ABSTRACT OF THE DISCLOSURE

Process for suppressing caking tendencies of nonsoap detergents in which the detergent active is an alkali metal or ammonium, secondary alkyl sulfate or alkyl sulfonate. The process includes combining the alkyl sulfonate or sulfates with inorganic sodium salt detergent builders. The presence of such inorganic salt detergent builders has been found to result in a considerably reduced caking tendency. In order to achieve this result, the ratio of alkyl sulfonate and sulfates to inorganic salt detergent builders should be at least 2:1.

The present invention relates to a process for suppressing the caking tendencies of alkyl sulfonate and alkyl sulfate detergents, and to the resulting detergent compositions having improved noncaking properties. More particularly, it relates to the preparation of a particulate solid detergent composition containing alkyl sulfonate or sulfate organic detergent, the alkyl group of the detergent being essentially of straightchain structure, said detergent composition having uniformly dispersed therethrough a minor proportion of 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.

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 specified requirements of biodegradability. As a result, in order to make available a more biodegradable material, commercial emphasis is being placed on synthetic detergents such as the alkyl sulfates and alkyl sulfonates in which the alkyl group is more linear; i.e., one in which branching is at a minimum and the alkyl or hydrocarbyl group is essentially of straight structure.

Like the branched-chain polypropylene-based detergents, the linear secondary alkyl sulfonates and sulfates possess undesirable caking tendencies. Indeed, the caking problem seems to be aggravated with the linear alkyl sulfonates and sulfates. This is one of the reasons why they have not heretofore been commercialized to the same extent as the branched-chain alkyl benzene sulfonates. (See the book by P. A. R. Pulette, Synthetic Detergents, published by Sidgwick and Jackson, London, 1957.) Thus, 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 the straight-chain materials. Conversely, the presently contemplated caking inhibitors, although eminently effective in linear alkyl sulfonate and in linear alkyl sulfate and alkyl sulfonate detergent compositions, are unexpectedly not so effective as the known inhibitors when incorporated in the branched-chain alkyl benzene sulfonates.

It has now been found that the caking tendencies of particulate solid linear alkyl sulfonate and alkyl sulfate detergent can be suppressed by intimately admixing therewith a but small effective proportion of an anticaking agent selected from the group consisting of sodium sulfosuccinate and potassium sulfosuccinate of the formula

$$\text{SO}_3\text{M}$$

wherein M represents either sodium or potassium alkali metal. The anticaking additive can be prepared by adding sodium bisulfite to an aqueous solution of the disodium salt or maleic acid. If desired, the sodium bisulfite can be formed in situ by adding sodium hydroxide and SO$_2$ to the maleic acid salt. In general a satisfactory amount of anticaking agent can range from about 2 to 25%, preferably 8 to 20%, by weight, based on alkyl sulfate or alkyl sulfonate detergent.

The nonsoap alkyl sulfonate or alkyl sulfate that can be used in practicing the present invention can be represented by the formula

$$\text{R}^-\text{CH}=-\text{CH}^-\text{R}'^-\text{X}^-$$

in which R and R’ are hydrocarbyl radicals, the sum of the carbon atoms in R and R’ ranging from 9 to 20 atoms; and X is a group that can be —OSO$_2$Y, —SO$_3$Y or —CH$_2$OSO$_3$Y, Y being a salt-forming cation or metal that can be an alkali metal, such as lithium, sodium, and potassium; or ammonium.

These secondary alkyl sulfonates or alkyl sulfonates are known compounds available commercially.

Thus, the compound having the group OSO$_2$Y, i.e., the alkyl sulfate, can be prepared in known fashion by sulfating a secondary alcohol or by adding sulfuric acid to straight-chain α-olefins or internal olefins, as shown, for example, in U.S. Patents Nos. 2,587,990 and 2,573,730, followed by neutralization. Alkyl sulfonates can be prepared by the sulfidation reaction of saturated aliphatic hydrocarbons, or by the sulfochlorination reaction of saturated aliphatic hydrocarbons followed by hydrolysis and neutralization. Detergent materials containing the group —CH$_2$OSO$_3$Y may be prepared from olefins by the Oxo reaction, followed by sulfation, and neutralization. However prepared, the detergent precursor material containing the —SO$_3$H group or the —O—SO$_3$H group is neutralized, as indicated, with appropriate base material to give the finished detergent or surface active product. Preferred bases are the alkali metal hydroxides, such as sodium hydroxide, lithium hydroxide or potassium hydroxide; or ammonium hydroxide.

