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LINEAR ALKYL ARYL SULFONATE DETERGENT COMPOSITIONS

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The present invention relates to a process for treating straight-chain alkyl aryl sulfonates useful as detergents, and to the resulting detergent compositions having improved non-caking properties. In a more specific aspect, it relates to the preparation of a particulate solid detergent composition containing alkyl-substituted aryl sulfonate organic detergent, the alkyl radical substituted on the nucleus being of linear or straight-chain structure, said detergent composition having uniformly dispersed therethrough a minor proportion of an additive capable of acting as an anticaking agent to suppress the caking tendencies of said organic detergent.

For a great number of years the bulk of detergent alkylate used to make the finished detergent composition by conversion to the sulfonic acid, followed by neutralization, has been the monophenyl substituted propylene polymers, as described in U.S. Patents Nos. 2,477,382 and 2,477,383 to Lewis. While these detergent compositions have superior detersive powers, it was recognized early in their development that in the particulate solid forms they were hygroscopic and possessed undesirable caking tendencies. These defects were particularly noticeable in built alkyl benzene sulfonate detergent formulations or compositions useful as household washing powders. To inhibit or prevent the undesirable caking phenomenon use was made of a number of anticaking agents, particularly satisfactory being sodium benzene sulfonate or sodium toluene sulfonate, as shown in U.S. Patent No. 2,773,833.

Because of the branched-chain nature of the alkyl polypropylene precursor used in making detergent alkylate, the subsequently sulfonated and neutralized detergent does not meet the recently specified requirements of biodegradability. Therefore, in order to produce a more biodegradable detergent, there is being promoted a so-called linear alkyl benzene sulfonate (LAS), i.e., one derived from the sulfonation and neutralization of detergent alkylate in which the hydrocarbyl or alkyl radical is derived from straight-chain or normal hydrocarbons instead of polypropylene. To make the biodegradable detergent, conventional reactions involve catalytic alkylation of benzene or some other aryl compound, such as toluene or xylene, with either an n-alkane or an n-alkyl halide alkylating agent of the desired molecular weight range, i.e., corresponding to a carbon content of 9 to 18 carbon atoms. The alkylating agent can be derived from petroleum distillate cracking or petroleum wax cracking, catalytic dehydrogenation of n-paraffins, chlorination-dehydrochlorination of n-paraffins, ethylene polymerization, and chlorination of n-paraffins. In addition, the raw materials from which the straight-chain stock is to be derived may be, and often is, subjected to iso-normal separation processes, such as those involving molecular sieves and urea clathration to produce a more linear product than could otherwise be obtained.

Like the branched-chain polypropylene-based detergents, the linear alkyl benzene sulfonates possess undesirable caking tendencies. Indeed, the caking problem seems to be aggravated with the linear alkyl benzene sulfonates to the extent that known anticaking additives, although regarded as being satisfactorily effective in branched-chain alkyl benzene sulfonates, are often, on the other hand, not quite so effective with currently produced linear alkyl benzene sulfonates. Conversely, the presently contemplated anticaking inhibitors, although eminently effective in linear alkyl benzene sulfonate detergent compositions, are unexpectedly not so effective, when incorporated in the branched-chain alkyl benzene sulfonates, as the known inhibitors.

It has now been found that the tackiness or caking tendencies of particulate solid linear alkyl benzene sulfonate detergent can be suppressed by incorporating therewith a small but effective proportion of an anticaking agent salt selected from the group consisting of the sodium and potassium salts of oxalic acid, maleic acid, fumaric acid, thiodisuccinic acid and sulfoacetic acid. In general a satisfactory amount of organic acid salt additive can range from about 2 to 25%, preferably 8 to 20%, by weight, based on alkyl benzene sulfonate detergent.

The invention is applicable to built detergent compositions, i.e., compositions containing nonsoap linear alkyl benzene sulfonate synthetic detergent, and an inorganic salt detergent builder, such as a sulfate, carbonate, silicate, borate, or condensed phosphate sodium salt.

