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MIXTURES OF ALKYL ARYL SULFONATES

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

Compositions comprising mixtures of nuclearly substituted aryl sulfonates which contain as nuclear substituents radicals corresponding to hydrocarbons of the type present in petroleum distillates are valuable for use as detergents, wetting agents, emulsifying agents, soap substitutes, and the like. The substituted aryl sulfonates present in such mixtures are conveniently referred to as "alkyl aryl sulfonates," the term "alkyl" being used in its broad sense to include generically: open-chain aliphatic hydrocarbon radicals (whether straight-chain or branched-chain), and radicals derived from cycloaliphatic and aromatic-aliphatic hydrocarbons which may be present in petroleum distillates. Depending upon the purpose for which they are to be used, the alkyl aryl sulfonate mixtures are derived from selected petroleum fractions, such as fractions within the upper gasoline range, the kerosene range, and higher ranges, or from selected fractions of related unsaturated hydrocarbon mixtures.

For example, where compositions are desired particularly adapted for use as wetting agents, petroleum distillates or related unsaturated hydrocarbon mixtures 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 petroleum distillate or olefin mixture useful for the manufacture of alkyl aryl sulfonate mixtures for use as wetting agents is one boiling within the range 140° to 180° C. Where it is desired to prepare a composition containing alkyl

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aryl sulfonates in which the substituent alkyl radicals contain an average of more than 20 carbon atoms, a petroleum distillate or olefin mixture 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 or olefin mixtures which boil within the kerosene range are preferable; that is, those which boil within the range 180° to 320° C. Those which boil for the most part (i. e., at least 80% thereof) within the range 210° to 320° C. are preferred, especially when composed predominantly of aliphatic and/or alicyclic saturated or unsaturated hydrocarbons which boil within the range 210° to 290° C.

In general the manufacture of the compositions in question involves forming the aromatic condensation product of a non-aromatic hydrocarbon mixture of mineral origin by condensing an aromatic compound with a chlorinated petroleum fraction (e. g., chlorinated kerosene) or with an olefin (e. g., dehydrochlorinated kerosene chlorides, cracking products, dehydrogenation products, polymerized lower olefins, etc.) and sulfonating the mixture of alkyl aromatic compounds thus produced. The alkyl groups introduced into the aromatic nucleus are principally hydrocarbon groups containing at least seven carbon atoms per molecule and the mixtures may comprise isomeric and homologous hydrocarbon groups. In addition to straight-chain and branched-chain alkyl groups, aralkyl and cycloalkyl groups may be present. The aromatic nucleus may be benzene, naphthalene, or diphenyl nucleus which may contain one or two substituents of the group consisting of halogens and hydroxy, alkoxy, lower alkyl, and phenoxy radicals.

One process for preparing the alkyl aryl sulfonates 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), sulfonat-

ing the resulting substituted aromatic compounds, converting the resulting sulfonic acids in the sulfonation mass to salts by treatment with a suitable alkaline compound, usually aqueous caustic soda, and drying the mixture of salts thus produced. Thus, one method for the manufacture of wetting, dispersing, emulsifying, and cleansing agents from kerosene and similar distillate fractions involves chlorinating a selected distillate fraction, for example a fraction of Pennsylvania, Michigan (Mt. Pleasant), or similar petroleum kerosene, so selected that the hydrocarbons therein contain for the most part between 7 and 19, and preferably 10 to 16, carbon atoms to the molecule, to obtain a mixture which comprises chlorinated hydrocaryons, and which for convenience may be called a "keryl" chloride. The keryl chloride is then condensed with an aromatic compound (for example, benzene, toluene, naphthalene, diphenyl, chlorobenzene, phenol, cresol, anisole, phenetole, hydroxydiphenyl, alpha-naphthol or beta-naphthol) to form a corresponding keryl aryl compound (e. g., keryl benzene, keryl phenol, etc.), and the keryl aryl compound is then sulfonated, with or without intermediate purification treatments.

