Patented Mar. 16, 1943

2,314,255

UNITED STATES PATENT OFFICE

2,314,255

PRODUCTION OF ALKYL ARYL SULPHONATES

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No Drawing. Application June 13, 1940, Serial No. 340,325

11 Claims. (Cl. 260—505)

This invention relates to a process for improving the storage properties of mixtures of substituted aryl sulphonates which contain as as nuclear substituents radicals corresponding to the hydrocarbons present in a petroleum distillate. More particularly it relates to a process for improving the storage properties of mixed alkyl benzene sulphonates which contain as nuclear substituents radicals derived from the hydrocarbons present in a kerosene fraction of petroleum.

As a comparatively recent development in the field of synthetic detergents, wetting agents, emulsifying agents, soap substitutes, and the like, there have been developed composition consisting of mixtures of aryl sulphonates which contain as nuclear substituents radicals corresponding to the hydrocarbons present in petroleum distillates. The aryl sulphonates present in such mixtures are conveniently referred to as alkyl aryl sulphonates, the term "alkyl" being used in its broad sense to include cycloalkyl radicals as well as straight or branched open-chain alkyl radicals. Depending upon the purpose for which they are to be used, these mixed alkyl aryl sulphonates are derived from petroleum fractions such as fractions within the upper gasoline range, the kerosene range, and higher ranges.

For example, where compositions are desired particularly adapted for use as wetting agents, petroleum distillates may be employed which boil as low as 100° C. In general, however, petroleum distillates are not employed having a boiling point lower than the boiling point corresponding to nonane. Thus, a useful petroleum distillate for the manufacture of mixed alkyl aryl sulphonates for use as wetting agents is one boiling within the range of 140° to 180° C.

Where it is desired to prepare a composition containing mixed alkyl aryl sulphonates in which the substituent alkyl radicals contain an average of more than 20 carbon atoms, a petroleum distillate having an upper boiling point as high as 300° C. at 25 mm. absolute pressure may be used. For most purposes, particularly for use as a general detergent, products derived from petroleum distillates within the kerosene range are preferable; i. e., petroleum distillates boiling for the most part within the range of 180° to 300° C. and preferably composed predominantly of aliphatic and/or alicyclic hydrocarbons which boil within the range of 180° to 280° C.

One process for preparing these mixed alkyl aryl sulphonates involves chlorinating the selected petroleum distillate, condensing resulting chlorhydrocarbons with an aromatic compound, usually in the presence of a Friedel-Crafts condensing agent such as aluminum chloride or zinc chloride, sulphonating the resulting substituted aromatic compounds, reacting the sulphonation mass with a suitable alkaline compound to form salts of the sulphonic acids therein, usually aqueous caustic soda, and drying the resulting mixture. It will be understood that this process is subject to many minor variations, such as distillation of the reaction mixtures at various points. United States Patent 2,233,408, of March 4, 1941, to Lawrence H. Flett, discloses methods for making mixed alkyl aryl sulphonates of this class.

These mixed alkyl aryl sulphonates offer several important advantages over other available synthetic detergents. First, because of the relatively inexpensive raw materials used in their manufacture, they may be produced economically. Also due to the fact that they consist of not one compound but of a mixture of compounds having properties varying among themselves, they are capable of a wider variety of uses than many other synthetic detergents, which are usually relatively specific in their action. In view of these facts, the mixed alkyl aryl sulphonates, particularly the alkyl benzene sulphonates, are the class of products which should be most satisfactory for general household uses. However, the mixed alkyl aryl sulphonates have the property of developing a rancid odor on being stored. While this characteristic of the mixed alkyl aryl sulphonates is not a decisive disadvantage in so far as their acceptance by those engaged in using synthetic detergents in industrial applications is concerned, this property would have an adverse effect upon the popularization of the mixed alkyl aryl sulphonates as general household detergents.

It is an object of the present invention to provide a process for preparing mixed alkyl aryl sulphonates of the class referred to above having improved storage properties, whereby the mixed alkyl aryl sulphonates may be stored for a relatively long period of time without developing rancid odors to an important degree. A more specific object of the invention is to provide a process for the treatment of mixed alkyl benzene compounds wherein the alkyl groups have been derived from a keroseene fraction of petroleum by a process including chlorination of the kerosene and condensation of re-

sulting chlorhydrocarbons with benzene, whereby upon sulphonation of resulting alkyl benzenes and neutralization and drying of the sulphonation product, mixed alkyl benzene sulphonates having improved storage properties are obtained.

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

It has been discovered in accordance with the present invention that mixed alkyl aryl sulphonates of the above type having improved storage properties can be obtained by subjecting the mixed alkyl aryl compounds from which the sulphonates are derived to the action of a phosphorus compound of the class set out below. The treatment of the mixed alkyl aryl compounds with the phosphorus compound can be effected at any time prior to the sulphonation of the compounds. The phosphorus compounds which I have found to be adapted for use in the process are members of the group consisting of hypo-, ortho-, meta-, and pyrophosphorous acids; hypo-, ortho-, metal-, and pyrophosphoric acids; phosphorus trioxide; phosphorus tetroxide; phosphorus pentoxide; phosphorus oxychloride; phosphorus trichloride; and phosphorus pentachloride. In referring to the above phosphorous and phosphoric acids, it will be understood that I intend to include compositions which are equivalent to these acids, for example a mixture of sulphuric acid and one or more salts of phosphorous and/or phosphoric acids, such as the alkali metal, ammonium and/or alkaline earth metal hypophosphites, orthophosphites, metaphosphites, pyrophosphites, hypophosphates, orthophosphates, metaphosphates, pyrophosphates, and polyphosphates.

