removed from the lower layer, and the mixture of alkyl aromatic compounds is subjected to sulphonation. The resulting mixture of sulphonic acids is preferably converted into a mixture of their corresponding salts. If inorganic salts are simultaneously formed, they may be left in the mixture of said sulphonic acid salts, or they may be separated therefrom, as the use of the product may determine.

I have found, in accordance with one feature of the present invention, that the use of a total amount of aluminum chloride equal to 5 to 20 per cent of the weight of the alkyl halide mixture at a temperature not exceeding 130° C., in conjunction with separation of the mixed alkyl aromatic compounds from the sludge formed as a by-product, results in a product which when sulphonated has superior properties with respect to color and surface active action, as compared with products obtained with a smaller amount of aluminum chloride and/or at higher temperatures. I have further found, in accordance with another feature of the present invention, that the halogenation of the non-aromatic hydrocarbon mixture to an extent such that the resuling 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, results in commercially satisfactory yields of alkyl aromatic sulphonates notwithstanding the use of the relatively large amounts of aluminum chloride employed in accordance with the present invention, especially when amounts of aluminum chloride not exceeding 15 per cent of the weight of the alkyl halide mixture are employed.

It was heretofore known to condense an alkyl halide with an aromatic hydrocarbon with the aid of anhydrous aluminum chloride as a catalyst, but in order to avoid low yields of alkyl aromatic product the amount of aluminum chloride employed was limited to amounts just adequate to effect the condensation, generally below 4 per cent of the weight of alkyl halide or alkyl halide mixture. When a halogenated fraction of petroleum distillate containing an amount of organically combined halogen substantially corresponding with 75 per cent to 175 per cent complete monohalogenation of the hydrocarbon mixture, as for example chlorinated kerosene containing an amount of organically combined chlorine corresponding with about 125 per cent monochlorination of the kerosene is condensed with an aromatic hydrocarbon, for example, benzene, toluene, etc., with the aid of anhydrous aluminum chloride in a catalytic amount, for example, less than 4 per cent by weight of the alkyl halide mixture, the resulting alkyl aromatic condensation products are inferior in quality and the sulphonated mixtures derived therefrom are highly colored.

The present invention comprehends a procedure in which the condensation of the alkyl halide mixture with the aromatic constituent is carried out at a temperature below 130° C. with a small amount of anhydrous aluminum chloride (4 per cent or less of the weight of the alkyl halide mixture) and the resulting condensation product is then subjected to further treatment at a temperature below 130° C. with additional anhydrous aluminum chloride, to effect the improved result of the present invention.

The invention will be illustrated by the following specific 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. For convenience a product obtained by chlorinating a kerosene fraction of petroleum is termed "keryl chloride" and the product obtained by condensing the keryl chloride with toluene, for example, is termed "keryl toluene."

### EXAMPLE 1

*Part 1.*—A kerosene fraction of Pennsylvania petroleum distillate of the type employed in Example 1 of my U. S. Patent No. 2,223,364 to which a small amount of iodine (0.05 part per 100) was added as a halogenating catalyst, was chlorinated by passing therethrough a stream of chlorine gas while the mixture was maintained at about 60° until organically combined chlorine in the mixture corresponded to about 125 per cent of the amount theoretically required for complete monochlorination. 150 parts of this chlorinated oil were added in a small stream to a well agitated mixture of 100 parts of benzene and 6 parts of anhydrous aluminum chloride. The reaction mixture was maintained throughout the addition from about 30° to about 60° and, after the addition of the chlorinated oil, was stirred for about 6 hours, and then allowed to stand for about 10 hours. The upper layer of oil was separated from the lower tarry mass, and heated to remove therefrom unreacted benzene by distillation. The resulting product was a dark brown oil consisting mainly of nuclearly alkylated benzenes in which the alkyl groups averaged about 13 to 14 carbon atoms.