These mixtures of alkyl aryl sulfonates 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 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 alkyl aryl sulfonate mixtures, particularly the keryl benzene sulfonates, in the form of the free acids or their sodium, potassium, ammonium, alkyl-ammonium, or hydroxy-alkyl-ammonium salts, are a class of products which are most satisfactory for general household uses.

However, the alkyl aryl sulfonates, which in the pure form are substantially white, colorless and tasteless products, are ordinarily obtained in the form of impure mixtures containing impurities of various types and in varying amounts when prepared from hydrocarbon mixtures of mineral origin by processes such as those described above. Thus, they have an unpleasant odor and a disagreeable taste, and are frequently discolored.

I have developed a number of improvements in the preparation and treatment of alkyl aryl sulfonates derived from hydrocarbons of mineral origin, and especially from kerosene fractions of petroleum distillates, which lead to products of improved properties, particularly with respect to color and odor. Processes for making keryl benzene sulfonates of improved properties are disclosed, for example, in my United States Patents 2,233,408, 2,223,364, 2,247,365, 2,267,725, 2,317,986, and 2,387,572.

While in some cases, as when freshly prepared, the alkyl aryl sulfonate mixtures may accordingly be obtained as substantially odorless products, they have the undesirable property of developing a rancid odor on standing. Thus, a synthetic detergent comprising a mixture of alkyl benzene sulfonates 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 referred to above, develops an objectionable odor upon standing, even in closed containers in the dark at room temperature.

The present invention has for an object improvement in storage properties of alkyl aryl sulfonate mixtures of the type discussed above, whereby said mixtures 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 alkyl benzene sulfonate mixtures, the alkyl groups of which have been derived from a kerosene fraction of petroleum by a process including chlorination of the kerosene, condensation of resulting chlorhydrocarbons with benzene, and sulfonation of the resulting alkyl benzenes, whereby the properties of the alkyl benzene sulfonate mixtures are improved with respect to development of odor during storage.

Other objects in part will be obvious and in part will appear hereinafter.

It has been discovered in accordance with the present invention that the stability to storage of alkyl aryl sulfonate mixtures of the above class, and particularly alkyl benzene sulfonate mixtures 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 alkyl aryl sulfonate mixtures a very small amount of one or more oxidation inhibitors of a particular class, namely, non-benzenoid organic oxidation inhibitors. The term "non-benzenoid," as employed herein (including the claims), denotes, generically, acyclic (i. e., open-chain) organic compounds and alicyclic organic compounds.

The class of non-benzenoid organic oxidation inhibitors includes various types of compounds. Thus it includes, for example, compounds which contain only carbon, hydrogen, and oxygen, and which owe their activity to the presence of the oxygen atom in the form of an oxy radical (which term generically includes an —OH radical and a >C=O radical) and which are further activated by the presence in said compounds, in proximity to the activated oxygen atom, of an unsaturated carbon atom or an activating functional radical. Activating functional radicals are, for example, hydroxyl, carbonyl, amino and imino radicals and combinations thereof (e. g., carboxyl and amide radicals); and they may be linked to the same carbon atom as the oxygen atom, or to an adjacent atom. The class of non-benzenoid organic oxidation inhibitors also includes compounds which owe their activity to the presence therein of a nitrogen atom or a sulfur atom linked to a carbon atom of a non-benzenoid hydrocarbon or derivative. Of the latter group, those compounds containing an open-chain organic nitrogen or sulfur compound in which a nitrogen atom or a sulfur atom is linked to a carbon atom to form a radical which is activated by the proximity of another functional radical (and especially those compounds containing at least one activated amino radical) are of particular value as oxidation inhibitors for use in accordance with the present invention. Activating functional radicals include those mentioned above. Activation may be effected by linkage of the activating radical to the nitrogen atom of the C—N radical, by linkage to the sulfur atom of the C—S radical, by linkage to the

carbon atom of the C—N radical, or by linkage to an atom adjacent to the activated carbon atom. Such activated compounds include amino-alcohols, carboxylic acid amides, ureas, thioureas, thioalcohols, guanidines, and the like.