As stated above, a particularly valuable product of the class with which the present invention is concerned contains mixed alkyl benzene compounds in which the substituent groups are derived from a paraffinic hydrocarbon petroleum distillate within the kerosene range, as by a procedure including chlorination of the distillate.

An advantageous process for preparing such mixed alkyl benzene sulphonates, which may also be termed sulphonates of benzene condensation products, includes the step of treating the mixed alkyl benzene compounds with sulphuric acid or oleum (hereinafter referred to as "a sulphuric acid wash), prior to their sulphonation, so as to put them in condition for use in the production of mixed alkyl benzene sulphonates of particularly good color characteristics, as described and claimed in the application of Lawrence H. Flett, Serial No. 340,468, filed June 14, 1940. The sulphuric acid wash may be carried out by mixing the mixed alkyl benzene compounds with sulphuric acid of 80% to 100% strength under conditions, including the strength and proportion of sulphuric acid, adapted to make a portion of the mixture soluble in water. The water-soluble portion of the mixture is then separated from the remainder of the mixture which is in such condition that, upon subsequent sulphonation followed by neutralization, sulphonates of improved color are obtained. (In this connection it is pointed out that the term "neutralization" is employed herein in the broad sense to mean conversion of the sulphonic acids to salts, the aqueous solutions of which may or may not have a pH of 7.) The treatment with a phosphorus compound of the above class in accordance with the present invention when incorporated in this process is preferably effected before the sulphuric acid wash although, if desired, there may be two such treatments: one before and one after the sulphuric acid wash. The treatment with a phosphorus compound may be employed also with particularly advantageous results in a process for manufacturing mixed alkyl aryl sulphonates which does not include a sulphuric acid wash.

The treatment with the phosphorus compound to achieve the improvement in the storage characteristics of the resulting alkyl aryl sulphonates can be carried out in a simple manner. For example, it has been found that it is sufficient merely to mix the phosphorus compound with the mixed alkyl aryl compounds and permit the mixture to stand for a relatively short period of time. The amount of a phosphorus compound preferably employed in the present process will vary depending upon the particular products subjected to treatment and the phosphorus compound employed. In general, however, it has been found to be preferable to use at least an amount of a phosphorus compound corresponding to 0.02 atomic equivalent of phosphorus for each molecular equivalent of the mixed alkyl aryl compounds if an important improvement in the storage characteristics of the mixed alkyl aryl sulphonates is to be obtained.

As a feature of the invention it has been found that often it is unnecessary to take any steps to remove the phosphorus compound after the expiration of the treatment. For example, where the phosphorus treatment precedes a sulphuric acid wash, the mixed alkyl aryl compounds containing the phosphorus compounds can be subjected to a sulphuric acid wash in the usual way. However, when a phosphorus compound is employed which possesses relatively low miscibility with the alkyl aryl compounds, after the treatment the mixtures may be permitted to settle and thereby separate the phosphorus compounds before proceeding with the next process step. In this connection it is pointed out that when a phosphorus or a phosphoric acid of less concentration than 100 per cent is employed in the treatment it is generally desirable to separate and withdraw said acid before subjecting the mixed substituted aryl compounds to a sulphuric acid wash or to sulphonation, in order to avoid dilution of the sulphuric acid. The phosphorous or phosphoric acid may be allowed to remain in the mixture if the amount of water in the acid is insufficient to dilute the sulphuric acid below its effective working strength.

Thus the present process may be carried out in various ways. The process has been found to effect a change in the properties of the mixed substituted aryl compounds so that such compounds upon sulphonation, neutralization, and drying are converted to dry compositions which are characterized by better storing and aging properties as compared with compositions prepared by the same process but omitting the treatment with a phosphorus compound. In general, it has been found that dry compositions most satisfactory for long storage are obtained either by employing a process which does not involve a sulphuric acid wash, the sulphonation following immediately after the treatment with the phosphorus compound, which may or may not have been removed from the mixture, or by a process in which a phosphorus treatment with optional removal of the phosphorus compound both precedes and follows a sulphuric acid wash.

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present art it is believed to be unnecessary to enumerate all of the various types of petroleum distillates whose derivatives may be treated in accordance with the present process to improve the odor characteristics of the resulting mixed alkyl aryl sulphonates. It is sufficient to point out that derivatives of petroleum distillates which boil for the most part within ranges which have lower limits above 100° C. and the sulphonates of which have the undesirable property of developing odors upon being stored may be treated advantageously by the present process. As previously indicated, the most important compositions for general detergent use are those which are obtained from kerosenes that are composed predominantly of aliphatic and alicyclic hydrocarbons by a process involving chlorination of the kerosene, condensation of the chlorhydrocarbons with an aromatic compound, and sulphonation of resulting condensation products. The treatment with the phosphorus compound may also be applied with advantage to the treatment of mixed alkyl aryl compounds prepared by a process involving conversion of a hydrocarbon mixture of the type specified to mixtures containing a large proportion of olefines, and condensation of the olefines with a suitable aromatic compound.

