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MIXTURES OF ALKYL ARYL SULPHONATES

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This invention relates to a process for improving the storage properties of mixtures of substituted aryl sulphonates which contain 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 advance in the field of synthetic detergents, wetting agents, emulsifying agents, soap substitutes, and the like, there have been developed compositions comprising mixtures of nuclearly substituted aryl sulphonates which contain as nuclear substituents radicals corresponding to the hydrocarbons present in petroleum distillates. The substituted 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 straight or branched, open-chain aliphatic hydrocarbon radicals, as well as radicals derived from cycloaliphatic and aromatic-aliphatic hydrocarbons which may be present in the petroleum distillate. Depending upon the purpose for which they are to be used, these mixed alkyl aryl sulphonates are derived from selected 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, a petroleum distillate boiling substantially below the boiling point of any nonane is not employed. Thus, a useful petroleum distillate for the manufacture of mixed alkyl aryl sulphonates for use as wetting agents, is one boiling within the range 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 a boiling range which reaches a maximum temperature of 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; that is, petroleum distillates which boil within the range 180° to 320° C. Those which boil for the most part (i. e., at least 80 per cent thereof) within the range 210° to 320° C. are

preferred, especially when composed predominantly of aliphatic and/or alicyclic hydrocarbons which boil within the range 210° to 290° C.

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 condensation catalyst (such as, aluminum chloride or zinc chloride), sulphonating the resulting substituted aromatic compounds, neutralizing the sulphonation mass with a suitable alkaline compound, usually aqueous caustic soda, and drying the neutralized mixture. It will be understood that this process is subject to many minor variations, such as distillation of the reaction mixtures at various points. My United States Patents Nos. 2,223,364, 2,233,408, 2,247,365 and 2,283,199 disclose 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 a mixture of compounds having properties varying in degree, 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 a class of products which should be most satisfactory for general household uses. However, the mixed alkyl aryl sulphonates, which when freshly prepared may be obtained as substantially white and odorless products, have the property of developing a rancid odor and of assuming a yellowish tinge on being stored. Thus, a synthetic detergent comprising mixed alkyl benzene sulphonates derived from a kerosene of the above type obtained from Pennsylvania petroleum, which has been produced in an odor-free form by a process of the type described above, develops an objectionable odor upon standing, even in closed containers in the dark at room temperature. The malodorous substances can be removed by treatment of the product; but the resulting odor-free product again develops an objectionable odor upon standing. While this characteristic of the mixed alkyl aryl sulphonates is not a serious handicap to their acceptance by those engaged in using synthetic detergents in industrial applications, it 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 improve the storage properties of mixed alkyl aryl sulphonates of the class referred to above whereby the mixed alkyl aryl sulphonates may be stored for a relatively long period of time without developing rancid odors to an objectionable degree. A more specific object of the invention is to provide a process for the treatment of mixed alkyl benzene sulphonates wherein the alkyl groups have been derived from a kerosene fraction of petroleum by a process including chlorination of the kerosene, condensation of resulting chlorhydrocarbons with benzene, and sulphonation of resulting alkyl benzenes, to improve the storage properties thereof so as to make the mixed alkyl benzene sulphonates suitable for general household use.

It has been discovered, in accordance with the present invention, that the stability to storage of mixed alkyl aryl sulphonates of the above class, and particularly mixed alkyl benzene sulphonates in which the substituent alkyl groups correspond to aliphatic and alicyclic hydrocarbons of a kerosene fraction of petroleum, which have the property of developing undesirable odors upon being stored, can be improved by incorporating with the mixed alkyl aryl sulphonates a small amount of one or more organic compounds which are characterized by a critical oxidation-reduction potential (E_c at 25° C.) not exceeding 1.10 volts. Preferred odor inhibitors have a critical oxidation-reduction potential not exceeding 1.00 volt, and especially not exceeding 0.80 volt. The meaning of the term "critical oxidation-reduction potential" represented by the symbol, E_c at 25° C., and methods of determining the value of E_c at 25° C. are described by Louis F. Fieser in vol. 52, J. Amer. Chem. Soc. (1930), pages 5209-12 and 5226-32.

Thus it has been found, in accordance with the present invention, that the tendency of such mixtures of alkyl aryl sulphonates to develop rancid odors can be inhibited by incorporating therewith small amounts of the following compounds having respectively, the following critical oxidation-reduction potentials in volts at 25° C., as well as other organic compounds of said class, so that the resulting mixed alkyl aryl sulphonates containing the said compounds may be stored over a relatively long period of time without developing undesirable odors to an unpleasant degree: alpha-naphthol 0.80, p-phenylenediamine 0.71, phenylglycine potassium salt 0.83 (for the free acid), mercaptobenzothiazole 0.79, sodium 1-naphthol-2-sulphonate 0.88, phenol 1.09, trichlorophenol 1.10, diphenylamine 1.01, and beta-naphthylamine 1.06.