*Part 2.*—110 parts of the dark brown oil were agitated with 10 parts of anhydrous aluminum chloride and 70 parts of kerosene as a diluent, for about 3 hours while maintaining the temperature at about 55° to about 60°. The mixture was then allowed to stand and to separate into two layers. The upper layer of yellow oil was decanted from the lower layer of black tarry matter. After being washed with about half its volume of water, the decanted oil was distilled until all volatile material therein boiling below 120° at 5 mm. mercury was removed. The residual oil was a pale yellow mobile liquid weighing 97 parts. For the production of a sulphonated product, 1 part of the resulting oil was mixed with about 1.1 to about 1.3 parts of 26 per cent oleum at a temperature of 5° to 15° and was further treated to obtain the sulphonated product in the form of the sodium salt by pouring the sulphonation mixture (when 1 part of a test portion, after neutralizing with sodium hydroxide, was soluble in 20 parts of water) into approximately 12.5 parts of an ice-water mixture, neutralizing the resulting solution to Brilliant yellow and Congo red papers with concentrated aqueous caustic alkali (e. g., a 50% aqueous solution of sodium hydroxide), and evaporating the neutralized solution to dryness on a rotary drum drier. The dry sulphonated product was a faintly yellow, friable solid which dissolved readily in water to give clear, substantially colorless solutions having excellent wetting and detergent properties.

When the dark brown oil, resulting from the procedure of Part 1 of this example, was sulphonated and recovered in the same manner, the resulting product was a dark brownish solid which dissolved in water to form brownish colored solutions which, on the basis of equal concentrations of alkyl aromatic sulphonates, possessed inferior wetting and washing properties as compared with the product obtained by the further treatment in accordance with Part 2 of this example.

The procedure of Example 1 may be applied in a similar manner to the preparation of the other alkyl aromatic sulphonates disclosed in the present application and especially those disclosed in Examples 1 to 5 inclusive of my United States Patent 2,223,364. Instead of carrying out the process in two stages, as disclosed in Parts 1 and 2 of Example 1, the process may be carried out in three or more stages. Further, the invention includes procedures in which residual benzene or residual other aromatic compounds employed as starting material are not removed by distillation prior to the additional treatment with aluminum chloride, and/or lower boiling constituents are not removed from the alkyl aromatic compounds resulting from the aluminum chloride treatment.

### EXAMPLE 2

1200 grams of a kerosene fraction of Pennsylvania petroleum distillate, having a boiling range of approximately 185° to 280° and a specific gravity of 0.7888 at 24° which on the basis of its source and properties was considered to be a mixture of hydrocarbons (mainly open chain aliphatic hydrocarbons) having an average molecular carbon content of 13 to 14 carbon atoms and a range from about 11 to about 16 carbon atoms per molecule, were chlorinated by passing therethrough chlorine gas at such a rate that about 4.25 grams per minute reacted with the kerosene. During the chlorination, the kerosene was agitated and maintained at a temperature between 60° and 62°. After about 2 hours of chlorination, a current of air was passed through the agitated charge to sweep out dissolved hydrogen chloride and chlorine. The charge had gained in weight by 257 grams and had a specific gravity of 0.917 at 24°.

Four condensations, which were alike in all respects except with regard to the treatment with anhydrous aluminum chloride, were made from the foregoing chlorinated kerosene mixture (keryl chloride).

In run #1, 608 grams toluene and 27.4 grams anhydrous aluminum chloride were agitated, and 304 grams of the chlorinated kerosene mixture were run in over a period of about 20 minutes without heating or cooling the mixture. The reacting mass was then warmed to 45° and agitated at 44° to 46° for 1½ hours.

In runs #2, #3 and #4, this procedure was followed, but 9 grams instead of 27.4 grams of anhydrous aluminum chloride were used in each case.

From this point, the four condensations differed as follows:

Runs #1 and #4 were allowed to stand for about 16 hours before the next process step, which is described below.

Run #2 was treated with an additional 18.2 grams anhydrous aluminum chloride, and agitated at 44° to 46° for 1½ hours and allowed thereafter to stand for about 16 hours.

Run #3 was allowed to stand ½ hour; a tarry layer which separated on standing was removed and discarded; agitation was resumed and 9 grams of additional anhydrous aluminum chloride were added to the mass which was then agitated for 1½ hours at 44° to 46°; the mass was again allowed to stand ½ hour; a tarry layer was again removed; agitation was then resumed and another 9 grams anhydrous aluminum chloride were added; the mass was then stirred for 1½ hours at 44° to 46° and allowed to stand about 16 hours.

