Patented Mar. 4, 1941 2,233,408

UNITED STATES PATENT OFFICE

2,233,408

METHOD OF PRODUCING HIGHER ALKYL AROMATIC SULPHONATES

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No Drawing. Application March 11, 1938, Serial No. 195,414

14 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 non-aromatic hydrocarbons by processes involving condensation of mixtures of alkylating forms of non-aromatic hydrocarbons with aromatic compounds in the presence of condensing agents of the Friedel and Crafts type, followed by sulphonation of the condensation product. (The term "non-aromatic hydrocarbons" is employed herein in the generic sense, including acyclic aliphatic hydrocarbons and cyclic aliphatic hydrocarbons.)

An object of the present invention is to provide improvements in the method of producing higher alkyl aromatic sulphonates from non-aromatic hydrocarbons and aromatic compounds whereby sulphonated products are obtained having improved properties.

Another object of the present invention is to provide improvements in the method of producing higher alkyl aromatic sulphonates from readily available and cheap non-aromatic hydrocarbons by processes involving condensation of aromatic compounds with mixtures of the non-aromatic hydrocarbons in an alkylating form, in the presence of a condensing agent of the Friedel and Crafts type, followed by sulphonation, whereby the presence of undesirable by-products in the sulphonated products is overcome in a relatively simple and efficient manner.

A further object of the invention is to provide improvements in the method of producing higher alkyl aromatic sulphonates from halogenated non-aromatic hydrocarbon mixtures and aromatic compounds by condensation, with the aid of a metal halide condensing agent, followed by sulphonation, whereby undesirable constituents present in the original hydrocarbon material and/or formed as by-products of the reaction are removed in a simple and efficient manner from the sulphonated products.

An additional object of the invention is to provide improvements in the method of producing higher alkyl aromatic sulphonates from halogenated hydrocarbon fractions of petroleum distillates and aromatic compounds by condensation, with the aid of metal halide condensing agents, followed by sulphonation, whereby sulphonated products are obtained having improved detergent action.

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

Alkyl aromatic sulphonates, particularly in the form of their alkali metal and organic ammonium salts, in which a higher alkyl group is present as a substituent in the aromatic nucleus represent a desirable class of products for use as substitutes for soaps in view of certain of their advantageous properties, as for example, resistance to acids and hard water, washing and lathering ability in hard water and sea water, and freedom from hydrolysis.

One method for producing such alkyl aromatic sulphonates involves halogenating a non-aromatic hydrocarbon or mixture of non-aromatic hydrocarbons, to form a mixture of halogenated 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 its conversion to the salt form 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 in the presence of anhydrous aluminum chloride or zinc chloride as a catalyst, sulphonating the resulting mixture of alkyl benzenes, neutralizing the alkyl benzene sulphonic acid mixture with aqueous sodium hydroxide solution, and recovering the resulting mixture of sodium alkyl benzene sulphonates.

Naturally - occurring and synthetically - prepared non-aromatic hydrocarbon mixtures (for example, the various fractions of petroleum distillates, hydrogenated coal distillates, polymerized olefines, etc.), represent available and inexpensive sources of alkylating agents for the preparation of higher alkyl aromatic sulphonates. They possess the disadvantages that they are complex mixtures which can be resolved only with great difficulty, if at all, into relatively pure fractions of simple hydrocarbons; and, when they are employed in the form of mixtures of relatively wide distillation range, they include constituents which are unlike in their reactivity to reagents employed in their conversion to useful products.

Attempts have been made to develop processes for the utilization of these non-aromatic hydrocarbon mixtures in connection with the production of higher alkyl aromatic sulphonates, but the said mixtures have disadvantages which decrease their usefulness. For example, in the preparation of higher alkyl aromatic sulphonates from

petroleum distillates which are chiefly non-aromatic hydrocarbons with at least 10 carbon atoms per hydrocarbon molecule, and particularly 10 to 20 carbon atoms per molecule, by processes involving halogenation of the petroleum distillate, the reactivity of the various hydrocarbons present in a given distillate to the halogenating agent is different, with the result that the halogenated product contains a mixture of various halogenated bodies in which the degree of halogenation is non-uniform, together with unhalogenated hydrocarbons. When such a mixture is employed for condensation with an aromatic compound and the resulting condensation product is sulphonated, the presence of the various constituents in the chlorination product leads to a wide variety of impurities and by-products in the sulphonation product.