The invention is applicable to built detergent compositions, i.e., compositions containing the nonsoap synthetic detergent, particularly those containing the groups —OSO$_2$Y and —SO$_3$Y as above defined, 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 particular solid detergent composition consisting essentially of nonsoap linear alkyl sodium sulfonate and sodium carbonate, such as sodium carbonate, as an inorganic sodium salt detergent builder, and a small but effective amount to suppress said caking tendencies of the aforesaid sodium or potassium sulfosuccinate anti-caking 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 anti-caking 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 tetrasodium 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 salt detergent builders as well can be present to the extent that the total inorganic salt builder including the phosphate, to synthetic detergent weight ratio can be as high as 10:1. Further, as is known in the art, the anti-caking additive such as a bleach, perfume, foam booster, etc., may be present in the finished composition, in a combined amount up to 30% by weight of the finished composition.

Accordingly, a particularly useful embodiment of the invention is the preparation of a heavy-duty particular solid detergent composition, consisting essentially of nonsoap linear alkyl sulfonate or sulfate organic detergent, an inorganic salt detergent builder in a weight ratio to organic detergent ranging from 1:1 to 1:1.1, said inorganic salt detergent builders including a condensed sodium sulfate phosphate, such as tripotassium pyrophosphate and/or sodium tripolyphosphate, present in a weight ratio to the organic detergent ranging from about 1:1 to 3:1.

The anti-caking 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 anti-caking additive and other components of the composition, and then drying the dispersion. Another way of effecting uniform dispersions of the caking inhibitor throughout the composition is to integrate its incorporation with the process of making the nonsoap detergent by adding the inhibitor at the neutralization step.

It is often the practice to leave all or a part of the unreacted acid material used in the sulphonate and sulfonation steps, admixed with the alkyl sulfonic acids or alkyl sulfates, and to neutralize them together to form an aqueous dispersion or slurry of organic detergent 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 anti-caking agent of the present invention can be incorporated into the detergent composition by adding preformed sodium or potassium sulfosuccinate either to the neutralizing basic solution or to the neutralization mixture prior to or during the neutralization step.

As hereinafore indicated, in addition to inorganic sodium sulfate detergent builder, other inorganic salt detergent builders, such as the condensed phosphates, carbonates, silicates, and borates, can be incorporated in the detergent composition. These may be added for example to the neutralized slurry prior to drying in accordance with the specifications desired in the ultimate or finished composition. The slurry thus built is then converted to the particular 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 synthetic detergent, for example, sodium alkyl sulfate detergent, and a condensed phosphate ordinarily used in conjunction with a 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 polyphosphate, from orthophosphate. The polyphosphates may 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 phosphates, for example, 80% tripolyphosphate and 20% polyphosphate.

In addition to the detergent builders, other ingredients or fillers, in combined amounts up to about 30 weight percent of the final composition, can be incorporated. Examples of other ingredients are those customarily present in heavy-duty detergent formulations. These include in weight amounts based on final composition, an anti-foaming and stabilizing agent, such as sodium silicate, wherein the SiO2 to Na2O ratio can range from 1/2 to 2/1 in proportion of, for example, 5%; an anti-redeposition agent, such as carboxymethyl cellulose, proportions of about 1 to 3% being cited as illustrative; a foam modifier, such as a mono- or di-ethanolamide of a fatty acid, such as lauric isopropanolamide, in proportions, for example, of 5%; a chemical bleaching agent, such as sodium peroxide or sodium percarbonate, for example, in an amount of 2 to 5%, optical whiteners, in amounts of the order 0.1 to 0.2%, such as the triazinyl- and aroyl-stilbenes.

In the tabulated experiments below a specified nonpolyphosphate was subjected to the visual tackiness test. Except where indicated, the test samples were in the form of unbuilt detergent compositions, i.e., the detergent formed substantially the whole of the sample. According to the test, the dried powder with or without anti-caking agent was placed in an uncovered jar and exposed to: room conditions of temperature and humidity, i.e., 24°C and 55% relative humidity, for 16 hours. The results are summarized in the following table:

<table>
<thead>
<tr>
<th>Example</th>
<th>Sample identification</th>
<th>Visual tackiness test (additives)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>C6-C14 oxo sulfates from 1-octene</td>
<td>Sticky, but less than LAB</td>
</tr>
<tr>
<td>2.</td>
<td>C6-C14 oxo sulfates from internal olefins</td>
<td>Sticky, but less than Example 1</td>
</tr>
<tr>
<td>3.</td>
<td>C6-C14 see-alcohol sulfates 16% active</td>
<td>Tacky and plastic</td>
</tr>
<tr>
<td>4.</td>
<td>C6-C14 see-alcohol sulfates, sodium salt</td>
<td>On drying on hot plate, product turns sticky</td>
</tr>
<tr>
<td>5.</td>
<td>C6-C14 see-polyphenol sulfonate</td>
<td>Flakes which stick to container</td>
</tr>
<tr>
<td>6.</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

