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METHOD OF PRODUCING HIGHER ALKYL
AROMATIC SULPHONATES

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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, chlor hydrocarbons 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-pro-

ducts 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.

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 5 per cent to 20 per cent 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 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 an 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., followed by separation of the mixed alkyl aromatic compounds from the sludge formed as a by-product of the condensation, 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 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, 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.

Thus 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 mixed alkyl benzenes from the dark-colored sludge produced as a by-product, distilling off excess benzene from the mixed alkyl benzenes, then reacting the mixed alkyl benzenes with a sulphonating agent, and neutralizing the sulphonated product with sodium hydroxide in aqueous solution. The oily mixed 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.

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 halogenation 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. Even when the alkyl aromatic condensation products are substantially decolorized by a decolorizing treatment of the type above mentioned, they generally produce sulphonated products in which the undesirable color again develops as a result of the sulphonation.

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.

Example 1

Part 1.—553 parts of a kerosene fraction of Pennsylvania petroleum distillate, boiling over the range of approximately 180° to 300° and having a specific gravity of 0.79, 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 10 to about 17 carbon atoms per molecule, were chlorinated by passing therethrough a stream of chlorine gas while the mixture was maintained around 50° to 60° and exposed to diffused daylight, until the organically combined chlorine in the mixture amounted to about 125 parts, corresponding to about 125 per cent of the amount theoretically required for complete monochlorination. 600 parts of this chlorinated oil were added in a small stream to a well agitated mixture of 395 parts of benzene and 35 parts of anhydrous aluminum chloride. The reaction mixture was maintained throughout the addition at about 30 to 35° and, after the addition of the chlorinated oil, was stirred for about three-quarters of an hour, and then allowed to stand about 20 minutes. The mixture separated into two layers. The upper layer, consisting of a brown mobile oil, was decanted from the lower layer of black tarry matter and washed with one-half its volume of 5 per cent muriatic acid. The washed product, a pale yellow oil, was distilled until a vapor temperature of 123° of 5 mm. mercury pressure was reached, to remove unreacted material. The residue, consisting of a light amber oil, weighed 363 parts. It comprised a mixture of alkyl benzenes in which the number of carbon atoms in the alkyl groups averaged about 13 to 14.

Part 2.—For the production of a sulphonated product, 200 parts of the oil were agitated well with 245 parts of 26 per cent oleum at a temperature of 5 to 15° until 1 part of a test portion, after neutralizing with sodium hydroxide, was soluble in 20 parts of water. The mixture was then poured into approximately 2500 parts of an ice-water mixture, and the resulting solution was made neutral to Brilliant Yellow and Congo Red papers with concentrated aqueous caustic alkali (e. g. a 50% aqueous solution of sodium hydroxide). The neutralized solution, when evaporated to dryness on a rotary drum dryer, resulted in a pale yellow friable solid, readily soluble in water to form solutions which were clear and tinged very faintly yellow. The solutions possessed excellent wetting and washing properties. The product comprised chiefly nuclearly alkylated benzene sulphonates in which the alkyl groups averaged about 13 to 14 carbon atoms.

Example 2

400 parts of a chlorinated kerosene containing approximately 16 per cent organically combined chlorine (corresponding to about 100 per cent of the amount theoretically required for complete monochlorination) and prepared from a kerosene of the type employed in Example 1 by the process described in Example 1, were added as a small stream to an agitated mixture of 35 parts of anhydrous aluminum chloride and 350 parts of toluene, which initially was at a temperature of about 12°. The temperature of the reaction mixture spontaneously rose to 45° and then slowly subsided as the evolution of hydrogen chloride gas diminished. After being stirred for about 1½ hours the mixture was allowed to stand and to separate into two layers. The upper layer was decanted and washed with one-half its volume of 5 per cent muriatic acid. It was then distilled until a vapor temperature of 120° at 4 mm. was reached. The residue (238 parts) was a pale yellow mobile oil, similar to that produced in Example 1, part 1. 20 parts of the oil were sulphonated by mixing it with 25 parts of 26% oleum and agitating the mixture

for about 1¼ hours at a temperature from about 10° to about 15° until 1 part of a test portion, after being neutralized with caustic soda was soluble in 20 parts of water. The mixture was then diluted in about 250 parts of ice-water, neutralized with concentrated aqueous caustic soda, and dried. The resulting product was a pale yellow to white solid which gave clear substantially colorless aqueous solutions having desirable wetting and washing properties. The product was chiefly a mixture of nuclearly alkylated toluene sulphonates in which the introduced alkyl groups averaged about 13 to 14 carbon atoms.