Thus it has been found in accordance with the present invention that the tendency of mixtures of alkyl aryl sulfonates of the above type to develop rancid odors can be inhibited by incorporating therewith very small amounts of non-benzenoid organic oxidation inhibitors of the following types, so that the mixtures of alkyl aryl sulfonates containing said non-benzenoid organic oxidation inhibitors may be stored over a relatively long period of time without developing undesirable odors to an unpleasant degree:

Unsaturated alcohols
Polyhydric alcohols
Hydroxy-carboxylic acids and esters
Keto-carboxylic acids and esters
Amino-carboxylic acids and esters
Unsaturated carboxylic acids and esters
Aldehydes
Unsaturated ketones
Terpene alcohols
Terpene ketones
Mercaptans
Hydrazines
Oximes
Monoamines
Polyamines
Amino-alcohols
Ureas (including thioureas)
Guanidines
Carbamates
Amides
Sulfones
Thiocyanates
Disulfides

It has further been found, in accordance with the present invention, that the presence of any of the said non-benzenoid organic oxidation inhibitors 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 alkyl aromatic sulfonate compositions to which the odor-inhibiting compounds are added.

The non-benzenoid organic oxidation inhibitors can be incorporated with the mixtures of alkyl aromatic sulfonates in any suitable manner and in the presence or absence of a solvent or diluent. Inasmuch as the amount of non-benzenoid organic oxidation inhibitor employed, relative to the mixture of alkyl aryl sulfonates, is very small (i. e., a fraction of a percent of the weight of the alkyl aryl sulfonate mixture), an advantageous procedure is to mix the non-benzenoid organic oxidation inhibitor with an aqueous solution of the alkyl aryl sulfonate mixture. For example, in the preparation of alkyl aryl sulfonate products by a procedure involving, as the final operation, evaporation of an aqueous solution of an alkyl aryl sulfonate mixture of the above type to dryness, a non-benzenoid organic oxidation inhibitor can be added to the solution prior to evaporation of the latter, whereby a dry product can be produced having increased stability against the development of undesirable odors upon being stored. Preferably, the non-benzenoid organic oxidation inhibitor is a solid or liquid which is high-boiling or relatively non-volatile under the drying conditions.

The present invention accordingly makes possible the production of a mixture of alkyl benzene sulfonates, in which the substituent alkyl groups are derived from kerosene or related olefins, which can be marketed for many purposes for which the untreated material is not suitable.

The particular type of non-benzenoid organic oxidation inhibitor employed in a particular case will depend upon the extent to which the particular mixture of alkyl aromatic sulfonates 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 solutions making contact with the skins of animals and human beings, it is important that the non-benzenoid organic oxidation inhibitors used and the amounts thereof incorporated with such compositions 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 were colored, or tended to become colored or to impart color to their solutions, non-benzenoid organic oxidation inhibitors are preferably employed which are colorless or which, upon oxidation, do not develop objectionable color.

On the other hand, when the mixtures of alkyl aryl sulfonates are 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 uses thereof, any of the non-benzenoid organic oxidation inhibitors can be used.

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 hydrocarbon mixtures whose alkyl aryl sulfonate 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 sulfonates which have the undesirable property of developing odors upon being stored and are derivatives of hydrocarbon mixtures 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 predominately of aliphatic and alicyclic hydrocarbons, by a process involving chlorination of the kerosene, condensation of resulting chlorhydrocarbons with an aromatic compound, and sulfonation 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 and percentages are by weight, the temperatures are in degrees centigrade and the pressure is atmospheric, unless otherwise indicated.

Example 1

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 dis-

solved 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 until the specific gravity of the chlorinated kerosene had become 0.918 at 24°.