Although for most purposes the more valuable compositions of the type with which the present invention is concerned are derivatives of benzene, the invention is not restricted to the treatment of mixed alkyl benzene compounds (that is, derivatives of benzene itself) but may be applied with advantage to the treatment of other mixed alkyl aryl compounds such as, for example, other mononuclear aryl compounds such as phenol, toluene, phenetole, cresol, resorcinol, and polynuclear aryl compounds such as diphenyl, hydroxydiphenyl, diphenyloxide, naphthalene, and naphthol. For most purposes the compositions are prepared in the form of their sodium salts, but they may also be prepared in the form of their other alkali metal salts, or their ammonium or organic amine salts.

In order that the invention may be understood more fully, reference should be had to the following examples which illustrate various embodiments of the present invention. Where parts are referred to in the examples, they are by weight:

EXAMPLE 1.—*Part 1.*—10,620 pounds Pennsylvania kerosene (having a specific gravity of 0.788 at 24° C. and boiling range 185° to 275° C.) were filtered through porous stoneware into a lead-lined kettle fitted with lead-covered agitator, thermometer well, and other accessories. 4.4 pounds iodine were dissolved in the agitated kerosene charge which was warmed to about 60° C. and maintained between 60° and 70° C. while chlorine gas, also filtered through porous stoneware, was passed into the liquid at an average rate of about 300 pounds per hour, until the specific gravity of the chlorinated kerosene was 0.918 at 24° C., corresponding with 115 per cent monochlorination of the kerosene. The amount of chlorine required for the purpose was about 4,825 pounds. The final chlorinated kerosene mixture weighed 12,834 pounds. The chlorinated hydrocarbon thus obtained was condensed in portions with benzene as follows:

A mixture of 13,272 pounds of benzene and 332 pounds of anhydrous aluminum chloride was agitated and 6,636 pounds of the chlorinated kerosene mixture were added thereto over a period of three hours, during which the temperature of the mass rose to about 35° C. The mixture was then heated to 45° C. and held there for about one and one-half hours. Agitation was then stopped, the mixture was allowed to stand for about two hours; thereafter the lower tarry layer was withdrawn. The upper layer was conveyed to a stripping kettle in which the liquid was stripped of low-boiling hydrocarbons, chiefly benzene, by boiling the liquid until its temperature reached 150° C. at atmospheric pressure, then reducing the pressure in the distilling system to a pressure of three to four inches of mercury absolute pressure and continuing the boiling without further supply of heat for about one hour, until the temperature of the distilland was about 120° C. The material left after this stripping was distilled in vacuo until about 7 per cent of the charge in the still had been removed as distillate. The remaining distilland was distilled, and distillate therefrom was collected separately until the boiling point of the distilland was 250° C. at 14 mm. mercury pressure. This last distillate was chiefly the condensation product of the chlorinated hydrocarbons of the kerosene fraction and the benzene; and for convenience it is called "keryl benzene."

Part 2.—100 parts of the keryl benzene prepared as above described and 20 parts of 85 per cent orthophosphoric acid were mixed and agitated for about one hour during which the temperature of the mixture was maintained between 25° and 30° C. Then the mixture was allowed to stratify; the lower layer of acid was withdrawn, and the remaining organic oil was washed by stirring it with 20 parts of 100 per cent sulphuric acid for about one hour at 25° to 30° C. The mixture was allowed to stand, the lower stratum of acid was withdrawn, and the remaining oil was sulphonated by mixing it with 100 parts of 100 per cent sulphuric acid, maintaining the mixture for 30 minutes at 25° to 35° C. and then for one hour at 55° to 60° C. The mixture was allowed to stratify again, and the lower layer of spent acid was withdrawn. The middle layer of sulphonated oil was drowned in water and ice and neutralized with aqueous caustic soda. The solute in the solution was adjusted by suitable addition of anhydrous sodium sulphate to contain about 38 per cent of the sodium salts of the organic sulphonates, and the solution was then dried on a double drum drier.

In dry sodium keryl benzene sulphonate prepared without the pretreatment with phosphoric acid, a rancid, unpleasant odor can be developed by accelerated "aging" which is effected by keeping the product at about 85° C. for about 16 hours, or longer. Distinctly less rancidity was developed by a similar aging treatment of the dry sodium keryl benzene sulphonate which had been prepared as described in the foregoing example.

EXAMPLE 2.—100 parts of a keryl benzene prepared as described in Example 1, Part 1, were agitated at room temperature with 21 parts of 100 per cent orthophosphoric acid for about one hour. The mixture was allowed to stand about one-half hour, then the lower layer of acid was withdrawn. The remaining oil was agitated with 20 parts of 100 per cent sulphuric acid at room temperature for about one hour. The mass was again allowed to stand for about one-half hour and the lower acid layer was withdrawn. Thereafter the washed oil was sulphonated with 100 parts of 100 per cent sulphuric acid by agitating

this oil-acid mixture for about one-half hour at room temperature and for about one hour at about 55° to about 60° C. Thereafter the sulphonation mixture was permitted to stand for two hours during which three layers of material separated; the top layer was chiefly unsulphonated material; the middle layer was chiefly sulphonated keryl benzene; and the bottom layer was spent sulphuric acid. The middle layer was separated from the others, drowned in ice water, neutralized with caustic soda (aqueous solution), and dried on a rotary drum drier.

The dried product, when heated to 85° C. to obtain accelerated aging effects, developed a rancid odor at a slower rate than a corresponding dry product made by the same process from similar keryl benzene oil which was not treated with a phosphorus compound of the above class.