From this point, each of the runs was treated in the same manner.

After the 16 hour period of standing, a separated lower tarry layer of the mixture was removed, and the upper layer of oily liquid was distilled, first at atmospheric pressure to a vapor temperature of 125° to remove most of the unreacted toluene and then at reduced pressure to a vapor temperature of 80° at 4 millimeters of mercury absolute pressure. In each run, the residual distilland was a light-amber oil comprising a mixture of alkyl toluene condensation products. The residual distillands from runs 1, 2, 3 and 4, in the order named, weighed 223, 238, 227 and 284 grams, respectively.

Each of the four residual distillands comprising mixtures of alkyl toluene condensation products was then sulphonated by the following procedure. 100 grams of the distilland were agitated at room temperature for about ¾ hour with 10 cc. of 100 per cent sulphuric acid. After standing for about ½ hour, the acid layer was drawn off and discarded. The refined oily material was then agitated and sulphonated by adding 100 cc. of sulphuric acid monohydrate at room temperature during 10 to 20 minutes, and then agitating for one hour at 55 to 60°. After adding 2 cc. of water to the sulphonation mixture and agitating briefly, the mass was allowed to stratify for one hour. Two layers formed. The upper sulphonic acid layer was separated from the lower spent acid layer which was discarded. The sulphonic acid layer was poured onto about 250 grams of cracked ice and the resulting solution neutralized. Sufficient sodium sulphate was added to adjust the inorganic salt content of the solute to 60 per cent and the resulting solution was dried on a double drum drier.

The four detergent preparations so obtained were tested for solution color, wetting power and detergency for dirty wool.

The results are given in the table.

The method of comparing colors of solutions and determining the percentage values of colors as given in the table was as follows: 100 cc. of a 5 per cent solution of the dry 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 and the color was expressed in terms of the percentage which the volume of the diluted solution of the sample represented with respect to the volume of the standard solution. In the event that a solution of the dry product was less colored than that of the standard light-colored solution, a 100 cc. sample of the latter solution was diluted with water and compared with 100 cc. of solution of the sample undergoing examination until the color of the diluted standard solution was substantially equal to that of the sample, and the color of the sample was expressed in terms of the percentage of the sample volume with respect to the volume of the diluted standard solution. Thus, a product is said to have a color of 195%, when on starting with a solution of the same concentration as the standard solution it is necessary to dilute the solution to 1.95 times its original volume before its color matches that of the standard; similarly a product is said to have a color of 75 per cent when it is necessary to dilute the standard solution to 1.33 times its original volume before its color matches that of the sample.

Wetting power was measured by determining the length of time necessary to wet out a standard sized sample of standard fabric with a solution of the product at definite temperature and concentration. 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°. A No. 10 canvas disk 1 inch in diameter was placed on the surface of the solution and immediately cupped in a long-stem inverted funnel and forced below the liquid level to a depth of 5 to 6 centimeters. The time from cupping until the disk commenced to fall out of the funnel was measured and is given as the wetting time.

The wool-washing tests were conducted as follows: A sample of wool cloth was uniformly soiled with lamp black, tallow and mineral oil. It was then cut into pieces of approximately equal size (4 inches by 4 inches) which were washed in a Launderometer in 200 cc. of solution of product for a standard period of 30 minutes at 45°. Two series of washings were made. In one series, the solutions used for the washing tests contained 0.1% of product dissolved in distilled water, and in the other series, the solutions contained 0.18% of product dissolved in water of 12° hardness (American scale). The degree of washing was determined by taking readings of reflected light (brightness) from the washed cloth with a Pfaltz and Bauer universal photoelectric reflectometer. The readings determined increased brightness which was measured by the difference in the readings obtained with the reflectometer on the soiled cloth before and after washing.