Many of the odor-inhibiting compounds belong to the categories of hydroxy-, amino-, and amino-hydroxy-aromatic compounds of the benzene and naphthalene series (that is, compounds derived from a member of the group consisting of benzene and its homologues and naphthalene and its homologues), substituted ureas, substituted hydrazines, and organic thiocyanates.

It has further been found, in accordance with the present invention, that the presence of any of the said organic odor-inhibiting compounds in small but sufficient amount to inhibit the development of objectionable odor has no appreciable harmful effect upon the wetting, detergent

and emulsifying properties of the mixed alkyl aromatic sulphonate compositions to which the odor-inhibiting compounds are added.

The odor inhibitors can be incorporated with the mixtures of alkyl aromatic sulphonates in any suitable manner and in the presence or absence of a solvent or diluent. Inasmuch as the amount of odor inhibitor employed, relative to the mixture of alkyl aryl sulphonates, is small, an advantageous procedure is to mix the odor inhibitor with an aqueous solution of the alkyl aryl sulphonates. For example, in the preparation of mixed alkyl aryl sulphonates by a procedure involving, as the final operation, evaporating to dryness an aqueous solution of the mixed alkyl aryl sulphonates, an odor inhibitor can be added to the solution prior to evaporation of the latter and a dry product can thereby be produced having increased stability against the development of undesirable odors upon being stored. Thus a mixture of alkyl benzene sulphonates in which the substituent alkyl groups are derived from kerosene and which has been treated by the process of the present invention can be marketed for many purposes for which the untreated material is not suitable.

The particular odor inhibitor employed will depend upon the extent to which the particular mixture of alkyl aromatic sulphonates tends to develop rancid odors, the length of time the product is to be stored and the use to which the product is to be put. Thus, for the preparation of detergent compositions which are to be used extensively in the household arts and frequently in solution making contact with the skins of animals and human beings, it is important that the odor inhibitors used and the amounts thereof incorporated with such compositions, in accordance with the present invention, should be non-toxic and non-irritating to animal and human skins. Further, for the production of compositions which, in solid form, or when used in solution, would be objectionable if they tended to become colored or to impart color to their solutions, odor inhibitors are preferably employed which, upon oxidation, do not develop objectionable color. The preferred odor inhibitors which are free from objectionable toxic effects and which, upon oxidation, do not form highly colored compounds are monohydroxy naphthols, and of these alpha-naphthol is especially preferred because of its effective odor-inhibiting properties even when used in very small amounts.

On the other hand, odor-inhibiting compounds, such as para-amino-phenol, metatolylene-diamine, para-toluidine and pyrogallol may be employed in a mixed alkyl aryl sulphonate composition when it is intended for uses in which the physical appearance and/or toxicity of the composition and/or its solution are of little importance and are not objectionable to the users thereof.

Because of the state of the development of the present art, it is believed to be unnecessary to enumerate all of the various types of petroleum distillates whose alkyl aryl sulphonate derivatives may be treated in accordance with the present process to improve their odor characteristics. It is sufficient to point out that treatment by the present process may be applied advantageously to alkyl aromatic sulphonates, which have the undesirable property of developing odors upon being stored and are derivatives of petroleum distillates which boil for the most part within ranges whose lower limits are above

100° C. 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 resulting chlorhydrocarbons with an aromatic compound, and sulphonation of resulting condensation products.

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.—Each of the two identical solutions was prepared by dissolving in 300 ccs. of water 50 grams of a commercial detergent composition containing about 20 grams of a mixture of sodium alkyl benzene sulphonates and about 30 grams of inorganic salts, chiefly sodium sulphate. The detergent composition had been prepared by chlorinating 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, at a temperature of about 55° to 60° in the presence of a small amount of iodine as a catalyst until about 1½ times the amount of chlorine theoretically necessary to yield the monochlor-substitution products of the hydrocarbon mixture had been absorbed; reacting 10 parts of the resulting chlorination product with 5.8 parts of benzene in the presence of 0.6 part of anhydrous aluminum chloride, for about 2 hours with vigorous agitation at about 45°; permitting the mixture to stand; decanting off the upper oily layer containing a crude mixture of higher alkyl benzenes; heating the resulting oil in a still until the vapor temperature of the distillate reached about 115° at about 45 mm. pressure, to remove unreacted benzene, low boiling hydrocarbons and low boiling by-products; adding to the remaining oil (crude higher alkyl benzenes) 6.6 parts of 26% oleum over a period of about one-half hour, and maintaining the mixture during addition of the acid at 10° to 15°, warming the mass to between 20° and 30° and keeping it at this temperature for 1½ hours; permitting the mixture to stand quiescent for about 2 hours until it separated into two layers; removing the upper oily layer; drowning the lower layer in about 50 parts of ice and water; neutralizing the aqueous solution with 50 per cent aqueous sodium hydroxide; and evaporating the resulting solution to dryness on a rotary drum drier.