EXAMPLE 3.—100 parts of keryl benzene prepared as described in Example 1, Part 1, were agitated with 15 parts of 93 per cent orthophosphoric acid for about 15 minutes; then five grams of 100 per cent sulphuric acid were added, and the mixture was stirred for another 45 minutes. It was allowed to stand for about one-half hour and the lower layer of separated acid was withdrawn. The remaining oil was sulphonated by agitating it with about 100 parts of 100 per cent sulphuric acid at room temperature (about 20° to 30° C.) for about 25 minutes, thereafter warming the mixture to a temperature within the range 55° to 60° C. and stirring it for about one hour. The mixture was then allowed to stratify; the middle organic sulphonate layer was separated, drowned, neutralized with caustic soda, adjusted to a content of organic sulphonate and inorganic salts (substantially sodium sulphate) corresponding to 38 per cent of organic sulphonate and 62 per cent of inorganic salts, and evaporated to dryness on a rotary drum drier.

The dried product, when heated to 85° C. to obtain accelerated aging effects, developed a rancid odor at a slower rate than a corresponding dry product made by the same process from a similar keryl benzene oil which was not treated with a phosphorus compound of the above class.

The following example illustrates a process which includes treatment of the keryl benzene oil with phosphoric acid, but without a sulphuric acid wash before sulphonation:

EXAMPLE 4.—100 parts keryl benzene prepared as described in Example 1, Part 1, were mixed with 10 parts of 100 per cent phosphoric acid. The mixture was adjusted to a temperature of 25° to 30° C. and agitated at that temperature for about 30 minutes. Thereafter, at a temperature around 25° C., it was treated with about 132 parts of 100 per cent sulphuric acid, and stirred while its temperature was maintained at about 20° to 30° C. Thereafter, the sulphonation was completed and the remaining processing steps to obtain a dry detergent composition were carried out in the manner described in Example 3. The final dry composition contained about 62 per cent by weight of inorganic salts, chiefly sodium sulphate, and about 38 per cent sodium keryl benzene sulphonate.

The mixture thus obtained was found to be more stable than the one made by a process omitting the treatment with the phosphorus compound.

As before stated, the treatment with a phosphorus compound may be applied before a sulphuric acid wash and repeated before sulphonation. The following example illustrates applying the present improvement in this way using orthophosphoric acid. It will be noted that the phosphoric acid and sulphuric acid used in the sulphuric acid wash are removed from the mixed substituted benzene compounds but that the phosphoric acid employed after the sulphuric acid wash is retained in the mixture during sulphonation. In proceeding in this way it is necessary of course to take into account the amount of water added with the phosphoric acid, and if the amount of water thus added be sufficient to dilute the sulphuric acid below the strength necessary for sulphonation, either a greater quantity of sulphonating agent or a stronger sulphonating agent must be used.

EXAMPLE 5.—100 parts keryl benzene prepared as described in Example 1, Part 1, were agitated with 15 parts of 93 per cent orthophosphoric acid for 15 minutes at 20° to 30° C. Then 5 parts 100 per cent sulphuric acid were added and the mixture was agitated about 45 minutes. The mass was then allowed to stratify and the lower separated layer of acid was withdrawn.

To the remaining oil, 5 parts of 93 per cent orthophosphoric acid were added; the mixture was agitated about 10 minutes, then 100 parts of 100 per cent sulphuric acid were added, and the mixture was stirred at room temperature for about 30 minutes, then at 55° to 60° C. for about one hour. Thereafter the sulphonated product was recovered as described in Example 3 as a dry mixture containing sodium keryl benzene sulphonate.

The dry product under the influence of accelerated aging by keeping it at 85° C., developed rancid odor much more slowly than a control sample which was aged similarly and was made from a similar keryl benzene not treated with a phosphorus compound.

In modifications of the foregoing treatments of keryl benzene oils with orthrophosphoric acid, it has been found that the strength of the treating phosphoric acid, the temperatures at which the treatments may be applied, the ratio of phosphoric acid to keryl benzene oil treated, and the period of treatment with the acid may be varied considerably without seriously disturbing the beneficial effects of the treatments. The following examples illustrate the effects of such variations.

EXAMPLE 6.—100 parts keryl benzene prepared as described in Example 1, Part 1, were mixed with 20 parts of 100 per cent orthophosphoric acid for one hour at 20° to 25° C. The mixture was permitted to settle and the lower phosphoric acid layer was withdrawn. To the remaining oil sufficient 100 per cent sulphuric acid was added to effect the sulphonation of the oil by the above method of warming and agitating the oil-sulphuric acid mixture. The sulphonated mass was drowned, neutralized with caustic soda, adjusted to the ratio of sodium keryl benzene sulphonate to inorganic salts in the solute described in Example 3, and dried on a rotary drum drier.

Similar preparations were made using respectively 60 per cent, 75 per cent, 85 per cent, and 90 per cent orthophosphoric acid.

The results were substantially the same in the cases in which 75 per cent and 85 per cent phosphoric acid were used. The compositions from keryl benzene treated with 60 per cent, 90 per cent, and 100 per cent phosphoric acid in comparison with those treated with 75 per cent and 85 per cent phosphoric acid, were characterized by slightly inferior stability during storage. However, all developed a rancid odor more slowly

than a preparation made without the phosphoric acid treatment. Preferred treatments are effected with phosphoric acids of concentrations from 75 per cent to 85 per cent.