TABLE

*Data on preparation and testing of keryl toluene sulphonates produced with different amounts of anhydrous aluminum chloride*

| Run No. | Detergent yield (1) (Expressed as G. of keryl toluene sulphonate produced per kilogram of kerosene consumed) | Aluminum chloride used (expressed as percent based on keryl chloride) | | | Color of detergent product | Wetting time | Detergency expressed as brightness increase (orig. brightness of soiled wool was 19) | |
|---|---|---|---|---|---|---|---|---|
| | | During condensation | For subsequent treating | Total | | | 0.1% concn. in soft water | 0.18% concn. in 12° hard water |
| | | *Per cent* | | *Per cent* | *Per cent* | *Minutes* | | |
| 1 | 884 | 9 | ---------------- | 9 | 75 | 0.63 | 21 | 38 |
| 2 | 961 | 3 | 6% without first sepg. tar from catalyst. | 9 | 110 | 0.77 | 22.5 | 38 |
| 3 | 920 | 3 | Two 3% increments with intermediate tar separation. | 9 | 100 | 0.68 | 22 | 37 |
| 4 | 1015 | 3 | ---------------- | 3 | 195 | 0.70 | 14 | 29 |

Data on yield presented in the table show that the highest yields of organic detergnet material were obtained in run #4 in which 3% aluminum chloride was used to effect the condensation and no subsequent treatment with aluminum chloride was carried out. Evidently 3% aluminum chloride is adequate to insure completion of the condensation reaction of keryl chloride with benzene. Treatment with more than 3% aluminum chloride as in runs 1, 2 and 3 causes the yield of organic detergent material to be decreased by about 10%. The surprising discovery has been made that this loss in yield is more than compensated for by improvement in detergent quality.

It is evident from the table that the detergent derived from a condensation product, made with an amount of aluminum chloride equal to 3 per cent of the weight of chlorinated kerosene used in the condensation is characterized by lesser washing action and darker color than the detergent which was made with an amount of aluminum chloride equal to 9 per cent of the kerosene chloride used in the condensation; and that the inferiority of the former detergent can be overcome and avoided by treating the condensation reaction mass (made with 3% aluminum chloride) with an additional amount (6%) of aluminum chloride. This treatment with the additional amount of aluminum chloride may be effected equally well with or without preliminary removal of spent catalyst from the condensation reaction. The treatment with the additional aluminum chloride is also equally effective as far as quality of final detergent composition is concerned if the additional aluminum chloride is added all at one time or in increments with intermediate separation of tarry sludges produced between additions of the said increments.

In the above examples the amount of aluminum chloride employed can be increased up to 20 per cent of the weight of the alkyl chloride mixture, but amounts in excess of about 15 per cent are not preferred for the obtainment of desirable yields.

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 hydrocarbon mixtures which may be employed as starting materials in accordance with the present invention are non-aromatic hydrocarbon mixtures, preferably aliphatic hydrocarbon mixtures, and especially mineral oil distillates, containing from 10 carbon atoms to 30 carbon atoms, and preferably from 12 to 28 carbon atoms. The particular type of hydrocarbon mixture employed will vary, depending upon the specific use for which the product is designed and the particular aromatic nucleus with which it is combined, as will be evident to those acquainted with the art. (By the term "non-aromatic hydrocarbon mixtures" as employed herein, I mean hydrocarbon mixtures containing essentially straight and/or branched open chain saturated hydrocarbons and/or alicyclic hydrocarbons and which may contain other hydrocarbons but not more than 20 per cent of aryl hydrocarbons, such as petroleum, petroleum distillates, artificially or synthetically prepared mixtures, etc.)

As is well known in the art, petroleum distillates are mainly mixtures of aliphatic hydrocarbons, including both saturated acyclic aliphatic hydrocarbons containing straight or branched carbon chains and cyclic aliphatic hydrocarbons, as well as some aromatic hydrocarbons and 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 products of the present invention, mixtures of various halogenated derivatives of the said aliphatic hydrocarbons (alkyl halides) are produced 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 sulphonated, compositions are produced which contain mixtures of sulphonated alkyl aromatic compounds differing from each other in the alkyl groups, which groups correspond with the aliphatic hydrocarbons of the mixture employed.

The preferred hydrocarbon mixtures employed in accordance with the present invention are exemplified by fractions of Pennsylvania and Michigan (Mount Pleasant) petroleum distillates. These distillates consist essentially of open chain aliphatic (paraffinic) hydrocarbons a large portion of which are 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 halogenation of the non-aromatic hydrocarbon mixture 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.