To one of these solutions, there was added 0.05 gram of alpha-naphthol, which has a critical oxidation-reduction potential (E_0 at 25° C.) equal to 0.80. The solutions were dried separately on a rotary drum drier which was heated internally with steam at about 70 pounds pressure. The dry products were placed in separate loosely-corked glass bottles. After being stored for six days in the said containers, the product containing alpha-naphthol had changed little in odor, and was definitely less rancid or unpleasantly odorous than the other product, which had acquired an offensive odor that seriously impaired its marketability. When tested for detergency, both products showed the same detergency.

Example 2.—Two 300 cc. portions were withdrawn from a large uniform batch of an aqueous

solution of mixed sodium alkyl benzene sulphonates containing about 12 per cent by weight of a mixture of sodium alkyl benzene sulphonates and about 18 per cent of inorganic salts, mainly sodium sulphate, which had been prepared from kerosene of Pennsylvania origin in the manner described in Example 1. To one portion of the solution, 0.09 gram of alpha-naphthol was added. The two solutions were drum-dried and the dry products were placed in separate, loosely-corked containers and stored. After two days the dry product which contained alpha-naphthol was substantially unchanged, whereas the dry product which did not contain alpha-naphthol had an offensive odor and was distinctly more tainted by undesirable odor than the other product.

Example 3.—Two 1260 cc. portions were withdrawn from a uniform solution of mixed sodium alkyl benzene sulphonates containing about 32 per cent by weight of a commercial detergent composition consisting of about 38 parts of a mixture of sodium alkyl benzene sulphonates and 62 parts of inorganic salts (mainly sodium sulphate) per 100 parts of detergent composition. The solution of the detergent composition had been prepared by chlorinating a kerosene fraction of Pennsylvania petroleum distillate of the type employed in Example 1, condensing 10 parts of the resulting chlorination product with 5.8 parts benzene and 0.8 part anhydrous aluminum chloride and removing unreacted benzene, lower boiling hydrocarbons and lower boiling by-products from the resulting crude mixture of higher alkyl benzenes, all in the manner set out in Example 1; then vacuum distilling the remaining oil (crude higher alkyl benzenes) until the vapor temperature of the distillate reached 240° at 20 mm. pressure; agitating 5 parts of the resulting higher alkyl benzene distillate with 1 part of 100 per cent sulphuric acid for about one hour at 25° to 35°; permitting the mixture to stand quiescent for half an hour; withdrawing the lower layer of spent acid; agitating the remaining acid-treated oil with 5 parts of 100 per cent sulphuric acid for about 20 minutes at room temperature, then heating the mixture to 60° and maintaining it at the temperature for an hour and twenty minutes; permitting the mixture to stand undisturbed until it separated into three layers; separating the middle layer from the other two layers and drowning it in about 20 parts of cold water; neutralizing the resulting aqueous solution with 50 per cent aqueous sodium hydroxide; adding sodium sulphate thereto; and evaporating the resulting solution to dryness on a rotary drum drier.

To one portion of the solution, an amount of alpha-naphthol corresponding to 7.9 parts per 10,000 parts of mixed alkyl benzene sulphonates (0.03 per cent of the weight of detergent composition) was added and thoroughly dispersed therein. The treated and untreated portions of solution were then drum-dried separately under the same conditions. Separate samples each of which represented one of the dry products and was placed in a loosely-corked glass bottle, were separately aged artificially by holding them at about 85° for about 16 hours. The sample representing the solution which contained alpha-naphthol had distinctly less odor than the sample representing the untreated solution. The remaining portions of the dry products were placed in separate, loosely-corked glass bottles and stored at ordinary atmospheric temperatures for about one year. The odor of the product which had been treated with alpha-naphthol was dis-

tinctly less unpleasant than that of the untreated product.