Therefore, a more specific embodiment of the invention is the preparation of a particulate solid detergent composition consisting essentially of nonsoap linear alkyl benzene sodium sulfonate detergent having caking tendencies, an inorganic sodium salt detergent builder, and a small but effective amount to suppress said caking tendencies of the aforesaid sodium or potassium salt anticaking agent. The proportions of nonsoap synthetic detergent can range from about 5 to 95%, preferably 10 to 40%, by weight, based on it and detergent builder; inorganic detergent salt builder, from 5 to 95%, preferably 60 to 90%, by weight, based on it and nonsoap detergent; and anticaking agent from about 2 to 25%, preferably 8 to 20%, by weight, based on nonsoap synthetic detergent.

The invention is particularly useful in connection with so-called heavy-duty detergent compositions or synthetics for household use, especially adapted for washing cotton. As is known these compositions consist essentially of the nonsoap synthetic detergent and a condensed phosphate such as tetra-sodium pyrophosphate and/or sodium tripolyphosphate, usually in a weight ratio of phosphate to synthetic detergent ranging from less than 1:1 to more than 3:1. Other inorganic salts as well can be present to the extent that the total inorganic salt content, including the phosphate, to synthetic detergent weight ratio can be as high as 10:1.

Accordingly, a particularly useful embodiment of the invention is the preparation of a heavy-duty particulate solid detergent composition, at least 70% by weight thereof consisting essentially of linear C_9–C_{18} alkyl benzene sulfonate organic detergent, an inorganic salt detergent builder in a weight ratio to organic detergent ranging from 1:1 to 10:1, said inorganic salt detergent builders including a condensed sodium phosphate, such as tetrasodium pyrophosphate and/or sodium tripolyphosphate, present in a weight ratio to the organic detergent ranging from about 1:1 to 3:1.

The anticaking agent is incorporated in the detergent composition in such fashion as to effect intimate and thorough admixture with, or uniform dispersion throughout, the other components of the detergent composition. This can be accomplished by wet-mixing, such as by forming an aqueous dispersion or slurry comprising the anticaking additive and other components of the composition, and then drying the dispersion. Another way of effecting uniform dispersions of the anticaking agent throughout the composition is to integrate its incorporation with the process of making the linear alkyl benzene sulfonate

detergent by adding the inhibitor at the neutralization step, as follows.

The appropriate aryl compound such as benzene or toluene, benzene hereinafter being taken as representative, is alkylated with an alkylating agent in the presence of an alkylating catalyst. Thus, benzene can be alkylated with a straight-chain olefin mixture, for example, a C_9–C_{18} α-olefin mixture, or any desired olefin fraction, such as a C_{10}–C_{13} or a C_{11}–C_{14} α-olefin fraction, or mixtures thereof, in the presence of HF catalyst; or with a chloroparaffin of similarly varying carbon range in the presence of a Friedel-Crafts catalyst, such as $AlCl_3$.

The resulting mixture of C_9–C_{18} monoalkyl benzenes is then sulfonated by means of a suitable sulfonating agent, such as sulfuric acid, oleum, or SO_3, to produce the alkyl benzene sulfonic acids.

Following the sulfonation step, excess sulfonating agent can be removed from the sulfonation mixture by adjusting the water content of the mixture, settling to obtain a top sulfonic acid phase and a lower spent acid phase, which is discarded, The sulfonic acid phase is then neutralized with a suitable base, such as caustic or sodium carbonate to give the alkyl benzene sodium sulfonate.

It is often the practice to leave all or a part of the unreacted sulfuric acid used in the sulfonation step, admixed with the alkyl benzene sulfonic acids and to neutralize them together to form an aqueous dispersion or slurry of organic sodium alkyl benzene sulfonate and inorganic sodium sulfate salt, the inorganic sulfate later serving as a builder in the finished detergent composition. The slurry is then dried as by spray-drying or drum-drying and reduced to the desired particle shape and size.