The aromatic compounds preferably employed in accordance with the present invention are the various aromatic hydrocarbons and their alkoxy and halogen derivatives, as for example benzene, toluene, xylene, diphenyl, naphthalene, monochlorbenzene, anisole, phenetole.

To effect the improved results of the present invention, the temperature at which the mixed alkyl halides and the aromatic compounds are condensed in the presence of the relatively large amounts of anhydrous aluminum chloride ought not exceed 130 C., and is preferably between about 20° and 80° C. In general at temperatures below 80° C., the condensations are slow, incomplete and cause lower yields of desired condensation products; while condensations effected at temperatures above 130° C. result in compositions which comprise undesirable compounds that increase in amount and in undesirable properties as the temperature of condensation increases, until at temperatures above about 160° C. the compositions are of little if any value for the manufacture of commercially acceptable alkyl aromatic sulphonates.

The proportion of mixed alkyl halides employed with respect to the aromatic compound in the preparation of the alkylated aromatic compounds may be varied. Preferably the proportion of mixed halogenated hydrocarbons employed with respect to the aromatic compound is such that only one higher alkyl radical is contained in the resulting alkyl aromatic compounds. Thus, at least 1.25 mols of aromatic compound per mol of mixed halogenated hydrocarbons is ordinarily employed in the condensation. A molar ratio as low as 1 to 1 may be employed, but the yield of the resulting mixed alkyl aromatic compounds containing one long alkyl group will be less.

The sulphonation of the mixture of alkyl aromatic compounds may be carried out with any suitable agent; as for example, sulphuric acids of various strengths (66° Be., 100 per cent, 26 per cent oleum, 65 per cent oleum, etc.), chlorsulphonic acid, etc. The sulphonation may be carried out in the presence of inert solvents or diluents, as for example, the halogenated aliphatic or aromatic hydrocarbons (carbon tetrachloride, tetrachlor ethane, ethylene dichloride, dichlorbenzene, etc.) or sulphonation may be carried out in their absence. When an inert solvent or diluent is used, it may be separated mechanically or by evaporation from the alkaline aqueous solution of the sulphonic acid salts of the alkyl aromatic compounds which results upon diluting the sulphonation mass with water and adding an alkali. If desired, sulphonation assistants may be employed, as for example the lower fatty acids and their anhydrides (e. g., acetic acid, acetic anhydride, etc.) or the alkali metal sulphates (e. g., sodium or potassium sulphate, etc.).

The temperature at which the sulphonation is carried out may vary within wide limits. For example, temperatures as low as about 0° and as high as about 140° may be employed. In general the more vigorous the sulphonation agent the lower is the preferred temperature. Preferred sulphonation temperatures lie between about 5° and about 90°.

The ratio of sulphonating agent employed with respect to the mixture of alkyl aromatic compounds also may be varied. Thus, for complete sulphonation, the sulphonating agent in terms of 100 per cent sulphuric acid may range from 0.3 to 5 times or more the weight of the alkyl aromatic compounds to be sulphonated. The extent to which the sulphonation is carried out may vary with the individual material being sulphonated, the duration or time of sulphonation, and the use to be made of the sulphonated product. In some cases, a degree of sulphonation which corresponds with a product having maximum detergent properties is not completely soluble in water to form a clear solution and/or may cause some precipitation of lime salts. On the other hand, a product which causes no precipitation of lime salts may not have maximum obtainable detergent properties because of excessive sulphonation. Furthermore, in some cases the degree of sulphonation may not be the same for products to be used as detergents in soft water, in hard water and in alkaline solutions. (As a standard of comparison, an aqueous solution of calcium chloride equivalent to 0.224 gram calcium oxide per liter of solution is employed as a standard hard water.)

The sulphonated products may be prepared in the form of their free sulphonic acids or in the form of salts. They are preferably prepared in accordance with the present invention in the form of salts of the alkali metals. The salts may be obtained in any suitable manner; for example, by reacting the sulphonated product with a metal oxide or hydroxide, ammonia or an organic base, or of a suitable salt of one of these, in an amount adapted to form a neutral product. Among the bases, oxides and salts which may be combined with the sulphonated products to produce salts in accordance with the present invention are, for example, sodium, potassium and ammonium hydroxides; sodium potassium and ammonium carbonates and bicarbonates; ammonia; magnesium oxide; ethylamine; pyridine; triethanolamine; propanolamines; butanolamines; diamino propanol; ethylene diamine; triethylene tetramine; aniline; o-toluidine; etc.