The ordinary procedure for the recovery of the sulphonation products in useful form involves a dilution of the sulphonation reaction mixture with water and/or ice, followed by conversion of the sulphonic acids in the product to salts by neutralization (for example, with an alkali, ammonia or an organic base or equivalent), with or without an intermediate separation of the sulphonic acids from the diluted sulphonation product. The presence of unreacted constituents of the non-aromatic hydrocarbon starting material, and/or of by-products formed during the preparation of the alkyl aromatic sulphonates from the non-aromatic hydrocarbon materials, leads to complications in the recovery of the sulphonation product in dry form from the aqueous solutions resulting from dilution of the sulphonation product. By reason of their excellent emulsifying and solubilizing qualities, the higher alkyl aromatic sulphonates emulsify and/or solubilize the water-insoluble oily material in the said aqueous solutions of the sulphonation product. Elimination of undesired constituents from the diluted sulphonation products is commercially impractical owing to this emulsifying or solubilizing action. The constituents which are carried over from the non-aromatic hydrocarbon starting material (e. g., the petroleum distillate) and/or are formed as by-products of the foregoing reaction remain in these aqueous solutions or emulsions and evaporate only in part, when the said emulsions are dried; they make it difficult to obtain the sulphonated product in dry friable form; they cause the dry products to be discolored and to be sticky, and to lump rapidly when stored, particularly when in a moist atmosphere; and they impart to the products and their aqueous solutions undesirable odors which become more disagreeable when the products are stored. More particularly these impurities are undesirable because of their adverse effect on the washing action of the products containing them. Removal of the impurities from the recovered higher alkyl aromatic sulphonates is not commercially practical and does not result in a satisfactory product.

According to the present invention, alkyl aromatic sulphonates of improved quality, and of efficient detergent and surface active action, are obtained from non-aromatic hydrocarbon materials 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 method of procedure, a mixture of non-aromatic hydrocarbons in an alkylating form (for example, in the form of the alkyl halides, or in the form of the unsaturated hydrocarbons, or both) containing at least 10 carbon atoms, more particularly 10 to 20 carbon atoms, and preferably from 12 to 16 carbon atoms, per molecule is reacted with the aromatic compound to be alkylated in the presence of a condensing agent of the Friedel and Crafts type, the resulting product of the condensation (containing higher alkyl aromatic compounds together with other constituents formed as by-products of the foregoing reactions or present as impurities in the reacting ingredients) is reacted with a sulphonating agent, and, when the sulphonation is complete, the sulphonation mass (containing higher alkyl aromatic sulphonic acids together with unsulphonated constituents, and residual sulphonating agent, if any) is subjected to conditions which favor stratification. The mass separates into two and sometimes more layers. The topmost layer is largely composed of unreacted hydrocarbons, some by-products which do not sulphonate under the conditions extant during the sulphonation, and some aromatic sulphonates. This layer is removed. (Although the removal of this layer somewhat decreases the weight yield of total desired alkylated aromatic sulphonate ultimately obtained, the removal of the material in this layer from the desired final mixture of sulphonates greatly enhances the properties and quality of the latter.) When there are only two layers, the lower one contains the desired higher alkyl aromatic sulfonic acids and the spent sulphonating acid. When there are three layers, the middle layer contains most of the desired higher alkyl aromatic sulphonic acids and part of the spent sulphonating acid, and the bottom or third layer contains the spent sulphonating acid with small amounts of the aromatic sulphonic acids. The layer containing the higher alkyl aromatic sulphonic acids, with or without the spent acid layer if present, is treated in any suitable manner to recover them and/or convert them to a desired final product; e. g., a salt in the dry form.

In accordance with the present invention, it has been found that, although the finished sulphonation mix appears homogeneous, if it is allowed to stand for considerable periods of time a layer of the unsulphonated material will slowly form which can be mechanically removed.

This separation step is effective in removing impurities which have not been successfully removed in previous purifications, and better still makes possible the production of a good washing agent without even a partial separation of the hydrocarbon impurities. Although the art indicates that organic solvents have a beneficial action in washing operations, I have found the presence of the removed hydrocarbon impurities inimical to a good washing action with products of the type covered in this invention.

I have found by subjecting the reaction mass resulting from the sulphonation treatment to conditions favoring stratification (for example, permitting the mixture to stand quiescent) followed by removal of the layer containing the alkyl aromatic sulphonic acids from the layer of non-sulphonated constituents (for example by decantation or by drawing off the lower layer), a highly satisfactory purification of the alkyl aromatic sulphonates is effected, with the results that, upon dilution of the separated layer containing the higher alkyl aromatic sulphonic acids, the formation of objectionable emulsions does not occur, and sulphonated products in the form

of sulphonic acids and in the form of salts thereof are obtainable in a light-colored, dry, friable form having improved properties as detergents and surface active agents.

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

Part 2.—10 parts of the resulting chlorination product were reacted with 6 parts of benzene in the presence of 0.8 part of anhydrous aluminum chloride, for about 2 hours with vigorous agitation at 42° to 45°. The reaction mixture was then allowed to stand for about 2 hours. It separated into two layers. The upper oily layer was decanted. It contained a mixture of higher alkyl benzenes resulting from the condensation, together with unreacted benzene, unreacted petroleum hydrocarbons and chlorinated petroleum hydrocarbons, and by-products of the reaction. The oil was heated in a still until the vapor temperature of the distillate reached about 115° at about 45 mm. pressure, to remove from the distilland a distillate comprising unreacted benzene, low boiling hydrocarbons, and low boiling by-products and to leave an oil containing the higher boiling alkyl benzenes and higher boiling impurities initially present in the distilland.