Example 4.—Alpha-naphthol was added in increasing amounts to solutions each consisting of 200 ccs. of water in which 38 grams of a detergent composition containing about 60 per cent of sodium alkyl benzene sulphonates and about 40 per cent of inorganic salts, chiefly sodium sulphate, had been dissolved. The detergent composition had been prepared in the manner set out in Example 3, but without the incorporation of sodium sulphate in addition to that present from the neutralization of the sulphonation mass. The resulting solutions and a similar untreated solution were dried, and the dry products were aged artificially by keeping them in loosely-corked bottles at about 85° for the same period of time—approximately 16 hours. Then the samples were examined for developed odor. The results of this test are summarized in the following table:

Table I

Sol. No.	Gms. sodium alkyl benzene sulphonate in sol. = A	Gms. of alpha-naphthol added = B	$\frac{B}{A} \times 100$	Odor after aging
1.....	22.8	0	0	Strong, rancid, unpleasant odor.
2.....	22.8	0.0038	0.017	Very slightly better than sample #1.
3.....	22.8	0.0114	0.050	Better than sample #1
4.....	22.8	0.0190	0.083	Better than sample #1
5.....	22.8	0.0285	0.125	Better than sample #1
6.....	22.8	0.0380	0.167	Better than sample #1
7.....	22.8	0.0570	0.25	Much better than sample #1, but definitely had an odor of alpha-naphthol.

Example 5.—Pennsylvania kerosene boiling from 185° to 275° was chlorinated between 60° and 70° in the presence of 3.8 parts iodine per 1000 parts kerosene, until the specific gravity of the latter had increased from 0.788 at 24° to 0.918 at 24°, corresponding to a weight increase due to absorbed chlorine of about 21 per cent. 10 parts of the resulting chlorinated hydrocarbon mixture, 20 parts of benzene and 0.5 part of anhydrous aluminum chloride were mixed at 35°; the mixture was held for about 1½ hours at 45°, then allowed to stratify; the upper layer of oil was removed from the tarry lower layer and distilled; and the fraction boiling between 150° at 75 to 100 mm. of mercury absolute pressure and 250° at 14 mm. of mercury absolute pressure was collected separately as the part which was chiefly alkyl aromatic compounds. The collected fraction was washed with 100 per cent sulphuric acid by agitating it with 18.4 per cent of its weight of the acid at 25° to 30° for 45 minutes, allowing the mass to settle 30 minutes and discarding the lower acid layer. The washed oil was mixed with 1.32 times its weight of 100 per cent sulphuric acid at 30° to 35°. The mixture was warmed to 55° to 60°, agitated at that temperature for 1 hour, allowed to stratify for about 1 hour, and the middle stratum which was separated from an upper layer of oil and from a lower layer of spent acid, was drowned in 4½ parts of a mixture of ice and water. The resulting aqueous solution was neutralized with 50 per cent aqueous caustic soda, and anhydrous sodium sulphate was added in such amount that the solute in the solution contained about 62 per cent inorganic salts, chiefly sodium sulphate, and 38 per cent sodium alkyl benzene sulphonates. The solution was then diluted to such an extent that it contained 20 parts by weight of solute per 100 cc. of solution.

Two liters of this solution were divided into four equal portions which were treated as follows and subjected to accelerated aging at 85°. Their condition after 16 hours was as shown in the following Table II:

Table II

Portion	Treatment	Odor after aging
10 A.....	Drum-dried without treatment.	Considerable amount of a rancid unpleasant odor.
B.....	0.1 gram of alpha-naphthol added, and then drum-dried.	No rancid odor.
15 C.....	0.1 gram of m-tolylene-diamine added, and then drum-dried.	Slightly more rancid than D, but less rancid than A.
D.....	0.1 gram of phenyl-alpha-naphthylamine added, and then drum-dried.	Slightly more rancid than B but considerably less rancid than A.

20 The results of these tests show that these odor

inhibitors, in decreasing order of effectiveness for retarding the development of unpleasant odor, are: alpha-naphthol, phenyl-alpha-naphthylamine and m-tolylene-diamine.

Example 6.—Each of two identical aqueous solutions were prepared by dissolving in 200 ccs. of water 61 grams of a detergent composition consisting of about 60 per cent of a mixture of sodium alkyl benzene sulphonates and about 40 per cent of inorganic salts (chiefly sodium sulphate). The detergent composition was prepared by the process described in Example 3, but omitting the incorporation of additional sodium sulphate. To one solution, 0.061 gram of thymol was added (i. e., the amount of thymol was 0.1 per cent of the detergent composition in solution). The solutions were dried on a drum-drier, and the dry products were aged by keeping them for about 16 hours in a loosely-stoppered bottle at about 85°. The odor of the aged sample containing the thymol was much less rancid than the odor of the other aged sample.