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 6,417 lbs. of the 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% of the charge in the still had been removed as distillate. The distillation was then continued 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 7,915 lbs. and was chiefly a mixture of alkylated benzenes, in which the alkyl groups were derived from the chlorinated kerosene.

600 parts of said mixture of alkylated benzenes were refined by mixing it with about 18% of its weight of 100% sulfuric 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 layer of refined oil (alkyl benzene mixture) there were added during 10 minutes about 840 parts of 100% sulfuric 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 unsulfonated material, the middle portion was chiefly sulfonated 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 sulfate was added to bring the inorganic salt content of the solute up to 58.4%. The resulting solution was then drum-dried. The solid detergent thus obtained was used in the following tests:

A stock solution was prepared which contained 28.4 parts of the solid detergent per 100 volume parts of solution. To 176 volume parts of this solution (containing 50 parts of solid detergent) there were aded 0.05 part of one of the oxidation inhibitors listed in the following Table 1. Thus, there were about 24 parts of oxidation inhibitor for each 10,000 parts of sodium alkyl benzene sulfonate in the solution. After agitating the aqueous mixture to insure dispersion of the oxidation inhibitor, the solution was dried on a double drum drier. A number of compositions were thus prepared, each employing a different one of the compounds in Table 1. A control composition, to which nothing was added, was similarly dried. Samples of the compositions so prepared were subjected to accelerated aging at 85°, to determine the extent of development of odor under conditions of accelerated aging, by placing a one-ounce sample of each composition in a two-ounce glass bottle, loosely stoppering it with a cork stopper, and heating the bottles (each containing a sample of one of the compositions undergoing test) at a controlled temperature in an oven for a specified period of time. At stated intervals, the bottles were removed and unstoppered, the odors were determined by smelling the contents of the bottles, the stoppers were replaced, and the bottles were returned to the oven. Odor which developed at the end of periods of 16, 40, 112 and 160 hours was noted and recorded. The effect of the added compounds as inhibitors of development of odor in the detergent mixture of sodium alkyl benzene sulfonates is shown in the following Table 1 in which odor is rated according to the following scale:

I=slight
II=moderate
III=bad
IV=extremely bad

Table 1

Oxidation Inhibitor	Degree of Odor Developed			
	16 Hrs.	40 Hrs.	112 Hrs.	160 Hrs.
None (control)	III	IV	IV	IV
Thiourea	I	I	I	I
Butyl-thiocyanate	I−	I−	II+	II−
Monobutyl-urea	I−	I−	II+	II
Dimethylhydrazine	I	II	II−	II−

EXAMPLE 2

A detergent composition of which 90% was a mixture of sodium alkyl benzene sulfonates derived from a kerosene containing mostly hydrocarbons having 10 to 16 carbon atoms in the molecule and 10% was sodium sulfate, and which had been prepared by a process of the type described above, was made into a plurality of aqueous solutions of about 20% strength, each solution containing 50 parts of the detergent composition. One solution was dried on a double drum drier without further treatment for use as a control. Acetyl methyl urea was added to a second of said solutions, and ethyl carbamate was added to a third of said solutions, the amount of each added being 0.05 part (0.1% of the dry detergent composition). The solutions were heated at 60° to 70° with agitation until the oxidation inhibitor was dispersed. The solutions were then dried on a double drum drier. A sample of each of the resulting dried products was subjected to accelerated aging at 85° in the manner described above. The effect of the oxidation inhibitors as inhibitors of development of odor is shown in the following Table 2 in which odor is rated according to the following scale:

A=no rancidity
B=slight trace of rancidity
C=mildly rancid
D=distinctly rancid
E=very strongly rancid

Table 2

Oxidation Inhibitor Added	Developed Odor	
	20 Hrs.	68 Hrs.
None (control)	A	D
Acetyl methyl urea	A	A
Ethyl carbamate	A	B