Part 3.—7 parts of the remaining oil (comprising a crude mixture of the higher alkyl benzenes, together with other, residual constituents and by-products of the foregoing procedure) were agitated with 12.8 parts of 100 per cent sulphuric acid for about 2 hours at a temperature of about 30°. The reaction mixture was then allowed to stand quiescent until it separated into three layers (about 1 hour). The upper layer, consisting of about 3.15 parts of oily material, was removed by decantation from the lower, acid layers containing higher alkyl benzene sulphonic acids and residual sulphuric acid. Substantially all of the residual petroleum hydrocarbons and chlor hydrocarbons as well as the greater portion of the water-insoluble by-products formed in the condensation and sulphonation operations were present in the upper oily layer. The lower, acid layers were then diluted by adding thereto about 2.5 parts of ice, while the vessel containing the mixture was cooled externally by means of cold water. Upon standing quiescent, the acid mixture separated into two layers: a lower, aqueous sulphuric acid layer weighing 13.5 parts, and an upper, higher alkyl benzene sulphonic acid layer, consisting of about 5 to 6 parts of sulphonic acids. The upper sulphonic acid layer was drawn off and was neutralized with aqueous ammonium hydroxide. A paste was obtained which had the characteristic properties of a good detergent and foaming agent. It contained principally the ammonium salts of alkyl benzene sulphonic acids in which the alkyl groups averaged about 13 to about 14 carbon atoms. When evaporated to dryness on a rotary drum drier, a pale yellow friable solid was obtained which was readily soluble in water to form solutions possessing excellent wetting and washing properties.

Example 2

8 parts of 26 per cent oleum were added to 10 parts of the oil obtained according to Part 2 of Example 1, and comprising a crude mixture of higher alkyl benzenes, maintained at a temperature between 5° and 8°. The reaction mixture was agitated, and the temperature was allowed to rise to between 25° and 30° and maintained within these limits for about 2 hours. The mixture was then allowed to stand quiescent for about 16 hours. The upper oily layer which formed was decanted. The remainder of the sulphonated mass was diluted by the addition of 2 to 7 parts of ice while cooling the mixture by external means. Upon standing quiescent for several hours, the acid mixture separated into two layers: a lower aqueous acid layer, which was drawn off and discarded; and a paste comprising a mixture of higher alkyl benzene sulphonic acids, and weighing 7.3 parts. The paste was neutralized with caustic soda; for example, by treatment with a 50 per cent aqueous solution of sodium hydroxide in an amount sufficient to render the resulting solution neutral to Brilliant Yellow and Congo Red papers. The neutralized solution, when evaporated to dryness on a rotary drum drier, resulted in a pale yellow friable solid, readily soluble in water to form solutions which were clear and which possessed excellent wetting and washing properties. The resulting product contained chiefly the sodium salts of alkyl benzene sulfonic acids in which the alkyl groups averaged about 13 to about 14 carbon atoms.

Example 3

Part 1.—10 parts of the chlorination product obtained according to Part 1 of Example 1, and comprising a mixture of monochlor hydrocarbons together with more highly chlorinated hydrocarbons and unchlorinated hydrocarbons, were reacted with 6 parts of benzene in the presence of 1.2 parts of anhydrous aluminum chloride, for about 45 minutes with vigorous agitation at 42° to 45°. The reaction mixture was then allowed to stand for about 2 hours. It separated into two layers. The upper oily layer was decanted. It contained a mixture of higher alkyl benzenes resulting from the condensation, together with unreacted benzene, unreacted petroleum hydrocarbons and chlorinated petroleum hydrocarbons, and by-products of the reaction. The oil was heated in a still until the liquid temperature reached 150°. After cooling slightly, vacuum was applied, and heating and distillation were con-

tinued until the vapor temperature reached 125° at 99 to 125 mm. mercury pressure, to remove from the distilland a distillate comprising chiefly unreacted benzene, with some low boiling hydrocarbons and low-boiling by-products, while leaving behind an oil containing the higher boiling alkyl benzenes and higher boiling impurities.