The reaction mixtures resulting from the sulphonation of the mixed alkyl aromatic compounds may also be directly employed for the formation of mixed products, as for example, mixtures of salts of the alkyl aromatic sulphonic acids and other acids present in said reaction mixtures. Thus, the sulphonation reaction mixture resulting from the treatment of the mixed alkyl aromatic compounds with an amount of sulphonating agent in excess of that theoretically required to effect the desired degree of sulphonation may be treated with a suitable inorganic or organic base or basic salt (as for example, one of those mentioned) and the resulting mixture of the salts of the sulphonated alkyl aromatic compounds and the inorganic salt (as for example, sodium sulphate) may be jointly isolated from the reaction mixture and employed as such. If it is desired to produce salts of the sulphonated alkyl aromatic compounds in a form substantially free from inorganic salts (for example, inorganic sulphates) this may be accomplished by taking advantage of their greater solubility than the inorganic salts in alcohol and other organic solvents, or by using an amount of chlorsulphonic acid such that no excess, or only a relatively small excess of it is present in the final sulphonation mass or mixture.

I claim:

1. In the method of producing higher alkyl aromatic sulphonates from non-aromatic hydrocarbons and aromatic compounds of the class consisting of hydrocarbons, monochlor hydrocarbons, and alkoxy-substituted hydrocarbons of the benzene and naphthalene series, by halogenation of the non-aromatic hydrocarbons, condensation of the alkyl halides with the aromatic compound with the aid of aluminum chloride as a condensation catalyst, followed by sulphonation, the improvement which comprises halogenating the non-aromatic hydrocarbons 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 non-aromatic hydrocarbons, condensing the resulting alkyl halide mixture with the aromatic compound and an amount of aluminum chloride equal to less than 5 per cent of the alkyl halide mixture at a temperature not exceeding 130° C., subjecting the resulting alkyl aromatic compounds to further treatment at a temperature not exceeding 130° C. with an additional amount of aluminum chloride, the total amount of aluminum chloride being 5 to 20 per cent of the alkyl halide mixture,

and separating the resulting alkyl aromatic compounds from the reaction product.

2. In the method of producing higher alkyl aromatic sulphonates from non-aromatic hydrocarbons and aromatic compounds of the class consisting of hydrocarbons, monochlor hydrocarbons, and alkoxy-substituted hydrocarbons of the benzene and naphthalene series, by chlorination of the non-aromatic hydrocarbons, condensation of the alkyl chlorides with an aromatic compound with the aid of aluminum chloride as a condensation catalyst, followed by sulphonation, the improvement which comprises chlorinating the non-aromatic hydrocarbons 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 non-aromatic hydrocarbons, condensing the resulting alkyl chloride mixture with the aromatic compound and an amount of aluminum chloride equal to not more than 4 per cent of the alkyl chloride mixture at a temperature not exceeding 130° C., subjecting the resulting alkyl aromatic compounds to further treatment at a temperature not exceeding 130° C. with an additional amount of aluminum chloride, the total amount of aluminum chloride being 5 to 20 per cent of the alkyl chloride mixture, and separating resulting alkyl aromatic compounds from the reaction product.

3. In the method of producing higher alkyl benzene sulphonates from non-aromatic hydrocarbons and benzene by chlorination of the non-aromatic hydrocarbons, condensation of the alkyl chlorides with benzene with the aid of aluminum chloride as a condensation catalyst, followed by sulphonation, the improvement which comprises chlorinating a petroleum hydrocarbon distillate containing 10 to 30 carbon atoms 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, condensing the resulting alkyl chloride mixture with benene and an amount of aluminum chloride equal to less than 5 per cent of the alkyl chloride mixture at a temperature not exceeding 130° C., subjecting the resulting alkyl benzene compounds to further treatment at a temperature not exceeding 130° C. with an additional amount of aluminum chloride, the total amount of aluminum chloride being 5 to 20 per cent of the alkyl chloride mixture, and separating resulting alkyl condensation compounds from the reaction product.