Example 7.—A solution containing about 30 per cent by weight of a detergent composition containing about 40 parts of a mixture of sodium alkyl benzene sulphonates and about 60 parts of sodium sulphate per 100 parts of detergent composition and prepared in the manner described in Example 5, was divided into equal portions. Each of four portions had incorporated therein one of the odor inhibitors shown in the following Table III, in an amount equal to 1 part per 1,000 parts of the detergent composition present in the portion of the solution, and no inhibitor was added to a fifth portion. The solutions were then drum-dried, and the dry products were aged artificially in loosely-stoppered glass bottles at about 85° for long periods. At specific time intervals, the dry compositions were examined for odor. The

results are summarized in the following Table III:

dried detergent composition contained about 90 per cent of sodium alkyl benzene sulphonates and

Table III

	Portion No.		
	1	2	3
Odor inhibitor.....	None.....	Alpha-naphthol.....	Hydroquinone.....
Aged odor 16 hrs.....	Strongly rancid.	Practically no odor.	Practically no odor.
Aged odor 48 hrs.....	do.....	do.....	Do.
Aged odor 117 hrs.....	do.....	do.....	Strongly rancid.
Aged odor 524 hrs.....	do.....	do.....	Do.

	Portion No.	
	4	5
Odor inhibitor.....	Para-amino phenol.....	Para-benzylamino phenol.
Aged odor 40 hrs.....	Practically no odor.....	Practically no odor.
Aged odor 230 hrs.....	do.....	Do.

Example 8.—1700 parts of a crude detergent composition which consisted of substantially 60 per cent of a mixture of sodium alkyl benzene sulphonates and about 40 per cent of inorganic salts (chiefly sodium sulphate), and which was prepared substantially in the manner described in Example 3 but without the addition of sodium sulphate, were dissolved in about 4500 parts of wash water obtained in the following manner from a previous practice of the process of this example, and which was heated to 60°. To the solution 50 parts of decolorizing charcoal ("Darco") and about 18 parts of "Filter Cel" were added. The solution was heated nearly to boiling (about 94°) and was filtered while hot. (The filter-cake was washed with water, and the wash-water was used in making up the next batch of solution.) To the filtrate 0.66 part of alpha-naphthol and 1150 parts of anhydrous sodium sulphate were added with stirring. After the mixture had been stirred for about an hour, it was drum-dried. The dry product weighed about 2520 parts. It contained approximately 40 per cent of mixed sodium alkyl benzene sulphonates and approximately 0.024 per cent of alpha-naphthol. It had greater stability during storage and less tendency to develop unpleasant odors than similar products prepared without addition of the readily oxidizable compounds of the present invention. In other respects the product had the normal and usual properties of mixed sodium alkyl benzene sulphonates prepared in the same manner, but without addition of alpha-naphthol.

Example 9.—In the manner described in Example 5, kerosene was chlorinated and condensed with benzene, and the fraction consisting chiefly of alkyl benzenes was separated by distillation, then acid washed, sulphonated and allowed to stratify. The middle layer of organic sulphonic acid was separated, and to it ice was added in the proportion of 10 parts of ice for each 100 parts of alkyl benzene oil which was sulphonated. The resulting aqueous mass was thoroughly mixed and allowed to stand for about three quarters of an hour, to stratify. The bottom layer of spent acid was then withdrawn and discarded, and the top layer of alkyl benzene sulphonic acids was poured into about four times its weight of water (to make an approximately 20 per cent solution). The aqueous mass was then neutralized with 50 per cent aqueous sodium hydroxide and dried on a drum drier. The

about 10 per cent of inorganic salts, chiefly sodium sulphate. A sample of this product was taken and identified as sample 1.

A 500 gram portion of this dried detergent composition was dissolved in 3,000 cc. of water. The solution was warmed to 70° to 80°, 20 grams of "Darco" (decolorizing carbon) were added, and the solution was agitated at this temperature for 2 hours. The mixture was filtered through "Super Cel." The clear filtrate was warmed again to 70° to 80°, 20 grams of "Darco" were added, and the solution was agitated at this temperature for 2 hours. The mixture was filtered through "Super Cel" and the clear filtrate was drum dried. A sample of this product was taken and identified as sample 2.

A 50 gram portion of this "Darco"-treated dried product was dissolved in water to make a 20 per cent solution, 0.05 gram of thymol was added (0.1 per cent of the weight of the detergent composition), and the solution was drum dried. A sample of this product was taken and identified as sample 3.