Part 2.—7 parts of the remaining oil (comprising a mixture of the higher alkyl benzenes, together with other, residual constituents and by-products of the foregoing procedure) were agitated at 30° to 40° with 1.4 parts of 100 per cent sulphuric acid for about 45 minutes. After standing quiescent for 1 to 2 hours, the lower layer of spent acid was withdrawn. The remaining acid-washed oil was agitated with 9 parts of 100 per cent sulphuric acid at 60° for about 1 hour. The reaction mixture was then allowed to stand quiescent until it separated into three layers (about 1 hour). The upper layer, consisting of oily material, was removed by decantation from the lower acid layers containing higher alkyl benzene sulphonic acids and residual sulphuric acid. Substantially all of the residual petroleum hydrocarbons and chlor hydrocarbons as well as the greater portion of the water-insoluble by-products formed in the condensation and sulphonation operations were present in the upper oily layer. The bottom sulphuric acid layer, containing principally spent sulphuric acid, was discarded. The original middle layer, containing the alkyl benzene sulphonic acids and some sulphuric acid, was drowned in about 50 parts of cold water, and neutralized with aqueous sodium hydroxide; for example, by treatment with a 50 per cent aqueous solution of caustic soda in an amount sufficient to render the resulting solution neutral to Brilliant Yellow and Congo Red. The neutralized solution when evaporated to dryness, on a rotary drum drier, resulted in a white flaked solid which was readily soluble in water to form solutions that were clear and that possessed excellent wetting and washing properties. The resulting product contained chiefly the sodium salts of alkyl benzene sulphonic acids, in which the alkyl groups averaged about 13 to about 14 carbon atoms, and sodium sulphate.

Example 4

Part 1.—10 parts of the chlorination product obtained according to Part 1 of Example 1, and comprising a mixture of monochlor hydrocarbons together with more highly chlorinated hydrocarbons and unchlorinated hydrocarbons, were reacted with 6 parts of benzene in the presence of 0.8 part of anhydrous aluminum chloride, for about 45 minutes with vigorous agitation at 42 to 45°. The reaction mixture was then allowed to stand for about 2 hours. It separated into two layers. The upper oily layer was decanted. It contained a mixture of higher alkyl benzenes resulting from the condensation, together with unreacted benzene, unreacted petroleum hydrocarbons and chlorinated petroleum hydrocarbons, and by-products of the reaction. The oil was heated in a still until the liquid temperature reached 150°. After cooling slightly, vacuum was applied and heating and distillation were continued until the vapor temperature reached 115° at an absolute pressure corresponding to 40 to 45 mm. mercury pressure, to remove a distillate comprising chiefly unreacted benzene, with some other low-boiling hydrocarbons. The receiver was then changed and distillation was continued until the vapor temperature reached 240° at 20 mm. mercury pressure, whereby a distillate was obtained comprising the alkyl benzenes.

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

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

The non-aromatic hydrocarbons which may be employed as sources of the alkyl groups in the final products are preferably those which contain a minimum of 10 carbon atoms per molecule. The process is particularly advantageous in connection with mixtures of such hydrocarbons, particularly those which boil over a temperature range greater than 50° C. They are further preferably aliphatic hydrocarbon mixtures, and especially mineral oil distillates, boiling above 100° C. and containing between 10 and 20 carbon atoms, and preferably between 12 and 16 carbon atoms, per molecule. The particular type of non-aromatic hydrocarbon mixture 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 cyclic aliphatic hydrocarbons and saturated, acyclic aliphatic hydrocarbons containing straight or branched carbon chains, 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 converted to an alkylating form, for example by

halogenation and/or by conversion to olefines, mixtures of various halogenated derivatives of the said aliphatic hydrocarbons (alkyl halides) and/or mixtures of various unsaturated derivatives of the said aliphatic hydrocarbons (olefines) are produced and the said mixtures, 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 sulfonated alkyl aromatic compounds differing from each other in the alkyl groups, which groups correspond with the aliphatic hydrocarbons of the original mixture employed.

The non-aromatic hydrocarbons may be converted into an alkylating form in various ways. They are preferably converted into a halogenated form for use in accordance with the present invention. If desired, the halogenated products may be converted into olefines by elimination of hydrogen halide by treatment of the halogenated hydrocarbon mixture with a dehalogenating agent (for example, zinc chloride, aluminum chloride, caustic alkali, ferric chloride, sodium phenolate or copper powder). Further, other sources of mixed non-aromatic hydrocarbons in an alkylating form are suitable in connection with the present invention; for example, the mixture of olefines containing more than 10 carbon atoms obtained by the cracking or reforming of hydrocarbon mixtures of the type of petroleum distillates, lignite tar oil and hydrogenated coal; or the olefines formed by polymerizing olefines of low molecular weight.

The preferred non-aromatic hydrocarbon mixtures employed in accordance with the present invention are exemplified by fractions of Pennsylvania and Michigan (Mount Pleasant) petroleum distillates, and especially the kerosene fractions of said distillates. These distillates consist essentially of open chain aliphatic (paraffinic) hydrocarbons of which a large portion have probably relatively long carbon chains rather than more condensed molecules. Such distillates will be referred to as "of the Pennsylvania type," whether derived from natural sources or derived by processing or by purification of less favorable distillates from other sources.