The anticaking agent of the present invention can be incorporated into the detergent composition by adding preformed sodium or potassium salt of the specified acids either to the neutralizing base solution, such as sodium or potassium hydroxide; or to the sulfonation mixture prior to or during the neutralization step. If desired, the anticaking agent salt can be formed in situ by adding the free acid either to the neutralizing base solution; or to the sulfonation mixture to be neutralized, whereby the acid is converted to the salt.

As hereinabove indicated, in addition to inorganic sodium sulfate, other inorganic salts such as the condensed phosphates, carbonates, silicates, and borates, can be incorporated in the detergent composition. These may be addded to the neutralized slurry prior to drying in accordance with the specifications desired in the ultimate or finished composition. The slurry is then converted to the particulate solid form and size by a suitable drying operation such as spray-drying or drum drying.

As stated, a particularly useful composition is one based on linear alkyl benzene sodium sulfonate detergent, and a condensed phosphate ordinarily used in conjunction with a synthetic surfactant to produce a heavy-duty detergent composition. The polyphosphates can be used in their commercially available anhydrous form, obtained by the high-temperature dehydration of the orthophosphates-tripolyphosphates, from a mixture of disodium orthophosphate and monoorthophosphate; tetrasodium pyrophosphate, from disodium orthophosphate; and sodium polymeta-phosphates, from orthophosphate. The various condensed phosphates can be used singly or in admixture. As is known in the detergent art, the proportions of the various phosphates are frequently altered in practice to meet the manufacturer's own specifications. Generally good results are obtained when sodium tripolyphosphate is essentially the sole condensed phosphate, or is admixed with the other condensed phosphate, for example, 80% tripolyphosphate and 20% pyrophosphate.

In addition to the inorganic salts already mentioned, other ingredients or fillers, in combined amounts up to about 30 weight percent of the final composition, can be incorporated. Examples of optional ingredients are those customarily present in heavy-duty detergent formulations. These include in weight amounts based on final composition, an anticorrosion and stabilizing agent, such as sodium silicate, wherein the SiO_2 to Na_2O ratio can range from 1/2 to 2/1 in proportion of, for example, 5 percent; an anti-redeposition agent, such as carboxymethyl cellulose, as described for example in U.S. Patent No. 2,568,334, proportions of about 1 to 3 percent being cited as illustrative; a chemical bleaching agent such as sodium perborate or sodium percarbonate, for example, in an amount of 2 to 5 percent, optical whiteners, in amounts of the order 0.1 to 0.2 percent, such as the triazinyl and aroylstilbenzene, such as benzidinesulphones, bisbenzimidazoles, triazoles, and amino coumarins; sequestering agents, in amounts, for example, of the order of less than one percent, such as tetrasodium ethylene diamine tetraacetic acid.

The following examples are given to illustrate the invention, parts being by weight:

Example 1

(a) A mixture of linear alkyl benzene sodium sulfonates having 11–14 carbon atoms in the alkyl groups, and obtained by the $AlCl_3$ alkylation of benzene with chlorinated C_{11}–C_{14} normal paraffins, is dried to a constant weight on a hot plate at about 135° C. to produce a free-flowing powder.

The dried powder is placed in an uncovered jar and exposed to room conditions of temperature and humidity, that is, 21° C. and 55% relative humidity.

After 15 minutes the jar is sealed. The material is observed to be stuck to the bottom of the jar and cannot be made to flow freely.

(b) Water solutions of the same detergent material as used in (a) and of sodium sulfate were mixed and dried to constant weight as above. The dried free-flowing mixture contains 50 parts linear alkyl benzene sodium sulfonates and 8 parts of sodium sulfate.

Under the same conditions as in (a), the free-flowing mixure is exposed in a jar for 15 minutes after which the jar is sealed. The mixture is found to be partly caked to the bottom of the jar, and cannot be made to flow freely.

(c) Under the same conditions as in (b), except that the sodium sulfate is replaced by an equal weight of sodium thiodisuccinate, after exposure for 15 minutes and sealing in the jar, no caking is observed, and the contents of the jar flow freely.