EXAMPLE 7.—Each of a series of four experiments was made in the manner described in Example 4, but the temperatures at which the keryl benzene was treated with the orthophosphoric acid were adjusted respectively at 10° C., 25° to 30° C., 45° to 50° C., and 75° to 80° C.; and before the sulphonating acid was added, the mixture in each case was warmed or cooled, as necessary, to about 25° C.

The resulting compositions were compared for stability during storage. It was found that the differences in the retardation effects upon development of rancidity in the four cases were measurable though small. The best result was obtained with a treatment at 45° to 50° C. The results of treatments at 10° C., 25° to 30° C., and 75° to 80° C. were less favorable than those at 45° to 50° C., but still much more favorable than where no phosphoric acid was used.

EXAMPLE 8.—A series of experiments, conducted in the manner of Example 4, was completed with the utilization of treatments with 100 per cent orthophosphoric acid in amounts ranging in the respective preparations from 2 to 50 parts of acid per 100 parts of keryl benzene oil. The compositions from these experiments in the series were compared by storage for retarding effects of the treatments on the development of objectionable odor in the products. It was found that in all cases an improvement in stability during storage was obtained, the best results being obtained with an amount of acid corresponding to from 10 to 30 per cent, and especially 20 per cent of the weight of the keryl benzene oil treated.

EXAMPLE 9.—100 parts keryl benzene prepared as described in Example 1, Part 1, were agitated with two parts phosphorus pentoxide for about one hour at 25° to 30° C. Part of the pentoxide dissolved in the oil, and part remained on the walls and bottom of the vessel. The oil was withdrawn and sulphonated without any intermediate wash with sulphuric acid. The sulphonating, drowning, neutralizing, adjusting and drying steps were effected substantially as described in Example 1.

The resulting dry composition containing sodium keryl benzene sulphonate was characterized by developing less rancidity and unpleasant odor than a similar sulphonate subjected to the same storage conditions and made from the same kind of keryl benzene which, however, had not been treated with a phosphorus compound.

EXAMPLE 10.—20 parts phosphorus pentachloride were agitated for 15 minutes with 100 parts of keryl benzene prepared as described in Example 1, Part 1, then five parts 100 per cent sulphuric acid were added to the mixture and agitated for one hour at 25° to 30° C. The liquid portion of the mixture was separated from solid material, and to the former 15 parts of 100 per cent sulphuric acid were added to facilitate stratification in the liquid mixture. The latter was allowed to stand about one-half hour, after which the separated acid layer was withdrawn. The remaining oil was sulphonated and converted to a dry composition containing about 38 per cent by weight of sodium keryl benzene sulphonate in a manner similar to that described in Example 1.

The dry product was characterized by developing less unpleasant odor than the dry product from untreated keryl benzene, when the dry products were stored under the same conditions for the same time.

EXAMPLE 11.—8 parts phosphorus trichloride were added to 400 parts of keryl benzene and the mixture was agitated at 25° to 30° C. for about 15 minutes; 60 parts of 100 per cent sulphuric acid were then added, and the mixture, after being agitated for about one hour at room temperature, was allowed to stand and stratify and the lower layer of acid was withdrawn. 8 parts of phosphorus trichloride were added to the remaining oil, and the mixture, at room temperature, was agitated for about 15 minutes. 460 parts of 100 per cent sulphuric acid were then added, and the mixture was stirred at 25° to 30° C. for about 30 minutes, then at 55° to 60° C. for about one hour. Again the mixture was permitted to stratify; the middle sulphonated layer was separated, drowned in ice water, and neutralized with caustic soda. After the proportion of sodium keryl benzene sulphonate to inorganic salts in the solute was adjusted so as to yield a dry product containing about 38 per cent by weight of sodium keryl benzene sulphonates, the solution was evaporated to dryness on a drum drier.

This dry composition did not develop any objectionable odor after 16 hours of accelerated aging at 85° C. A composition made similarly from a similar keryl benzene not treated with a phosphorus compound when aged for 16 hours at 85° C. became rancid to an undesirable degree. After the two compositions were aged artificially for 160 hours at 85° C., the composition which had been treated with a phosphorus compound was much less rancid than the composition which had not been treated with a phosphorus compound.

EXAMPLE 12.—100 parts keryl benzene were mixed with 4 parts phosphorus oxychloride and stirred at room temperature for five minutes. To the mixture, 15 parts 100 per cent sulphuric acid were added and agitation was continued at 25° to 30° C. for about one hour. The wash acid was separated; the acid-washed oil was treated with 4 parts phosphorus oxychloride at 25° to 30° C. for 10 minutes, then about 100 parts of 100 per cent sulphuric acid were added, and the mixture was stirred at room temperature for about 30 minutes and at 55° to 60° C. for about one hour. From the sulphonation mass dry sodium keryl benzene sulphonate was obtained by the previously described drowning, neutralizing, and drying steps.

The dry product, after being aged artificially for 160 hours at 85° C., was distinctly less rancid than a sample similarly aged and prepared from the same kind or keryl benzene which had not been treated with a phosphorus compound.

EXAMPLE 13.—Three mixtures of keryl benzene and phosphorus trichloride were made with equal amounts of keryl benzene prepared as described in Example 1, Part 1, the mixtures respectively contained 4 parts, 10 parts, and 20 parts phosphorus trichloride per 100 parts keryl benzene in them. The mixtures were agitated for about 15 minutes at 25° to 30° C.