The extent to which the non-aromatic hydrocarbons may be halogenated in converting them to an alkylating form may vary. In general chlorination of a petroleum hydrocarbon mixture may be carried out to an extent corresponding with a product containing a ratio of about ¼ to 2½ atoms of chlorine per molecule of petroleum hydrocarbon. Preferably the halogenation of the non-aromatic hydrocarbon mixture is carried out to an extent such that the resulting halogenation reaction mixture contains an amount of organically combined halogen substantially corresponding with 75 per cent to 175 per cent complete monohalogenation of the original non-aromatic hydrocarbon mixture. While the greater the amount or extent of halogenation, the greater is the amount of higher boiling residues obtained in the alkyl aromatic mixture produced therefrom, the present invention affords a simple and effective method for removal of such high boiling residues. Inasmuch as the present invention affords a simple and effective method for the removal of high boiling residues of whatever nature which remain unsulphonated in the sulphonated mass, it is possible, as a result of the present invention, to take advantage of whatever beneficial effects accrue from the use of higher halogenated hydrocarbons and yet avoid the undesirable presence in the final products of impurities which are not sulphonated or which are not soluble by themselves in water.

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

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

If desired the reaction mixture resulting from the halogenation may be subjected to fractional distillation to select portions of a narrower distillation range for further use in the process. The present invention makes such distillation unnecessary in the usual case, but even when such distillation is carried out the present invention effects improvements in the final product.

The aromatic compounds preferably employed in accordance with the present invention are various aromatic hydrocarbons and their simple substitutions products. They may contain as substituents in the aromatic nucleus one or more of the following: halogen, a hydroxyl group, an ether group (in which the hydrocarbon radical of the ether is an alkyl or aralkyl group containing 1 to 8 carbon atoms, or an aryl radical), or a carboxyl group (in the free acid or salt form). Examples of such aromatic compounds are: benzene, naphthalene, anthracene, diphenyl, and their homologues (such as, toluene, xylene, etc.); monochlorbenzene, phenol, cresols, naphthol, anisole, phenetol, benzoic acid, salicylic acid, resorcinol, and hydroxy diphenyl. Mixtures of aromatic compounds may be employed if desired; as for example, naturally-occurring mixtures (such as, commercial cresylic acid), or artificially prepared mixtures of two or more of the aromatic compounds. Unsubstituted lower aromatic hydrocarbons are preferred, since they can be readily removed from the higher alkyl derivatives by vaporization and they are less affected by side reactions.

The proportion of mixed alkyl halides or olefines 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 or mixed olefine 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.

In condensing the aromatic compounds with the nonaromatic hydrocarbons in alkylating form, or with other mixtures of impure alkylating agents, a catalyst of the Friedel and Crafts

type is employed; as for example, anhydrous aluminum chloride, anhydrous zinc chloride, anhydrous ferric chloride, etc. The amount of condensing agent employed may vary over a wide range, for example as low as 1 per cent or as high as 20 per cent or more by weight of the anhydrous metal chloride may be employed, based upon the weight of non-aromatic hydrocarbons in alkylating form. The temperature at which the condensation reaction is carried out may also vary over a wide range.

Aluminum chloride is preferably used for the condensation of a mixture of chlorinated petroleum hydrocarbons with an aromatic hydrocarbon; and preferably the amount of aluminum chloride corresponds with 5 to 20 per cent of the weight of the chlorinated petroleum hydrocarbon mixture. The use of aluminum chloride in such amounts in conjunction with a chlorinated petroleum hydrocarbon mixture which has been chlorinated 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 original petroleum hydrocarbon mixture, as disclosed and claimed in my application Serial No. 186,231, filed January 21, 1938, makes possible an additional improvement in the quality of the higher alkyl aromatic sulphonates obtained by the practice of the process of the present invention. Accordingly, the improved procedure of said application Serial No. 186,231, is included in the preferred practice of the present invention, as illustrated in the above specific examples. In this connection, the condensation is carried out at a temperature which preferably does not exceed 130° C., the condensation reaction mass is permitted to stratify into an upper layer containing mainly a crude mixture of aykyl aromatic compounds and a lower layer of darkly colored sludge, and the upper layer is removed from the lower layer and subjected to the further treatment. Preferably, the condensation is carried out at temperatures between 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 value, if any, for the manufacture of commercially acceptable alkyl aromatic sulphonates. Preferably, the condensation is carried out in a single stage, as illustrated in the above examples; but, if desired, it may be carried out in a plurality of stages in each of which a portion of the total amount of aluminum chloride is employed.

The treatment to which the condensation product is subjected prior to sulphonation may be varied, depending upon the nature of the product desired and the procedure and materials employed in the condensation. For example, metallic compounds may be washed out of the condensation product by treatment with water, or dilute hydrochloric acid or equivalent, and the oily product comprising crude alkyl aromatic compounds may be recovered for further treatment. In the preferred practice of the present invention, the reaction mixture resulting from the condensation above referred to is caused to stratify and the upper layer of crude alkyl aromatic compounds is separated from the lower layer of sludge comprising metallic compounds and colored impurities.