Example 3

562 parts of a kerosene fraction of Pennsylvania petroleum distillate, boiling over the range approximately 165 to 225° and having a specific gravity of 0.785, which, on the basis of its source and properties, was considered to be a mixture of hydrocarbons (mainly open chain aliphatic hydrocarbons) having a range from about 10 to about 13 carbon atoms per molecule, were chlorinated in diffused daylight until about 138 parts of chlorine had been absorbed (corresponding to about 107 per cent of the amount theoretically required for complete monochlorination). 400 parts of this mixture of chlorinated hydrocarbons were added as a small stream to an agitated mixture maintained at about 60° to about 70° of 30 parts of anhydrous aluminum chloride, 400 parts of naphthalene, and 240 parts of Pennsylvania kerosene. The mixture was stirred and allowed to cool for about one hour, then it was allowed to stand and separate into two layers of which the upper was decanted, washed and distilled until a vapor temperature of 120° at 4 mm. was reached. The residue (302 parts) was an amber-colored oil comprising chiefly a mixture of alkyl naphthalenes in which the alkyl groups contained from about 10 to about 13 carbon atoms. 20 parts of the oil were sulphonated by mixing it with 24½ parts sulphuric acid monohydrate, and agitating the mixture for about 1½ to 2 hours at a temperature from about 10° to about 15°, until 1 part of a test portion, after being neutralized with caustic soda was soluble in 20 parts water. The mixture was then diluted with about 250 parts ice-water, neutralized with concentrated aqueous caustic soda and dried. The resulting product was an almost white solid, soluble in water to form substantially colorless solutions having desirable wetting and washing properties. The product was chiefly a mixture of nuclearly alkylated naphthalene sulphonates in which the alkyl groups contained from about 10 to about 13 carbon atoms.

Example 4

Paraffin oil of the type known commercially as "white oil," having a specific gravity of about 0.848, and boiling over the range approximately 224° to 278° at 15 mm. mercury pressure, having an average molecular carbon content of 26 carbon atoms (determined by the cryoscopic method), and, on the basis of its source and properties, considered to be a mixture of hydrocarbons ranging in carbon content from about 22 to 28 carbon atoms per molecule, was chlorinated in a lead-lined vessel by passing chlorine gas into the oil at about 75° in the presence of about 0.05 per cent of iodine as catalyst until a gain in specific gravity of 0.09 had been realized. The resulting chlorinated oil contained approximately 1.3 times the amount of organically combined

chlorine theoretically required for complete monochlorination of the hydrocarbons in the white oil. 300 parts of the resulting chlorinated white oil were added to an agitated mixture, maintained at about 25° to about 30°, of 21 parts of anhydrous aluminum chloride and 150 parts of benzene. Hydrogen chloride gas was evolved. The mixture was agitated at about 25° to about 30° for one hour and then at 45° to 50° for one hour. The mixture was then allowed to stand for 16 hours. Two layers formed; a brown, mobile oily upper layer and a black, tarry, more viscous lower layer. The upper layer of brown mobile oil was decanted, washed with a 5 per cent aqueous NaHSO_3 solution, and distilled until volatile components boiling up to 100 at 4 mm. were removed. The residue of the distillation was about 200 parts of an amber oil comprising chiefly alkylated benzenes in which the alkyl groups ranged from about 22 to 28 in carbon content and averaged about 26 carbon atoms. 200 parts of the oil were sulphonated by slowly adding thereto 48½ parts of chlorosulphonic acid while the mixture was maintained at about 20° to about 25°. Thereafter the mixture was stirred for about 2 hours until 1 part of a test portion, after being neutralized with caustic soda, was soluble in 20 parts of water. The mixture was then diluted with about 4 parts of water, made neutral to Brilliant Yellow by addition of concentrated aqueous caustic soda, and dried. The resulting product was a practically yellowish solid which was clearly soluble in water to give almost colorless solutions and which was soluble in dry cleaner's naphtha, carbon tetrachloride, trichlorethylene and the like dry cleaning solvents.