(d) Upon repeating each part of (c), using potassium thiodisuccinate in place of the sodium thiodisuccinate, again no caking is observed, and the contents of the jar flow freely.

(e) The procedure of Example 1(c) is repeated separately using disodium maleate, disodium fumarate, disodium oxalate, and sodium sulfoacetate; in each case no caking is observed, and the contents of the jar flow freely.

Example 2

(a) A detergent like that of Example 1 containing 10 percent of sodium sulfate produced in the process of making the detergent is dried to constant weight as in Example 1 to produce a free-flowing granular composition. This composition is placed in a jar and exposed to the same atmospheric conditions as in Example 1 for 15 minutes, and then sealed. The detergent composition forms a cake which can be dislodged only by severe shaking of the jar.

(b) 100 parts of the detergent-sulfate mixture of (a) is dissolved in water. To this solution is added 13.5 parts of sodium oxalate dissolved in water. Similar solutions are prepared from 100 parts of the detergent and 13.5 parts of each of the following: sodium furmarate, sodium sulfoacetate, sodium maleate and sodium thiodisuccinate.

The resulting solutions are dried to constant weight as in (a) to produce free-flowing powders. These powders are placed in jars, and exposed to the same conditions of temperature and humidity. After 15 minutes each jar is sealed. No caking is observed, and the material in each jar is free-flowing.

A suitable method for determining the extent of cracking in a built detergent composition, and the one utilized in the examples below, is the lift-tackiness test.

According to this test, the ingredients of the composition to be tested are formed into a water slurry of approximately 50% solids content. This slurry is mixed with a mechanical stirrer for 15 minutes and then dried on a glass plate. The glass plate is kept on a steam plate or hot plate which is kept at constant temperature in the range of 135–150° C. The slurry is spread on with a large 31-mil doctor blade and allowed to dry until the dried product is readily scraped (2 to 4 minutes). The dried product is exposed to the atmosphere in order to attain an equilibrium moisture content, i.e., of the order of 5 to 10%, an amount normally present in commercial spray-dried detergent products.

The powder is then screened and that passing through a 20 mesh screen and retained on a 48 mesh screen is used for testing.

The apparatus used in the test comprises a stationary aluminum cylinder having a diameter of 1¼", mounted above a spring pan balance supported on a screw-type jack. The bottom of the aluminum cylinder is covered with double-sided adhesive tape, which is changed with each test. The underside of the adhesive tape is coated with a thin layer of the test sample.

30 ml. of screened sample prepared as above is weighed, and is poured in the form of a conical pile on a piece of filter paper in a Petri dish having a diameter of 9 cm., and supported on the pan of the balance. The top of the sample pile is spread level to the top of the Petri dish.

The jack is slowly raised and the test sample is made to impinge upon the treated bottom of the aluminum cylinder to a pressure of 100 g.

This pressure is maintained for 30 seconds, and then slowly released by lowering the jack. As soon as the Petri dish clears the sample adhering to the cylinder, a piece of siff weighing paper in slid under the cylinder to catch any sample falling off the cylinder while the Petri dish is being lowered out of the way.

The powder adhering to the cylinder is scraped onto the same weighing paper, and the total amount of sample that has been lifted is weighed.

Caking tendency as measured by this test is rated on the volume of solids sticking to the plunger, calculated as follows, the lower the value, the less pronounced is the caking tendency:

$$\text{Tackiness (ml.)} = \frac{\text{wt. lifted} \times 30}{\text{wt. of sample used}}$$

Example 3

(a) A detergent formulation having the following composition in parts by weight is prepared:

	Parts
Sodium alkyl benzene sulfonate (same as Example 1)	25
Sodium tripolyphosphate	40
Sodium silicate	7
Carboxy methyl cellulose	1
Sodium sulfate	19

This formulation when subjected to the lift-tackiness test is found to have a tackiness value of 8.1 ml. A moisture content of 6.7% by weight based on total composition is determined by drying to a constant weight.