A fourth sample of this keryl benzene was submitted to the ordinary sulphuric acid wash, and the sulphuric acid was separated and discarded in the usual manner before the sulphonating charge of acid was added.

Without separating and removing the phosphorus trichloride from the treated portions of keryl benzene oils, the three phosphorus trichlo-

ride keryl benzene mixtures, as well as the sulphuric acid washed keryl benzene, were severally sulphonated by the addition of 100 per cent sulphuric acid, followed by heating and stirring, separation of the sulphonated portion, dilution, neutralization, adjustment of ratio of sodium keryl benzene sulphonate to inorganic salts in the solute, and drying of the resulting solution. The dry compositions were compared by storing them under the same conditions and noting the development of rancid odors in the compositions.

It was found that the compositions derived from keryl benzenes treated with phosphorus trichloride could be stored for much longer periods than the product derived from the ordinary sulphuric acid washed keryl benzene; and the retardations of unpleasant odors in the former products were substantially of the same degree in the three compositions.

From the foregoing examples it will be seen that the conditions under which the present process may be carried out can vary within wide limits. For example, the temperature at which the mixed alkyl aryl compounds and the phosphorus compound are maintained in admixture in general is not an essential condition of the process. Thus, temperatures varying from 0° to 100° C. are suitable and it is generally unnecessary to use temperatures varying greatly from room temperatures. As shown by the above examples, when using orthophosphoric acid, temperatures varying from 10° to 80° C. have been found to be suitable and optimum results are obtained when maintaining the temperature at from 45° to 50° C. When using phosphorus trichloride, temperatures varying from 20° to 60° C. have been found to be entirely satisfactory, although it is generally preferred to maintain the temperature at from 20° to 30° C. If it is desired to shorten the time of the reaction, it is usually advisable to employ higher temperatures.

The period of time required for achieving optimum results from the phosphorus treatment will vary depending upon the composition subjected to treatment, the particular phosphorus compound employed, the temperature, and other factors. It has been found, however, that the reaction proceeds rapidly and generally short reaction periods (such as 5 or 10 minutes, for example) are entirely satisfactory. On the other hand, extended reaction periods may be employed if desired. In the case of orthophosphoric acid, it is preferred to employ a reaction period of 15 to 60 minutes and in the case of phosphorus trichloride, it is generally preferable to permit the reaction to continue for a period of 10 to 20 minutes. The principal reason for not employing longer periods is that no noticeable improvement in results is obtained. Thus, with phosphorus trichloride reaction periods up to five hours have been employed with satisfactory but not substantially improved results. In certain cases, prolonged reaction periods, say for 24 hours or more, are undesirable; for, while an improvement in the storage characteristics of the mixed alkyl aryl sulphonates as compared with the storage characteristics of similar sulphonates prepared without the use of a phosphorus treatment is obtained, this improvement is somewhat less than that obtained with the use of shorter reaction periods.

The amount of phosphorus compound used in the process may also be varied widely. As noted above it is preferred to use at least an amount of a phosphorus compound corresponding to 0.02 atomic equivalent of phosphorus for each molecular equivalent of the mixed alkyl aryl compounds, since otherwise an important improvement in the storage properties of the resulting mixed alkyl aryl sulphonates is not obtained. Ordinarily, however, it is preferred to use a greater quantity of a phosphorus compound. For example, when using orthophosphoric acid solutions, which as pointed out in the examples may vary in concentration, for the treatment of mixed alkyl benzene compounds derived from benzene and a paraffinic hydrocarbon distillate within the kerosene range by chlorination of the distillate and condensation of resulting chlorinated hydrocarbons with benzene with the aid of a Friedel-Crafts condensing agent, such as anhydrous aluminum chloride, it is preferred to employ the phosphoric acid in amounts based on 100 per cent acid corresponding to 10 to 30 per cent, and especially about 20 per cent of the weight by the mixed alkyl benzenes, as indicated in Example 8. In carrying out the present process using phosphorus trichloride by the treatment of mixed alkyl benzenes of the above class, it has been found that amounts of this compound corresponding to from one per cent to 20 per cent or more of the weight of the mixed alkyl benzenes are entirely satisfactory and that amounts corresponding to 2 to 4 per cent are preferable, larger amounts not producing superior results and hence representing a waste.

Because of its property of reducing odor efficiently and also because in many cases it also acts to improve the color of the products, phosphorus trichloride is preferred for use in the present process.

It will be understood that the foregoing examples are merely illustrative of the invention and that other mixed alkyl aryl compounds of the class hereinbefore disclosed may be treated in a similar manner with any of the phosphorus compounds adapted for use for the purposes of the present invention whereby, upon subsequent sulphonation and neutralization, mixed alkyl aryl sulphonates are obtained which can be stored for relatively long periods of time without developing an unpleasant odor to an undesirable degree.

Since changes may be made in the process described above without departing from the invention, it is intended that the description shall be taken as illustrative and not in a limiting sense.