EXAMPLE 3

A plurality of aqueous solutions of about 20% strength were prepared, each containing 50 parts of detergent composition of which 40% was a mixture of sodium alkyl benzene sulfonates derived from a kerosene containing mostly hydrocarbons having 10 to 16 carbon atoms in the molecule and 60% was sodium sulfate, and which had been prepared by a process of the type described above. One solution was dried on a double drum drier without further treatment, for use as a control. To one of each of the other solutions one of each of the oxidation inhibitors set out in the following Table 3 was added. The solutions were heated at 60° to 70° with agitation until the oxidation inhibitor was dispersed, and then were dried on a double drum drier. A sample of each of the resulting dried products was subjected to accelerated aging at 85° in the manner described above. Odor which developed at the end of periods of 24, 48, 72, and 120 hours was noted and recorded. The results are shown in the following Table 3, in which odor is rated according to the scale employed in Example 2:

Table 3

Oxidation Inhibitor Added	Developed Odor			
	24 Hrs.	48 Hrs.	72 Hrs.	120 Hrs.
None (control)	A	B	D	E
Tartaric acid	A	A	A	A
Pyruvic acid	A	A	A	A
Glycollic acid	A	A	A	A
Dibutyl tartrate	A	B	B	C
Ethyl levulinate	A	A	B	C
Di-n-octyl maleate	A	A	B	C
Mannitol	A	A	A	B
Oxamide	A	A	A	C
Dicyandiamide	A	A	A	B
Aspartic acid	A	A	A	A
Mono-2-ethyl-hexyl aspartate	A	A	B	B
Guanidine hydrochloride	A	A	A	A
Urea	A	A	A	B
Dimethyl-glyoxime	A	A	A	A
Heptaldoxime	A	A	B	D
Iso-leucine	A	A	A	A
2-Amino-2-methyl-propanol	A	A	A	A
S-amyl-thiomalic acid	A	A	A	A
Tributyl-phosphate	A	A	A	A

EXAMPLE 4

A plurality of aqueous solutions of about 20% strength were prepared, each containing 50 parts of detergent composition of the type employed in Example 3. One solution was dried on a double drum drier without further treatment, for use as a control. To one of each of the other solutions, 0.05 part (0.1%) of one of each of the oxidation inhibitors set out in the following Table 4 was added. The solutions were heated at 60° to 70° with agitation until the oxidation inhibitor was dispersed, and then were dried on a double drum drier. A sample of each of the resulting dried products was subjected to accelerated aging at 85° in the manner described above. Odor which developed at the end of periods of 24, 48, and 96 hours was noted and recorded. The results are shown in the following Table 4, in which odor is rated according to the scale employed in Example 2:

Table 4

Oxidation Inhibitor Added	Developed Odor		
	24 Hrs.	48 Hrs.	96 Hrs.
None (control)	A	C	E
Fumaric acid	A	A	A
Teraconic acid	A	A	A
Mucic Acid	A	A	B
Dioxytartaric acid	A	B	B
Sebacic acid	A	C	C
Malic acid	A	A	A
Diethyl teraconate	A	A	B
Ethyl acetoacetate	A	B	B
Cetyl alcohol	A	A	E
Geraniol	A	A	A
Cholesterol	A	A	B
Borneol	A	A	A
Terpinol hydrate	A	A	A
Glycerine	A	A	B
Carbowax 1500	A	A	B
Camphor	A	A	A
Phorone	A	A	A
Trichloropropionic acid	A	A	A
Acetyl butylamine	A	A	B
Acetamide	A	B	D
Laurylamine	A	A	A
Diethylaminoethyl alcohol	A	A	C
Monobutyl urea	A	A	A
Amyl carbamate	A	A	A
Keryl mercaptan [1]	A	A	C
Dibutyl sulfone	A	A	A
Tributyl phosphite	A	A	A

[1] A mixture of higher alkyl mercaptans derived from a chlorinated kerosene mixture produced as described in Example 1.

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 non-benzenoid organic oxidation inhibitors employed in the above examples, other compounds of the types referred to above can be used.