(b) To batches of a formulation having the same composition as in (a), there is added 3 parts by weight of one of the following additives. Tackiness values are determined as before. The following results are obtained.

Additive	Tackiness (ml.)	Moisture, Percent
Sodium Toluene Sulfonate	8.0	7.3
Sodium Oxalate	2.5	7.2
Sodium Maleate	2.6	7.6
Sodium Fumarate	2.5	8.2
Sodium Thiodisuccinate	2.5	10.0
Sodium Sulfoacetate	2.2	5.0

I claim:

1. Process for suppressing the caking tendencies of straight-chain soldium alkyl benzene sulfonate nonsoap detergent containing 9 to 18 carbon atoms in the alkyl portion of the molecule, which comprises uniformly dispersing throughout said detergent 2 to 25% by weight, based on said nonsoap detergent, of an anticaking agent selected from the group consisting of the sodium and potassium salts of oxalic acid, sulfoacetic acid, maleic acid, fumaric acid and thiodisuccinic acid.

2. Process according to claim 1, wherein the anticaking agent is present in an amount of about 8 to 25%, by weight, based on nonsoap detergent.

3. Process according to claim 1, wherein the anticaking agent is sodium thiodisuccinate.

4. Process according to claim 1, wherein the anticaking agent is potassium thiodisuccinate.

5. Particulate detergent composition consisting essentially of straight-chain sodium C_{10}–C_{18} alkyl benzene sulfonate and 2 to 25% by weight thereof of a salt selected from the group consisting of the sodium and potassium salts of oxalic acid, sulfoacetic acid, maleic acid, fumaric acid and thiodisuccinic acid.

6. A particulate solid detergent composition consisting essentially of straight-chain sodium C_9–C_{18} alkyl benzene sulfonate nonsoap detergent component, inorganic sodium salt detergent builder component, and as an anticaking agent a salt selected from the group consisting of the sodium and the potassium salts of oxalic acid, sulfoacetic acid, maleic acid, fumaric acid, and thiodisuccinic acid, the nonsoap detergent and the detergent builder each being present in a proportion within about the range of 5 to 95%, by weight, based on the two, and the anticaking agent, in the range of about 2 to 25%, by weight, based on the nonsoap detergent, said composition being obtained by drying an aqueous dispersion of the aforementioned components.

7. A built detergent according to claim 6, wherein the nonsoap detergent is present in a proportion in about the range of 10 to 40%, and the inorganic sodium salt detergent builder, in about the range 60 to 90%.

8. A built detergent according to claim 6, wherein the anticaking agent is present in an amount of about 8 to 20%, by weight, based on nonsoap detergent.

9. A built detergent composition according to claim 7, wherein the anticaking agent is sodium thiodisuccinate.

10. A built detergent composition according to claim 7, wherein the anticaking agent is sodium fumarate.

11. Heavy-duty particulate solid detergent composition at least about 70% by weight thereof consisting essentially of a mixture of (a) straight-chain sodium alkyl benzene sulfonate nonsoap detergent containing 9 to 18 carbon atoms in the alkyl portion of the molecule, and (b) inorganic sodium salt detergent builder, the weight ratio of inorganic sodium salt detergent builder to nonsoap detergent ranging from 1:1 to 10:1, and uniformly dispersed throughout the particles of said composition, an organic salt selected from the group consisting of the sodium and the potassium salts of oxalic acid, sulfoacetic acid, maleic acid, fumaric acid, and thiodisuccinic acid, said acid being present in an amount rang-

ing from about 2 to 25%, by weight, based on nonsoap detergent.

12. Composition according to claim **11**, wherein the straight-chain sodium alkyl benzene sulfonate nonsoap detergent contains 10 to 14 carbon atoms in the alkyl radical.

13. Composition according to claim **11**, wherein the organic salt is present in an amount of about 8–20%, by weight, based on the nonsoap detergent.

14. Composition according to claim **11**, wherein the organic salt is sodium thiodisuccinate.

15. Composition according to claim **11**, wherein the organic salt is sodium fumarate.

No references cited.

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