I claim:

1. In the process for the preparation of mixed alkyl aryl sulphonates in which the alkyl groups are derived from a petroleum distillate which boils for the most part above 100° C., involving sulphonation of corresponding mixed alkyl aryl compounds, the improvement which comprises treating the mixed alkyl aryl compounds, prior to the sulphonation, with a phosphorus compound selected from the group consisting of hypo-, ortho-, meta-, and pyrophosphorous acids; hypo-, ortho-, meta-, and pyrophosphoric acids; phosphorus trioxide; phosphorus tetroxide; phosphorus pentoxide; phosphorus oxychloride; phosphorus trichloride; and phosphorus pentachloride, whereby the treated mixed alkyl aryl compounds upon sulphonation, neutralization, and drying are converted into dry mixed alkyl aryl sulphonates which can be stored without developing unpleasant odors to an undesirable degree for a longer period of time than a mixture of alkyl aryl sulphonates which has been

prepared by the same process but omitting the treatment with a phosphorus compound.

2. In the process for the preparation of mixed alkyl aryl sulphonates in which the alkyl groups are derived from a petroleum distillate which boils for the most part within the range 180° to 300° C., involving sulphonation of corresponding mixed alkyl aryl compounds, the improvement which comprises treating the mixed alkyl aryl compounds, prior to the sulphonation, with a phosphorus compound selected from the group consisting of hypo-, ortho-, meta-, and pyrophosphorous acids; hypo-, ortho-, meta-, and pyrophosphoric acids; phosphorus trioxide; phosphorus tetroxide; phosphorus pentoxide; phosphorus oxychloride; phosphorus trichloride; and phosphorus pentachloride, the amount of phosphorus compound employed corresponding to at least 0.02 atomic equivalent of phosphorus for each molecular equivalent of the mixed alkyl aryl compounds, whereby the treated mixed alkyl aryl compounds upon sulphonation, neutralization, and drying are converted into dry mixed alkyl aryl sulphonates which can be stored without developing unpleasant odors to an undesirable degree for a longer period of time than a mixture of alkyl aryl sulphonates which has been prepared by the same process but omitting the treatment with a phosphorus compound.

3. In the process for the preparation of mixed alkyl mononuclear aryl sulphonates in which a petroleum distillate which boils for the most part above 100° C. is halogenated, resulting halogenated hydrocarbons are condensed with a mononuclear aromatic compound with the aid of a Friedel-Crafts condensing agent, and resulting mixed alkyl aryl compounds are sulphonated, the improvement which comprises treating the mixed alkyl aryl compounds resulting from the Friedel-Crafts condensation with a phosphorus compound selected from the group consisting of hypo-, ortho-, meta-, and pyrophosphorous acids; hypo-, ortho-, meta-, and pyrophosphoric acids; phosphorus trioxide; phosphorus tetroxide; phosphorus pentoxide; phosphorus oxychloride; phosphorus trichloride; and phosphorus pentachloride, the amount of phosphorus compound employed corresponding to at least 0.02 atomic equivalent of phosphorus for each molecular equivalent of the mixed alkyl aryl compounds, whereby the treated mixed alkyl aryl compounds upon sulphonation, neutralization, and drying are converted into dry mixed alkyl aryl sulphonates which can be stored without developing unpleasant odors to an undesirable degree for a longer period of time than a mixture of alkyl aryl sulphonates which has been prepared by the same process but omitting the treatment with a phosphorus compound.

4. In the process for the preparation of mixed alkyl aryl sulphonates in which the alkyl groups are derived from a petroleum distillate which boils for the most part above 100° C., involving sulphonation of corresponding mixed alkyl aryl compounds, the improvement which comprises treating the mixed alkyl aryl compounds, prior to the sulphonation, with phosphorus trichloride, whereby the treated mixed alkyl aryl compounds upon sulphonation, neutralization, and drying are converted into dry mixed alkyl aryl sulphonates which can be stored without developing unpleasant odors to an undesirable degree for a longer period of time than a mixture of alkyl aryl sulphonates which has been prepared by the same process but omitting the treatment with phosphorus trichloride.

5. In the process for the preparation of mixed alkyl benzene sulphonates in which the alkyl groups are derived from a petroleum distillate which boils for the most part within the range 180° to 300° C., involving sulphonation of corresponding mixed alkyl benzenes, the improvement which comprises treating the mixed alkyl benzenes with phosphorus trichloride at a temperature from 20° to 60° C., the phosphorus trichloride being employed in an amount corresponding to from 1 per cent to 20 per cent of the weight of the mixed alkyl benzenes, whereby the treated mixed alkyl benzenes upon sulphonation, neutralization, and drying are converted into dry mixed alkyl benzene sulphonates which can be stored without developing unpleasant odors to an undesirable degree for a longer period of time than a mixture of alkyl benzene sulphonates which has been prepared by the same process but omitting the treatment with a phosphorus compound.

6. In the process for the preparation of mixed alkyl benzene sulphonates in which a petroleum distillate which boils for the most part within the range 180° to 300° C. and is composed predominantly of hydrocarbons selected from the group consisting of aliphatic and alicyclic hydrocarbons is halogenated, resulting halogenated hydrocarbons are condensed with benzene with the aid of a Friedel-Crafts condensing agent, and resulting mixed alkyl benzenes are sulphonated, the improvement which comprises treating the mixed alkyl benzenes with phosphorus trichloride for 10 to 20 minutes at a temperature from 20° to 30° C., the phosphorus trichloride being employed in an amount corresponding to from 2 to 4 per cent of the weight of the mixed alkyl benzenes, whereby the treated mixed alkyl benzenes upon sulphonation, neutralization, and drying are converted into dry mixed alkyl benzene sulphonates which can be stored without developing unpleasant odors to an undesirable degree for a longer period of time than a mixture of alkyl benzene sulphonates which has been prepared by the same process but omitting the treatment with phosphorus trichloride.