Example 5

A kerosene fraction of Pennsylvania petroleum distillate boiling over the range about 172° to about 250°, which, on the basis of its source and properties, was considered to be a mixture of hydrocarbons (mainly open-chain aliphatic hydrocarbons) having a range from about 10 to about 15.5 carbon atoms per molecule, was chlorinated in diffused daylight at a temperature between 50° and 60° until about 21 parts of chlorine had been absorbed per 100 parts of kerosene (corresponding to about 109 per cent of the amount theoretically required for complete monochlorination). 200 parts of this mixture of chlorinated hydrocarbons were reacted at ordinary temperature with 150 parts of monochlorobenzene and 20 parts of anhydrous aluminum chloride. The temperature of the mixture was allowed to rise to about 60° with agitation and agitation was continued for about 1 additional hour after this temperature was reached. The mixture was allowed to stand and separate into two layers of which the upper was decanted, washed with dilute hydrochloric acid and distilled until a vapor temperature of 120° C. at 5 mm. was reached. The residue (85 parts) was an amber-colored oil comprising chiefly a mixture of alkyl chlorobenzenes in which the alkyl groups contained from about 10 to 15.5 carbon atoms. 20 parts of the oil were sulphonated by mixing it with 25½ parts of 26° Bé. oleum at a temperature from about 10° to 15° for about 3 hours. The mixture was then heated to 40° to 55°, where it was held for about ½ hour. The mixture was then diluted by drowning it in 6 to 7 times its weight of ice and water, neutralized with concentrated aqueous caustic soda and dried. The resulting product was an almost white solid soluble in water to form substantially

colorless solutions having desirable wetting and washing properties. The product was chiefly a mixture of nuclearly alkylated chlorobenzenes in which the alkyl groups contained from about 10 to about 15.5 carbon atoms.

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 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.

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 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 em-

ployed, 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, monochlorobenzene, 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 20° 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° Bé., 100 per cent, 26 per cent oleum, 65 per cent oleum, etc.), chlorosulphonic 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, dichlorobenzene, 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 chlorosulphonic acid such that no excess, or only a relatively small excess, of it is present in the final sulphonation mass or mixture.

The improvement in the properties of the al-

kyl aromatic sulphonates resulting from the use of the relatively large amounts of aluminum chloride at temperatures below 130° C. in accordance with the present invention are not limited to the unitary procedure above illustrated in the specific examples; although in view of economies in number of operations, equipment, and labor involved, the unitary procedure is preferred. Thus, the present invention comprehends a procedure in which the condensation of the alkyl halide mixture with the aromatic constituent may be 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 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 following example illustrates such a procedure:

Example 6

Part 1.—A kerosene fraction of Pennsylvania petroleum distillate of the type employed in Example 1, to which a small amount of iodine (0.05 part per 100) was added as a halogenating catalyst, was chlorinated by passing there-through 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. The resulting product was a dark brown oil consisting mainly of nuclearily 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 in the manner disclosed in Example 1, part 2. 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 sul-

phonated 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.

Where in the claims the process is defined as "reacting" the alkyl halide mixture with the aromatic compound and aluminum chloride, it will be understood that such claims generically include the treatment with aluminum chloride in a single stage, such as disclosed in Examples 1 to 5, and in a plurality of stages, such as disclosed in Example 6.

This application is a continuation-in-part of my application Serial No. 93,719, filed July 31, 1936, now U. S. Patent 2,195,409.

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, reacting the resulting alkyl halide mixture with the aromatic compound and an amount of aluminum chloride equal to 5 per cent to 20 per cent of the alkyl halide mixture at a temperature not exceeding 130° C., 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 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 in the presence of an amount of aluminum chloride equal to 5 per cent to 20 per cent of the alkyl halide mixture at a temperature not exceeding 130° C., and separating the resulting alkyl aromatic compounds from the reaction product.

3. 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 chlorina-

tion 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, reacting the resulting alkyl chloride mixture with the aromatic compound and an amount of aluminum chloride equal to 5 per cent to 20 per cent of the alkyl chloride mixture at a temperature not exceeding 130° C., and separating the resulting alkyl aromatic compounds from the reaction product.