The resulting crude mixture of alkyl aromatic compounds obtained by either of these procedures may then be sulphonated with or without an intermediate treatment for removal of some of the impurities, as for example by washing with water and/or by a distillation treatment. When the presence of unalkylated aromatic sulphonates is undesirable in the final product, residual unalkylated aromatic compound present in the crude mixture of alkyl aromatic compounds may be removed by subjecting the crude mixture to a distillation treatment adapted to distill off the residual unalkylated aromatic compound, which may be collected and reused in the manufacture of additional alkyl aromatic compound, while leaving behind the mixture of alkyl aromatic compounds and higher boiling impurities. It will be noted that this distillation does not involve the vaporization and fractionation of the alkyl aromatic compounds themselves but is a mere stripping operation. As illustrated in the above examples, such a stripping operation is preferably included in the practice of the present invention.

If desired, the alkyl aromatic compounds also may be distilled and a fraction thereof separately collected for sulphonation, as illustrated in Example 4. By such fractional distillation, high boiling impurities will be removed from the mixture of alkyl aromatic compounds, but the mixture will still contain impurities of boiling points similar to those of the alkyl aromatic compounds, carried over from preceding steps in the process and/or formed as by-products of preceding reactions; for, processes are not now known which make possible the separation of the components of such complex mixtures as the mixed hydrocarbons, or the halogenated mixtures of hydrocarbons, or the mixture of alkylated aromatic hydrocarbons, which are made and used in the course of preparing the alkylated aromatic sulphonates of this invention. Further, it is not known at the present time how to separate from each other these different species of chemical compounds, some of which distill within the same distillation ranges. While in view of the purification effected by the present invention such fractional distillation is ordinarily not required and is ordinarily undesirable in view of the added cost and decreased yields of alkyl aromatic sulphonates resulting therefrom, such fractional distillation operation finds utility in conjunction with the improvement of the present invention. Thus, fractional distillation, for the purpose of separating into fractions of narrow distillation ranges any of the petroleum oils or other non-aromatic hydrocarbon mixtures, from which the alkylating agents are derived, or the alkylating agents, or the alkylated aromatic compounds, is rendered unnecessary. Moreover, when fractional distillations have been applied to the said petroleum oils, and/or the alkylating agents derived from them, and/or the alkylated aromatic compounds made with their aid, to effect partial but not complete separations of unreacted products and by-products, and the fractions so obtained are converted into sulfonated alkyl aromatic sulphonates according to this invention, the final dry sulphonated products are highly desirable, light-colored friable products, which do not lump, are substantially free from odor, and impart strong detergent properties to their aqueous solutions.

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.), chlorsulphonic acid, sulphur trioxide, etc.

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

The ratio of sulphonating agent employed wtih 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 impure or technical 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.)

After stratification of the sulphonation reaction mixture and separation of the acid layer from the layer of impurities, in accordance with the present invention, the alkyl aromatic sulphonic acids may be recovered from the acid layer in any suitable manner; for example, they may be reacted with a metal oxide or hydroxide, ammonia, or an organic base, or a suitable salt of one of these, in an amount adapted to form a neutral product in aqueous solution, and the resulting alkyl aromatic sulphonates may be salted out; for example by addition of a highly ionized inorganic salt of the neutralizing base. 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; ethanolamines; propanolamines; butanolamines; diamino propanol; ethylene diamine; triethylene tetramine; aniline; o-toluidine; etc.

The acid layer may be directly employed for the formation of mixed products; for example, mixtures of salts of the alkyl aromatic sulphonic acids and other acids present in said 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 caused to stratify in accordance with the present invention, and the acid layer containing the desired alkyl aromatic sulphonates and residual sulphonating agent may be separated from the layer of impurities (e. g., by decantation or by drawing off) and then treated with a suitable inorganic or organic base or basic salt (as for example, one of those mentioned). 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 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 the greater solubility of the alkyl aromatic sulphonates 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 same is present in the final sulphonation mass or mixture. In the preferred practice of the invention the alkyl aromatic sulphonic acids in the acid layer are freed from residual sulphuric acid prior to recovery thereof, by partially diluting the acid layer with ice and/or water to a sufficient extent to render the alkyl aromatic sulphonic acids insoluble in the resulting dilute sulphuric acid. Ordinarily the higher alkyl aromatic sulphonic acids are insoluble in sulphuric acid of a concentration of 40 to 50 per cent. On standing, the mixture separates into two layers: an upper layer containing substantially all of the higher alkyl aromatic sulphonic acids and a lower layer containing most of the sulphuric acid. After separation of the layers, the higher alkyl aromatic sulphonic acids may be recovered as such or converted to salts by treatment with a suitable inorganic or organic base or basic salt (as for example, one of those above mentioned).

The salts of the alkylated aromatic sulphonic acids may be dried in any suitable manner. They are preferably dried on atmospheric or vacuum drum driers or in spray driers. Preferably the sulphonates derived from organic bases are dried under vacuum conditions.