Odor tests were made on three samples of products by accelerated aging at 85°. After 16 hours, sample 3 was found to have developed less rancid type of odor than sample 2 which developed less rancid type of odor than sample 1. As aging progressed, the differences in odor became more pronounced. After 250 hours, sample 3 had become slightly rancid. It was less rancid than sample 2 and far less rancid than sample 1.

Example 10.—10,620 lbs of Pennsylvania kerosene (specific gravity 0.788 at 24° and boiling range 179° to 265°) were charged into a lead-lined kettle fitted with a lead-covered agitator, thermometer well and other accessories. 4.4 lbs. of iodine were dissolved in the agitated kerosene charge. The resulting charge was warmed to about 63° and maintained at that temperature while chlorine gas was passed into it at an average rate of about 500 lbs. per hour for 5 hours and then at an average rate of 300 lbs. per hour for 6 hours and 50 minutes, or until the specific gravity of the chlorinated kerosene had become 0.918 at 24°. The amount of chlorine required for the purpose was about 4550 lbs. The final chlorinated kerosene mixture weighed about 12,834 lbs.

A mixture of 14,805 lbs. of benzene (part of which was recovered from a previous batch)

and 321 lbs. of anhydrous aluminum chloride was agitated, and 6417 lbs. of the foregoing chlorinated kerosene mixture were added thereto, over a period of three hours, during which the temperature of the mass rose to about 40°. The mixture was then heated to 45°, and held there for about 1½ hours with agitation. Agitation was then stopped, the mixture was allowed to stand for about 2 hours, and the lower tarry layer was then 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 first under atmospheric pressure and finally at 150° under reduced pressure of 3 to 4 inches of mercury absolute pressure. The material left after this stripping was distilled in vacuo until about 22 per cent of the charge in the still had been removed as distillate. The remaining distillate was then distilled further and distillate therefrom was collected separately until the boiling point of the distillate was 230° at 5 mm. mercury pressure. This last distillate weighed 7915 lbs. and was chiefly a mixture of alkylated benzenes, in which the alkyl groups were derived from the chlorinated kerosene.

A 600-gram portion of the mixture of alkyl benzenes was washed with 100 per cent sulphuric acid by mixing it with about 18 per cent of its weight (60 cc.) of the acid and agitating the mixture for about 45 minutes at about 20° to 25°. The mixture was allowed to stand for about a half hour to permit stratification, and the lower layer of spent acid was withdrawn and discarded. To the upper washed layer of mixed alkyl benzenes there were added during 10 minutes about 840 grams of 100 per cent sulphuric acid, the temperature being allowed to rise from about 25° to about 50°. The mixture was then warmed to 55° and agitated at 55° to 60° for 1 hour. It was then allowed to stand for 1 hour, during which time three layers formed. The upper layer was chiefly unsulphonated material, the middle portion was chiefly sulphonated alkyl benzenes, and the lower layer was spent acid. The middle layer was separated from the others, drowned in cracked ice, and neutralized with an aqueous solution of caustic soda. To the neutralized solution, sufficient sodium sulphate was added to bring the inorganic salt content of the solute up to 58.4 per cent. The resulting solution was then drum dried. The detergent mixture thus obtained was used in the following tests.

A stock solution was prepared which contained 28.4 grams of the solid detergent product of the preceding paragraph per 100 cc. of solution. To 176 cc. of this solution (containing 50 grams of solid detergent product) there were added 0.05 gram of one of the organic compounds (odor inhibitors) listed in Table IV. Thus, there were about 24 parts of odor inhibitor for each 10,000 parts of sodium alkyl benzene sulphonate in the solution. After agitating the aqueous mixture to insure solution of the odor inhibitor, the solution was drum dried. A large number of samples were thus prepared from the list of organic compounds shown in Table IV. Each sample so prepared was tested for development of offensive odors by storing portions thereof in loosely stoppered glass bottles at 85° for 40, 112 and 160 hours. Odor which developed at the end of these periods was rated as: A—slight; B—moderate; C—bad; D—extremely bad. Control samples to which no odor inhibitor was

added were prepared in the same way and used in these comparisons. The effects of the odor inhibiting compounds upon development of odor in the detergent mixture of sodium alkyl benzene sulphonates, as rated by the above mentioned scale, are shown in the following Table IV.