4. 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 in the presence of an amount of aluminum chloride equal to 5 per cent to 20 per cent of the alkyl halide mixture at a temperature not exceeding 130° C., and separating the resulting alkyl aromatic compounds from the reaction product

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, reacting the resulting alkyl chloride mixture with an aromatic hydrocarbon of the benzene and naphthalene series and an amount of aluminum chloride equal to 5 per cent to 20 per cent of the alkyl chloride mixture at a temperature not exceeding 130° C., separating the resulting alkyl aromatic compounds from the reaction product, and sulphonating the 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 of the hydrocarbon mixture, condensing the resulting alkyl chloride mixture with an aromatic hydrocarbon of the benzene and naphthalene series in the presence of an amount of aluminum chloride equal to 5 per cent to 20 per cent of the alkyl chloride

mixture at a temperature between 20° and 80° C., separating the resulting alkyl aromatic compounds from the reaction product, and sulphonating the alkyl aromatic compounds.

7. The method of producing sulphonated products having surface active properties, which comprises chlorinating a paraffinic 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, reacting the resulting alkyl chloride mixture with benzene and with anhydrous aluminum chloride in an amount equal to 5 per cent to 20 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 resulting alkyl benzene mixture to distillation to remove lower boiling substances than the alkyl benzenes, and sulphonating the alkyl benzenes.

8. The method of producing sulphonated products having surface active properties, which comprises chlorinating a 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 75 per cent to 175 per cent complete monochlorination, condensing the resulting alkyl chloride mixture with an aromatic hydrocarbon of the benzene and naphthalene series in the presence of anhydrous aluminum chloride in an amount equal to 5 per cent to 20 per cent of the weight of the alkyl chloride mixture at a temperature between 20° and 80° C., separating the resulting alkyl aromatic mixture from the sludge formed as a by-product of the reaction, subjecting the resulting alkyl aromatic mixture to distillation to remove lower boiling substances than the alkyl aromatic compounds, and sulphonating the remaining alkyl aromatic mixture.

9. 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 5 per cent to 20 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 resulting alkyl benzene mixture to distillation to remove lower boiling substances than the alkyl benzenes, and sulphonating the alkyl benzenes.

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, condensing the result-

ing alkyl chloride mixture with benzene in the presence of anhydrous aluminum chloride in an amount equal to 5.8 per cent to 15 per cent of the weight of the alkyl chloride mixture at a temperature between 20° and 80° C., separating the resulting alkyl benzene mixture from the sludge formed as a by-product of the reaction, subjecting the resulting alkyl benzene mixture to vacuum distillation to remove lower boiling substances than the alkyl benzenes, and sulphonating the remaining alkyl benzene mixture.

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 in the presence of anhydrous aluminum chloride in an amount equal to 5 per cent to 15 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 resulting alkyl benzene mixture to vacuum distillation to remove lower boiling substances than the alkyl benzenes, and sulphonating the alkyl benzenes.

12. 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, reacting the resulting alkyl chloride mixture with benzene and with anhydrous aluminum chloride in an amount equal to 5 per cent to 20 per cent of the weight of the alkyl chloride mixture at a temperature between 20° and 80° C., separating the resulting alkyl benzene mixture from the sludge formed as a by-product of the reaction,

subjecting the resulting alkyl benzene mixture to vacuum distillation to remove lower boiling substances than the alkyl benzenes, and sulphonating the remaining alkyl benzene mixture.

13. The method of producing sulphonated products having surface active properties, which comprises chlorinating a 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 about 125 per cent complete monochlorination, reacting the resulting alkyl chloride mixture with benzene and with anhydrous aluminum chloride in an amount equal to 5 per cent to 15 per cent of the weight of the alkyl chloride mixture at a temperature between 20° and 80° C., separating the resulting alkyl benzene mixture from the sludge formed as a by-product of the reaction, subjecting the resulting alkyl benzene mixture to vacuum distillation to remove lower boiling substances than the alkyl benzenes, and sulphonating the remaining alkyl benzene mixture.

14. The method of producing sulphonated products having surface active properties, which comprises chlorinating a kerosene fraction of Pennsylvania petroleum distillate, having a boiling range of approximately 180° to 300° C. and a specific gravity of 0.79, 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 in the presence of anhydrous aluminum chloride in an amount equal to 5 per cent to 15 per cent of the weight of the alkyl chloride mixture at a temperature between 20° and 80° C., separating the resulting alkyl benzene mixture from the sludge formed as a by-product of the reaction, subjecting the resulting alkyl benzene mixture to vacuum distillation to remove lower boiling substances than the alkyl benzenes, and sulphonating the remaining alkyl benzene mixture.

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