I claim:

1. In the method of producing higher alkyl aromatic sulphonates from non-aromatic hydrocarbons and aromatic compounds by condensation of a mixture of non-aromatic hydrocarbons in an alkylating form with an aromatic compound, followed by a sulphonation treatment with a sulphonating agent, the improvement which comprises separating the mixture resulting from the treatment with the sulphonating agent into masses of differing densities by means of the differences in densities of the constituents of the mixture, one of said masses comprising higher alkyl aromatic sulphonic acids resulting from the sulphonation treatment and another of said masses comprising oily impurities.

2. In the method of producing higher alkyl aromatic sulphonates from mixtures of petroleum hydrocarbons and aromatic compounds by condensation of an aromatic compound with a mixture of petroleum hydrocarbons which are in alkylating form and contain between 10 and 20 carbon atoms, with the aid of a metal halide condensing agent, followed by a sulphonation treatment with a sulphonating agent in excess of that theoretrically required for monosulphonation, the improvement which comprises stratifying the mixture resulting from the treatment with the sulphonating agent into layers of which

one comprises higher alkyl aromatic sulphonic acids resulting from the sulphonation treatment and sulphuric acid, and separating said layer comprising the higher alkyl aromatic sulphonic acids from the remainder.

3. In the method of producing higher alkyl aromatic sulphonates from mixtures of non-aromatic hydrocarbons and aromatic compounds by condensation of a mixture of non-aromatic hydrocarbons in an alkylating form with an aromatic compound with the aid of a condensing agent of the Friedel and Crafts type, followed by a sulphonation treatment with a sulphonating agent, whereby a sulphonation mixture is obtained containing higher alkyl aromatic sulfonic acids and impurities present as residual constituents from the mixture of non-aromatic hydrocarbons, the improvement which comprises separating the sulphonation mixture into masses of differing densities by means of the differences in the densities of the constituents of the mixture, one of said masses comprising higher alkyl aromatic sulphonic acids and another of said masses comprising said impurities.

4. In the method of producing higher alkyl aromatic sulphonates from mixtures of petroleum hydrocarbons and aromatic compounds by condensation of a mixture of petroleum hydrocarbons containing between 10 and 20 carbon atoms in an alkylating form with an aromatic compound with the aid of a metal halide condensing agent, followed by a sulphonation treatment with a sulphonating agent, whereby a sulphonation mixture is obtained containing higher alkyl aromatic sulphonic acids and impurities comprising by-products of the previous reactions and petroleum hydrocarbons, the improvement which comprises permitting the sulphonation mixture to stand quiescent for a sufficient period of time to produce stratification into an acid layer comprising higher alkyl aromatic sulphonic acids and a layer comprising said impurities, and separating said layers.

5. In the method of producing higher alkyl aromatic sulphonates from mixtures of non-aromatic hydrocarbons and aromatic compounds by halogenation of a mixture of non-aromatic hydrocarbons, cendensation of the resulting mixture of alkyl halides with the aromatic compound with the aid of a metal halide condensing agent, followed by a sulphonation treatment of the condensation product with a sulphonating agent, the improvements which comprise halogenating the mixture of non-aromatic hydrocarbons to produce a halogenation reaction mixture comprising a mixture of alkyl halides and unreacted non-aromatic hydrocarbons, reacting the resulting mixture of alkyl halides containing unreacted non-aromatic hydrocarbons as impurities with the aromatic compound and a metal halide condensing agent to effect condenastion of the alkyl halides with the aromatic compound, reacting a sulphonating agent with the resulting mixture of higher alkyl aromatic compounds containing impurities present as constituents of the mixture of non-aromatic hydrocarbons and formed as by-products of the foregoing reactions, whereby a sulphonation mixture is obtained containing higher alkyl aromatic sulphonic acids and said impurities, and separating the resulting sulphonation mixture into an acid mass of one density comprising resulting higher alkyl aromatic sulphonic acids and a mass of a different density comprising said impurities, by means of said differences in density.

6. The method of producing higher alkyl aromatic sulphonates which comprises chlorinating a petroleum hydrocarbon distillate containing 10 to 20 carbon atoms, condensing a resulting mixture of alkyl chlorides with an aromatic hydrocarbon with the aid of a metal halide condensing agent, treating the resulting alkyl aromatic hydrocarbon mixture with a sulphonating agent under sulphonating conditions, stratifying the resulting sulphonation reaction mixture into an acid layer of higher alkyl aromatic sulphonates and an oily layer of residual petroleum hydrocarbons, and separating said layers.

7. The method of producing higher alkyl aromatic sulphonates which comprises chlorinating a petroleum hydrocarbon distillate containing 10 to 20 carbon atoms to produce a chlorination reaction mixture comprising a mixture of alkyl chlorides and unreacted petroleum hydrocarbons, condensing the resulting chlorination reaction mixture with an aromatic hydrocarbon with the aid of a metal halide condensing agent, treating the resulting alkyl aromatic hydrocarbon mixture with a sulphonating agent under sulphonating conditions, whereby a sulphonation mixture is obtained containing sulphuric acid, higher alkyl aromatic sulphonic acids and oily impurities comprising petroleum hydrocarbons and by-products of the previous reactions, and separating the resulting sulphonation mixture into an acid mass of one density comprising higher alkyl aromatic sulphonic acids and a mass of a different density comprising said oily impurities, by means of said differences in density.