Table IV

Odor inhibitor used	Degree of odor developed on storing			
	16 hrs.	40 hrs.	112 hrs.	160 hrs.
10 Mercaptobenzothiazole.....	A—	A—	A—	A—
15 p-Phenylenediamine.....	A—	A—	A—	A—
Phenylglycine potassium salt.....	A—	B+	B+	B+
Beta-naphthylamine.....	A	A	A	A
Diphenylamine.....	A	A	A	A
N-ethylaniline.....	A—	B	B—	D
Trichlorophenol.....	A	A	C	C
Phenol.....	B	C	D	D
20 Potassium-1-naphthol-2-sulphonate.....	A	A—	B	C
Sodium-1-naphthol-2-sulphonate.....	A	B	B	C
Alpha-naphthol.....	A	A	A	A
Thiourea.....	A	A	A	A
Sym p-hydroxyphenyl-thiourea.....	A	A	A	A—
p-Tolylthiourea.....	A—	A—	A—	A—
Butylthiocyanate.....	A—	A—	B+	B—
25 Monobutyl-urea.....	A—	A—	B+	B
Dimethylhydrazine.....	A	B	B—	B—
Blank (untreated).....	C	D	D	D

It will be evident to those skilled in the art that the invention is not limited to the details of the foregoing illustrative examples and that changes can be made without departing from the scope of the invention.

Thus, instead of the odor inhibitors employed in the examples, other compounds which have a critical oxidation-reduction potential (E_c at 25° C.) not exceeding 1.10 volts can be used. The following compounds are additional illustrations of suitable odor inhibitors: catechol, pyrogallol, beta-naphthol, dihydroxynaphthalene, meta-tolylene-diamine, 1,8-naphthalenediamine, diamino-phenol, N-methyl-aminophenol and N-para-hydroxyphenyl-diisobutylaspartate.

The preferred odor inhibitors are phenolic compounds which do not form colored compounds upon being oxidized. The undesirable effect of using compounds which oxidize to colored compounds is exemplified by preparation No. 4 in Example 7 above, where the treated detergent composition became dark reddish-brown and, therefore, physically unattractive and unfit for normal use, even though the composition did not develop an odor during long periods of storage. When development of such color is not objectionable, and repression of development of odor is of paramount importance, odor inhibitors such as para-aminophenol which impart color to the compositions may be used.

The amount of odor inhibitor which is effective for this invention has been found to be very small in comparison with the mixture of alkyl aryl sulphonates with which it is incorporated. Because of the variance among different mixed alkyl aryl sulphonates, depending upon the petroleum distillates used in their preparation, the details of the process employed, the purpose for which they are to be used, and other variable factors, it is not possible to state definitely the amount of odor inhibitor to be used in all cases. In general, the incorporation of the odor inhibitors in amounts greater than 3 parts per 10,000 parts by weight of mixed alkyl benzene sulphonates is sufficient to repress the development of odor in the treated, dry compositions to the extent that the compositions can be stored for long periods of time before development of odors in

them takes place to an unpleasant degree. In the case of odor inhibitors which themselves have distinctive odors, it is ordinarily undesirable to add to the detergent composition an amount of inhibitor sufficient to impart its own odor to the treated composition. Thus, in the case of alpha-naphthol, amounts which range from 3 parts to 40 parts in 10,000 parts by weight of mixed alkyl benzene sulphonates are preferred. Amounts which are less than the above minimum amount may be desirable when the mixed alkyl aryl sulphonates are to be stored only for relatively short periods; while amounts greater than the above maximum amount may be used whenever the odor inhibitor does not itself impart detrimental effects, such as an undesired odor and/or color, toxicity, etc., or where one or more such effects is less objectionable than the rancid odors which in time develop in the untreated compositions.

While in the above examples the mixed alkyl aryl sulphonates treated are derivatives of benzene, other mixed alkyl aryl sulphonates which are derived from homologues of benzene and from other aromatic compounds may be similarly treated to inhibit the development of objectionable odors; as for example, mixed alkyl phenol sulphonates, mixed alkyl naphthalene sulphonates, mixed alkyl phenetole sulphonates, and mixed alkyl diphenyl sulphonates, in which the alkyl groups are derived from petroleum distillates which boil for the most part above 100° C. The treatment is particularly adapted to the compounds derived from aryl hydrocarbons. Compounds derived from phenol have less tendency to develop odor, presumably because of the presence of the phenolic group. Further, the mixed alkyl aryl sulphonates may be in the form of neutral salts other than the sodium salt, and especially in the form of other water-soluble salts; as for example, the potassium, magnesium, lithium nickel, ammonium and tri (hydroxyethyl) ammonium salts.