7. In the process for the preparation of mixed alkyl benzene sulphonates in which a petroleum distillate which boils for the most part within the range 180° to 300° C. and is composed predominantly of hydrocarbons selected from the group consisting of aliphatic and alicyclic hydrocarbons is halogenated, resulting halogenated hydrocarbons are condensed with benzene with the aid of a Friedel-Crafts condensing agent, and resulting mixed alkyl benzenes are sulphonated, the improvement which comprises treating the mixed alkyl benzenes with orthophosphoric acid of 60 to 100 per cent strength for 10 to 60 minutes at a temperature from 10° to 80° C., the orthophosphoric acid being employed in an amount based on 100 per cent acid corresponding to from 10 to 30 per cent of the weight of the mixed alkyl benzenes, whereby the treated mixed alkyl benzenes upon sulphonation, neutralization, and drying are converted into dry mixed alkyl benzene sulphonates which can be stored without developing unpleasant odors to an undesirable degree for a longer period of time than a mixture of alkyl benzene sulphonates which has been prepared by the same process but omitting the treatment with orthophosphoric acid.

8. The process for the preparation of mixed

alkyl aryl sulphonates having good storage properties which comprises chlorinating a petroleum distillate boiling for the most part within the range 180° to 300° C., condensing resulting chlorinated hydrocarbons with an aromatic compound with the aid of a Friedel-Crafts condensing agent, treating resulting mixed alkyl aryl compounds with a phosphorus compound selected from the group consisting of hypo-, ortho-, meta-, and pyrophosphorous acids; hypo-, ortho-, meta-, and pyrophosphoric acids; phosphorus trioxide; phosphorus tetroxide; phosphorus pentoxide; phosphorus oxychloride; phosphorus trichloride; and phosphorus pentachloride, adding sulphuric acid of sulphonating strength to the mixture resulting from said treatment, sulphonating the treated mixed alkyl aryl compounds, neutralizing the resulting sulphonic acids, and drying the resulting sulphonates.

9. The process for the preparation of mixed alkyl aryl sulphonates having good storage properties which comprises chlorinating a petroleum distillate boiling for the most part within the range 180° to 300° C. and composed predominantly of hydrocarbons selected from the group consisting of aliphatic and alicyclic hydrocarbons, condensing resulting chlorinated hydrocarbons with an aromatic compound with the aid of a Friedel-Crafts condensing agent, treating resulting mixed alkyl aryl compounds with a phosphorus compound selected from the group consisting of hypo-, ortho-, meta-, and pyrophosphorous acids; hypo-, ortho-, meta-, and pyrophosphoric acids; phosphorus trioxide; phosphorus tetroxide; phosphorus pentoxide; phosphorus oxychloride; phosphorus trichloride; and phosphorus pentachloride, washing the treated mixed alkyl aryl compounds with sulphuric acid, sulphonating the washed mixed alkyl aryl compounds, neutralizing the resulting sulphonic acids, and drying the resulting sulphonates.

10. The process for the preparation of mixed alkyl aryl sulphonates having good storage properties which comprises chlorinating a petroleum distillate boiling for the most part within the range 180° to 300° C. and composed predominantly of hydrocarbons selected from the group consisting of aliphatic and alicyclic hydrocarbons, condensing resulting chlorinated hydrocarbons with a mononuclear aromatic compound with the aid of a Friedel-Crafts condensing agent, treating resulting mixed alkyl aryl compounds with a phosphorus compound selected from the group consisting of hypo-, ortho-, meta-, and pyrophosphorous acids; hypo-, ortho-, meta-, and pyrophosphoric acids; phosphorus trioxide; phosphorus tetroxide; phosphorus pentoxide; phosphorus oxychloride; phosphorus trichloride; and phosphorus pentachloride, washing the treated mixed alkyl aryl compounds with sulphuric acid, subjecting the washed mixed alkyl aryl compounds to another treatment with a phosphorus compound of the said group, thereafter sulphonating the mixed alkyl aryl compounds, neutralizing the resulting sulphonic acids, and drying the resulting sulphonates.

11. The process for the preparation of mixed alkyl benzene sulphonates having good storage properties which comprises chlorinating a petroleum distillate boiling for the most part within the range 180° to 300° C. and composed predominantly of hydrocarbons selected from the group consisting of aliphatic and alicyclic hydrocarbons, condensing resulting chlorinated hydrocarbons with benzene with the aid of anhydrous aluminum chloride, treating resulting mixed alkyl benzenes with a phosphorus compound selected from the group consisting of hypo-, ortho-, meta-, and pyrophosphorous acids; hypo-, ortho-, meta-, and pyrophosphoric acids; phosphorus trioxide; phosphorus tetroxide; phosphorus pentoxide; phosphorus oxychloride; phosphorus trichloride; and phosphorus pentachloride, washing the treated mixed alkyl benzenes with sulphuric acid, subjecting the washed mixed alkyl benzenes to another treatment with a phosphorus compound of the said group, the amount of phosphorus compound employed for each of said treatments corresponding to at least 0.02 atomic equivalent of phosphorus for each molecular equivalent of the mixed alkyl benzenes, thereafter sulphonating the mixed alkyl benzenes, neutralizing the resulting sulphonic acids, and drying the resulting sulphonates.

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