4. The method of producing sulphonated products having surface active properties, which comprises chlorinating a petroleum hydrocarbon distillate containing 10 to 30 carbon atoms 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, condensating the resulting alkyl chloride mixture with an aromatic hydrocarbon of the benzene and naphthalene series at a temperature not exceeding 130° C. in the presence of an amount of anhydrous aluminum chloride equal to less than 5 per cent of the alkyl chloride mixture, separating the resulting condensation product from the reaction product, subjecting the condensation product to further treatment at a temperature not exceeding 130° C. with an additional amount of anhydrous aluminum chloride, the total amount of aluminum chloride being 5 to 20 per cent of the alkyl chloride mixture, separating resulting mixed alkyl aromatic compounds from the sludge formed as a by-product of the treatment, and sulphonating resulting mixed alkyl aromatic compounds.

5. The method of producing sulphonated products having surface active properties, which comprises chlorinating a petroleum hydrocarbon distillate containing 10 to 30 carbon atoms 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, condensating the resulting alkyl chloride mixture with an aromatic hydrocarbon of the benzene and naphthalene series at a temperature between 20° and 80° C. in the presence of an amount of anhydrous aluminum chloride equal to not more than 4 per cent of the alkyl chloride mixture, separating the resulting condensation product from the reaction product, subjecting the condensation production to further treatment at a temperature between 20° and 80° C. with an additional amount of anhydrous aluminum chloride, the total amount of aluminum chloride being 5 to 20 per cent of the alkyl chloride mixture, separating resulting mixed alkyl aromatic compounds from the sludge formed as a by-product of the treatment, subjecting the resulting mixed alkyl aromatic compounds to distillation to remove lower boiling substances than the alkyl aromatic compounds, and sulphonating resulting mixed alkyl aromatic compounds.

6. The method of producing sulphonated products having surface active properties, which comprises chlorinating a petroleum hydrocarbon distillate containing 10 to 30 carbon atoms 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, condensing the resulting alkyl chloride mixture with benzene in the presence of anhydrous aluminum chloride in an amount equal to less than 5 per cent of the weight of the alkyl chloride mixture at a temperature not exceeding 130° C., separating the resulting alkyl benzene mixture from the sludge formed as a by-product of the reaction, subjecting the alkyl benzene mixture to further treatment at a temperature not exceeding 130° C. with an additional amount of anhydrous aluminum chloride, the total amount of aluminum chloride being 5 to 20 per cent of the alkyl chloride mixture, separating resulting mixed alkyl benzenes from the sludge formed as a by-product of the treatment, subjecting the resulting mixed alkyl benzenes to distillation to remove lower boiling substances than the alkyl benzene, and sulfonating the alkyl benzenes.

7. The method of producing sulphonated products having surface active properties, which comprises chlorinating a petroleum hydrocarbon distillate containing 10 to 30 carbon atoms 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, condensing the resulting alkyl chloride mixture with benzene in the presence of anhydrous aluminum chloride in an amount equal to less than 5 per cent of the weight of the alkyl chloride mixture at a temperature not exceeding

130° C., separating the resulting condensation product from the sludge formed as a by-product of the reaction, distilling residual benzene from the condensation product, subjecting the resulting condensation product to further treatment at a temperature not exceeding 130° C. with an additional amount of anhydrous aluminum chloride, the total amount of aluminum chloride being 5 to 20 per cent of the alkyl chloride mixture, separating the resulting alkyl benzene mixture from the sludge formed as a by-product of the treatment, subjecting the alkyl benzene mixture to vacuum distillation to remove lower boiling substances than the alkyl benzenes, and sulfonating the remaining alkyl benzene mixture.