In general, the odor-inhibiting compounds used in accordance with the present invention may be employed individually, but sometimes they are advantageously employed as mixtures of two or more of said compounds. Moreover, they may be employed in addition to a treatment of the mixed alkyl aryl sulphonates with chemical agents adapted to react with the constituents of said mixed alkyl aryl sulphonates which tend to form substances having an objectionable odor, or in addition to other treatments such as a treatment with decolorizing carbon ("Darco") as in Example 9.

It will thus be seen that the present invention provides a simple and economical means for improving the storage properties of mixed alkyl aryl sulphonates derived from petroleum distillates, so that the mixed alkyl aryl sulphonates may be kept for a considerable period of time without developing rancid odors to an undesirable degree.

Since charges may be made in the above description without departing from the scope of the invention, it will be understood that the above description should be taken as illustrative and not in a limiting sense.

I claim:

1. A composition comprising a mixture of alkyl aryl sulphonates in which the alkyl groups are derived from a petroleum distillate which boils for the most part above 100° C., which mixture develops a rancid odor or being stored, and in

admixture therewith a very small amount of a hydroxy-aromatic compound derived from a member of the group consisting of benzene and its homologues and naphthalene and its homologues, as an odor inhibitor.

2. A composition comprising a mixture of alkyl aryl sulphonates in which the alkyl groups are derived from a kerosene fraction of petroleum which boils for the most part within the range 210° to 320° C., which mixture develops a rancid odor on being stored, and in admixture therewith a fraction of a per cent of its weight of a hydroxy-aromatic compound derived from a member of the group consisting of benzene and its homologues and naphthalene and its homologues, as an odor inhibitor.

3. A composition comprising a mixture of alkyl aryl sulphonates in which the alkyl groups are derived from a petroleum distillate which boils for the most part above 100° C., which mixture develops a rancid odor on being stored, and in admixture therewith a very small amount of alpha-naphthol, as an odor inhibitor.

4. A composition comprising a mixture of alkyl benzene sulphonates in which the alkyl groups are derived from a kerosene fraction of petroleum which boils for the most part within the range 180° to 320° C., which mixture develops a rancid odor on being stored, and in admixture therewith a fraction of a per cent of its weight of alpha-naphthol, as an odor inhibitor.

5. A composition comprising a mixture of sodium salts of sulphonated alkyl benzenes in which the alkyl groups are derived from a kerosene fraction of petroleum which boils for the most part within the range 210° to 320° C., which mixture develops a rancid odor on being stored, and in admixture therewith from 3 to 40 parts of alpha-naphthol per 10,000 parts by weight of said mixture of sodium salts, as an odor inhibitor.

6. A process of inhibiting the development of rancid odors in a mixture of alkyl benzene sulphonates in which the alkyl groups are derived from a kerosene fraction of petroleum which boils for the most part within the range 210° to 320° C., which comprises incorporating with said mixture of alkyl benzene sulphonates a fraction of a per cent of its weight of a hydroxy-aromatic compound derived from a member of the group consisting of benzene and its homologues and naphthalene and its homologues, as an odor inhibitor.

7. A process of inhibiting the development of rancid odors in a mixture of sodium alkyl mononuclear aryl sulphonates in which the alkyl groups are derived from a kerosene fraction of petroleum which boils for the most part within the range 210° to 320° C., which comprises adding to an aqueous solution of the mixture of sulphonates from 3 to 40 parts of alpha-naphthol per 10,000 parts by weight of said mixture of sulphonates, and drying the resulting solution.

8. In the manufacture of a mixture of alkyl benzene sulphonates by a process involving chlorinating a kerosene fraction of petroleum composed predominantly of hydrocarbons selected from the group consisting of aliphatic and alicyclic hydrocarbons which boils for the most part within the range 210° to 290° C., condensing the resulting chlorhydrocarbons with benzene in the presence of aluminum chloride, sulphonating the resulting condensation products, and neutralizing the sulphonation products with sodium hydroxide, the method of inhibiting the development of rancid odors in the resulting mix-

ture of alkyl benzene sulphonates which comprises adding to an aqueous solution of the mixture of sulphonates from 3 to 40 parts of alpha-naphthol per 10,000 parts by weight of said mixture of sulphonates, and drying the resulting solution.

9. A composition comprising a mixture of alkyl benzene sulphonates in which the alkyl groups

are derived from a kerosene fraction of petroleum which boils for the most part within the range 180° to 320° C., which mixture develops a rancid odor on being stored, and in admixture therewith a fraction of a per cent of its weight of thymol, as an odor inhibitor.

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