The amount of non-benzenoid organic oxidation inhibitor which is effective for this invention has been found to be very small in comparison with the amount of mixture of alkyl aryl sulfonates with which it is incorporated; it need be only a fraction of a percent of the weight of the mixture of alkyl aryl sulfonates. Because of the variance among different alkyl aryl sulfonate mixtures, depending upon the hydrocarbon mixtures 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 non-benzenoid organic oxidation inhibitor to be used in all cases. In general, incorporation of the non-benzenoid organic oxidation inhibitor in amounts greater than 3 parts per 10,000 parts by weight of mixtures of alkyl benzene sulfonates (exclusive of inorganic salts, when present) 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. Thus, amounts which range from 3 parts to 95 parts per 10,000 parts by weight of alkyl benzene sulfonate mixtures may be employed. In general, amounts ranging from 3 parts to 40 parts are preferred. Amounts which are less than the above minimum amount may be desirable when the alkyl aryl sulfonate mixtures are to be stored only for relatively short periods; while amounts greater than the above maximum amount may be used whenever the oxidation inhibitor does not itself impart

detrimental effects, such as an undesired odor and/or color, toxicity, etc., or where one or more such effects are less objectionable than the rancid odors which in time develop in the untreated compositions.

While in the above examples the mixtures of alkyl aryl sulfonates treated are derivatives of benzene, other alkyl aryl sulfonate mixtures which are derived from homologs of benzene and from other aromatic compounds may be similarly treated to inhibit the development of objectionable odors; as, for example, alkyl phenol sulfonate mixtures, alkyl naphthalene sulfonate mixtures, alkyl phenetole sulfonate mixtures, and alkyl diphenyl sulfonate mixtures, in which the alkyl groups are derived from petroleum distillates or olefins 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, because of the presence of the phenolic group. Further, the alkyl aryl sulfonate mixtures 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.

Instead of the mixtures of alkyl benzene sulfonates employed in the above examples, equal amounts of mixtures of sodium alkyl benzene sulfonates obtained by condensing benzene with higher olefins, especially olefins containing 10 to 16 carbon atoms and more particularly those obtained by polymerizing lower olefins (for example, tributylene, tetrapropylene, etc.), followed by sulfonation and neutralization with sodium hydroxide, can be employed. The resulting dried products have similar improved stability against the development of unpleasant odor.

In general, the non-benzenoid organic oxidation inhibitors 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 alkyl aryl sulfonate mixtures with chemical agents adapted to react with the constituents of said alkyl aryl sulfonates which tend to form substances having an objectionable odor, or in addition to other treatments, such as a treatment with decolorizing carbon.

While mercaptans are effective, as a class, as oxidation inhibitors, the lower mercaptans and other non-benzenoid organic oxidation inhibitors which would render the resulting products malodorous are not employed.

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

This application is a continuation-in-part of my application Serial No. 350,143, filed August 2, 1940, Patent No. 2,397,133, issued March 26, 1946.

I claim:

1. A composition comprising a solid mixture of alkyl aryl sulfonates in which the alkyl groups are derived from a hydrocarbon mixture which boils for the most part above 100° C., which solid mixture develops a rancid odor on being stored, and in admixture therewith a fraction of a percent of its weight of a non-benzenoid organic oxidation inhibitor, as an odor inhibitor.

2. A composition comprising a solid mixture of water-soluble alkyl benzene sulfonates in which the alkyl groups are derived from a hydrocarbon mixture which boils for the most part within the range 180° to 320° C., which solid mixture develops a rancid odor on being stored, and in admixture therewith a fraction of a percent of its weight of a non-benzenoid organic oxidation inhibitor, as an odor inhibitor.

3. A composition comprising a solid mixture of water soluble alkyl benzene sulfonates in which the alkyl groups are derived from a hydrocarbon mixture which boils for the most part within the range 180° to 320° C., which solid mixture develops a rancid odor on being stored, and in admixture therewith a fraction of a percent of its weight of an acyclic organic oxidation inhibitor, as an odor inhibitor.