8. The method of producing higher alkyl aromatic sulphonates which comprises chlorinating a petroleum hydrocarbon distillate containing 10 to 20 carbon atoms to produce a chlorination reaction mixture comprising a mixture of alkyl chlorides and unreacted petroleum hydrocarbons, condensing the resulting chlorination reaction mixture with an aromatic hydrocarbon of the benzene series with the aid of a metal halide condensing agent, treating the resulting alkyl benzene mixture with a sulphonating agent under sulphonating conditions, whereby a sulphonation mixture is obtained containing higher alkyl benzene sulphonic acids and impurities comprising petroleum hydrocarbons and by-products of the previous reactions, and separating said impurities from the higher alkyl benzene sulphonic acids by stratification.

9. The method of producing higher alkyl aromatic sulphonates which comprises chlorinating a petroleum hydrocarbon distillate of the Pennsylvania type containing 12 to 16 carbon atoms to produce a chlorination reaction mixture comprising a mixture of alkyl chlorides and unreacted petroleum hydrocarbons, condensing the resulting chlorination reaction mixture with benzene in the presence of aluminum chloride, separating the resulting mixture of higher alkyl benzenes from the sludge formed as a by-product of the reaction, reacting a sulphonating agent with a resulting mixture of higher alkyl benzenes containing as impurities residual petroleum hydrocarbons and by-products of the foregoing reactions, whereby a sulphonation mixture is obtained containing a mixture of higher alkyl benzene sulphonic acids and said impurities, permitting the sulphonation mixture to stand quiescent for a sufficient period of time to produce stratification into an acid layer comprising higher alkyl benzene sulphonic acids and a layer comprising said impurities, and separating the acid layer

comprising higher alkyl benzene sulphonic acids from the remainder.

10. The method of producing higher alkyl aromatic sulphonates which comprises sulphonating a crude mixture of higher alkyl aromatic compounds having as impurities oily bodies of a similar distillation range but a different density, and separating the resulting sulphonation reaction mixture into an acid mass of one density comprising resulting higher alkyl aromatic sulphonic acids and a mass of a different density comprising such oily bodies, by means of said differences in density.

11. The method of producing higher alkyl aromatic sulphonates which comprises sulphonating a crude mixture of higher alkyl aromatic compounds, containing between 10 and 20 carbon atoms in the alkyl group, having as impurities oily bodies of a similar distillation range, stratifying the resulting sulphonation reaction mixture into an acid layer of resulting higher alkyl aromatic sulphonic acids and an oily layer of such impurities, and separating said layers.

12. The method of producing higher alkyl aromatic sulphonates which comprises sulphonating a crude mixture of higher alkyl aromatic compounds, containing between 10 and 20 carbon atoms in the alkyl group, having as impurities oily bodies of a similar distillation range, permitting the resulting sulphonation reaction mixture to stand quiescent for a sufficient period of time to produce stratification into an acid layer comprising resulting higher alkyl aromatic sulphonic acids and a layer comprising such oily bodies, separating said layers, and recovering the higher alkyl aromatic sulphonic acids from the separated acid layer.

13. The method of producing higher alkyl aromatic sulphonates which comprises chlorinating a petroleum hydrocarbon distillate containing 10 to 20 carbon atoms, said distillate boiling over a temperature range greater than 50° C., condensing a resulting mixture of alkyl chlorides with an aromatic hydrocarbon with the aid of a metal halide condensing agent, treating the resulting alkyl aromatic hydrocarbon mixture with a sulphonating agent under sulphonating conditions, stratifying the resulting sulphonation reaction mixture into an acid layer of higher alkyl aromatic sulphonates and an oily layer comprising residual petroleum hydrocarbons, and separating said layers.

14. The method of producing higher alkyl aromatic sulphonates which comprises chlorinating a petroleum hydrocarbon distillate containing 12 to 16 carbon atoms to produce a chlorination reaction mixture comprising a mixture of alkyl chlorides and unreacted petroleum hydrocarbons, said distillate boiling over a temperature range greater than 50° C., condensing the resulting chlorination reaction mixture with benzene in the presence of aluminum chloride, recovering a mixture of higher alkyl benzenes containing as impurities residual petroleum hydrocarbons and by-products of the foregoing reactions, reacting the recovered mixture with a sulphonating agent to produce a sulphonation mixture containing a mixture of higher alkyl benzene sulphonic acids and said impurities, permitting the sulphonation mixture to stand quiescent for a sufficient period of time to produce stratification into an acid layer comprising higher alkyl benzene sulphonic acids and a layer comprising said impurities, and separating the acid layer comprising higher alkyl benzene sulphonic acids from the remainder.

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