8. The method of producing sulphonated products having surface active properties, which comprises chlorinating a paraffinic petroleum hydrocarbon distillate containing 12 to 30 carbon atoms to an extent such that the resulting chlorination reaction mixture contains an amount of organically combined chlorine substantially corresponding with 100 per cent to 140 per cent complete monochlorination, condensing the resulting alkyl chloride mixture with benzene at a temperature between 20° and 80° C. in the presence of anhydrous aluminum chloride in an amount equal to less than 5 per cent of the alkyl chloride mixture, separating the resulting condensation product from the sludge formed as a by-product of the reaction, subjecting the condensation product to further treatment at a temperature between 20° and 80° C. with an additional amount of anhydrous aluminum chloride, the total amount of aluminum chloride being 5 to 20 per cent of the alkyl chloride mixture, separating the resulting alkyl benzene mixture from the sludge formed as a by-product of the treatment, subjecting the alkyl benzene mixture to vacuum distillation to remove lower boiling substances than the alkyl benzenes, and sulphonating the remaining alkyl benzene mixture.

9. The method of producing sulphonated products having surface active properties, which comprises chlorinating a paraffinic petroleum hydrocarbon distillate of the Pennsylvania type containing 12 to 30 carbon atoms to an extent such that the resulting chlorination reaction mixture contains an amount of organically combined chlorine substantially corresponding with 100 per cent to 140 per cent complete monochlorination, condensing the resulting alkyl chloride mixture with benzene at a temperature between 20° and 80° C. in the presence of anhydrous aluminum chloride in an amount equal to not more than 4 per cent of the alkyl chloride mixture, separating the resulting condensation product from the sludge formed as a by-product of the reaction, distilling residual benzene from the condensation product, subjecting the condensation product to further treatment at a temperature between 20° and 80° C. with an additional amount of anhydrous aluminum chloride, the total amount of aluminum chloride being 5 to 15 per cent of the alkyl chloride mixture, separating the resulting alkyl benzene mixture from the sludge formed as a by-product of the treatment, subjecting the alkyl benzene mixture to vacuum distillation to remove lower boiling substances than the alkyl benzenes, and sulphonating the remaining alkyl benzene mixture.

10. The method of producing sulphonated products having surface active properties, which comprises chlorinating a petroleum hydrocarbon distillate containing 10 to 30 carbon atoms 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, condensing the resulting alkyl chloride mixture with an aromatic hydrocarbon of the benzene and naphthalene series at a temperature between 20° and 80° C. in the presence of an amount of anhydrous aluminum chloride equal to not more than 4 per cent of the alkyl chloride mixture, subjecting the condensation product to further treatment at a temperature between 20° and 80° C. with an additional amount of anhydrous aluminum chloride, the total amount of aluminum chloride being 5 to 20 per cent of the alkyl chloride mixture, separating a resulting liquid product containing mixed alkyl aromatic compounds from the sludge formed as a by-product of the treatment, subjecting the separated liquid product to distillation to remove lower boiling substances than the alkyl aromatic compounds, and sulphonating the mixed alkyl aromatic compounds.

11. The method of producing sulphonated products having surface active properties, which comprises chlorinating a paraffinic petroleum hydrocarbon distillate containing 12 to 30 carbon atoms to an extent such that the resulting chlorination reaction mixture contains an amount of organically combined chlorine substantially corresponding with 100 per cent to 140 per cent complete monochlorination, condensing the resulting alkyl chloride mixture with benzene at a temperature between 20° and 80° C. in the presence of anhydrous aluminum chloride in an amount equal to less than 5 per cent of the alkyl chloride mixture, subjecting the condensation product to further treatment at a temperature between 20° and 80° C. with an additional amount of anhydrous aluminum chloride, the total amount of aluminum chloride being 5 to 20 per cent of the alkyl chloride mixture, separating a resulting liquid product containing a mixture of alkyl benzenes from the sludge formed as a by-product of the treatment, subjecting the separated liquid product to vacuum distillation to remove lower boiling substances than the alkyl benzenes, and sulphonating resulting alkyl benzenes.

LAWRENCE H. FLETT.

# CERTIFICATE OF CORRECTION.

Patent No. 2,314,929. March 30, 1943.

LAWRENCE H. FLETT.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 5, first column, line 2, for "detergnet" read --detergent--; and second column, line 65, for "80° C." read --20° C.--; page 7, first column, line 46, claim 3, for "benene" read --benzene--; line 65-66, claim 4, and second column, line 16-17, claim 5, for "condensating" read --condensing--; line 25, claim 5, for "production" read --product--; 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 18th day of May, A. D. 1943.

Henry Van Arsdale,
(Seal) Acting Commissioner of Patents.