4. A composition comprising a solid mixture of alkyl mononuclear aryl sulfonates in which the alkyl groups are derived from a hydrocarbon mixture which boils for the most part within the range 180° to 320° C., which solid mixture develops a rancid odor on being stored, and in admixture therewith a fraction of a percent of its weight of an open-chain organic nitrogen compound containing in its molecule at least one nitrogen atom linked to a carbon atom which is activated by the proximity thereto of a member selected from the group consisting of an unsaturated carbon atom, an —OH radical, a >C=O radical, an amino radical, an imino radical and a combination of said radicals, as an odor inhibitor.

5. A composition comprising a solid mixture of alkyl mononuclear aryl sulfonates in which the alkyl groups are derived from a hydrocarbon mixture which boils for the most part within the range 180° to 320° C., which solid mixture develops a rancid odor on being stored, and in admixture therewith a fraction of a percent of its weight of an open-chain organic nitrogen compound containing in its molecule at least one activated amino radical, as an odor inhibitor.

6. A composition comprising a solid mixture of water-soluble alkyl mononuclear aryl sulfonates in which the alkyl groups are derived from a hydrocarbon mixture which boils for the most part within the range 180° to 320° C., which solid mixture develops a rancid odor on being stored, and in admixture therewith a fraction of a percent of its weight of an open-chain organic nitrogen compound containing in its molecule at least one amino-nitrogen atom linked to a carbon atom activated by the proximity of an oxy group, as an odor inhibitor.

7. A composition comprising a solid mixture of sodium alkyl benzene sulfonates 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 solid mixture develops a rancid odor on being stored, and in admixture therewith a fraction of a percent of its weight of an open-chain organic nitrogen compound containing in its molecule at least one nitrogen atom linked to a carbon atom which is activated by the proximity thereto of a member selected from the group consisting of an unsaturated carbon atom, an —OH radical, a >C=O radical, an amino radical, an imino radical and a combination of said radicals, as an odor inhibitor.

8. A composition comprising a solid mixture of sodium alkyl benzene sulfonates in which the

alkyl groups are derived from a mixture of olefins containing 10 to 16 carbon atoms, which solid mixture develops a rancid odor on being stored, and in admixture therewith a fraction of a per cent of its weight of an open-chain organic nitrogen compound containing in its molecule at least one nitrogen atom linked to a carbon atom which is activated by the proximity thereto of a member selected from the group consisting of an unsaturated carbon atom, an —OH radical, a >C=O radical, an amino radical, an imino radical and a combination of said radicals, as an odor inhibitor.

9. A composition comprising a solid mixture of sodium alkyl benzene sulfonates in which the alkyl groups are derived from polymerized olefins containing 10 to 16 carbon atoms, which solid mixture develops a rancid odor on being stored, and in admixture therewith a fraction of a percent of its weight of an open-chain organic nitrogen compound containing in its molecule at least one nitrogen atom linked to a carbon atom which is activated by the proximity thereto of a member selected from the group consisting of an unsaturated carbon atom, an —OH radical, a >C=O radical, an amino radical, and imino radical and a combination of said radicals, as an odor inhibitor.

10. A composition comprising a solid mixture of sodium alkyl benzene sulfonates in which the alkyl groups are derived from a hydrocarbon mixture which boils for the most part within the range 180° to 320° C., which solid mixture develops a rancid odor on being stored, and in admixture therewith a fraction of a percent of its weight of aspartic acid, as an odor inhibitor.

11. A composition comprising a solid mixture of sodium alkyl benzene sulfonates in which the alkyl groups are derived from a hydrocarbon mixture which boils for the most part within the range 180° to 320° C., which solid mixture develops a rancid odor on being stored, and in admixture therewith a fraction of a percent of its weight of geraniol, as an odor inhibitor.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,130,321	Kharasch	Sept. 13, 1938