1 Weight based on detergent active of sodium toluene sulfonate.
2 Commercial linear alkyl benzene sulfonate detergent.
3 This material could not be dried and then tested as the others due to decomposition. Therefore the anti-caking agent was observed as an aid to drying rapidly without decomposition.
4 Potassium sulfosuccinate used in place of sodium sulfosuccinate.
The straight chain 1-olefins used to make the detergent actives noted in Table I were commercially available mixtures derived from paraffin wax by a cracking process. Such a process yields a nearly monodisperse distribution of olefins. Either broad mixtures within the detergent range, e.g., C15-C20, may be used or in order to obtain special properties, narrower mixtures may be used. Thus the C15-C20 1-olefins which were subjected to the oxo reaction in known manner to give C15-C20 oxo sulfates were comprised of about 15–35% of each of the olefins from C14 through C20 along with minor amounts of C16 and C21. Fractionation of this olefin mixture, for instance by distillation at reduced pressure, in order to split it in half, gives as the lower boiling portion the C16-C17 and half of the C18 olefins. This mixture was also subjected to the oxo reaction to give the C16-C17 oxo sulfates.

The internal olefins required for preparation of secondary alkyl sulfates or oxo sulfates may be obtained by dehydrogenation of paraffins using a two step method of chlorination followed by dehydrochlorination. Alternatively, the internal olefins may be made by isomerizing 1-olefins by known processes.

In order to obtain high quality, i.e., straight chain paraffins to insure maximum biodegradability of the product, paraffins from petroleum sources must be treated to remove branched impurities. This may be done by several known processes, of which urea clathration and molecular sieve treatment are the most widely known. The thus purified paraffins may be used for sulfoxidation or sulfochlorination to produce secondary paraffin sulfonates.

The results of Table I indicate that sodium sulfosuccinate has the desirable feature of expediting the rate of drying as well as reducing the tallowiness of the final product. This is a particularly useful property for use with temperature sensitive materials such as secondary alkyl sulfates and mixtures containing relatively large amounts of detergent and accompanied only by sodium sulfate, for example, 40% to 90% detergent active and the balance sodium sulfate and water. The use of sodium sulfosuccinate will be especially efficacious for drum drying of such mixtures, wherein the mixtures are exposed to elevated temperatures for relatively long periods of time compared, for instance, to the times and temperatures involved in spray drying.

A suitable method for determining the extent of caking 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 a large 31-mil doctor blade and allowed to dry until the dried product is readily scraped off (2 to 4 minutes). The composition then contains about 1–2% moisture. In order to simulate commercial spray dried products which ordinarily contain about 10% moisture, the powders are left exposed to ambient conditions for 24 hours. This period of time is sufficient to allow them to attain the equilibrium moisture content. The ability to retain a high moisture content without exhibiting appreciable caking tendency is desirable in an additive which will reduce caking tendency while permitting more moisture to be left in the dried formulation is highly desirable.

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 114", 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 stiff weighing paper is 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 7**

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

<table>
<thead>
<tr>
<th>Parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium C15-C20 secondary alkyl sulfate (obtained by sulfation of C15-C20 α-olefins)</td>
</tr>
<tr>
<td>Sodium tripolyphosphates</td>
</tr>
<tr>
<td>Sodium silicate</td>
</tr>
<tr>
<td>Carboxymethyl cellulose</td>
</tr>
<tr>
<td>Sodium sulfate</td>
</tr>
</tbody>
</table>

This formulation had an equilibrium moisture content of 9.2%, and when subjected to the lift-tackiness test was found to have a tackiness value of 9.2 ml.

(b) A formulation was prepared as in (a), the only change being that 3 parts sodium sulfosuccinate replaced 3 parts of sodium sulfate. The formulation had an equilibrium moisture content of 10.0%, and gave a tackiness value of 8.4 ml.

**EXAMPLE 8**

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

<table>
<thead>
<tr>
<th>Parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium C15-C20 secondary alkyl sulfate</td>
</tr>
<tr>
<td>Sodium tripolyphosphates</td>
</tr>
<tr>
<td>Sodium silicate</td>
</tr>
<tr>
<td>Carboxymethyl cellulose</td>
</tr>
<tr>
<td>Sodium sulfate</td>
</tr>
</tbody>
</table>

This composition had a tackiness of 6.3 ml, and an equilibrium moisture content of 7.5%.

(b) A composition was prepared as in 8(a), except that 3 parts sodium sulfate were replaced with 3 parts sodium sulfosuccinate. The composition had a moisture content of 8.4% and a tackiness value of 4.2 ml.

In addition to the reduction in tackiness, it was also noticed in Examples 7 and 8 that each formulation containing the sodium sulfosuccinate, Examples 7b and 8b, dried more rapidly and showed no sign of decomposition, while the formulations containing an anticaking agent, Examples 7a and 8a showed varying degrees of decomposition on drying, as judged by color formulation.

I claim:

1. Process for suppressing the caking tendencies of a nonsoap detergent having caking tendencies, said nonsoap detergent being represented by the formula:

\[ R-\text{CHR}-R' \]

X
wherein R and R' are essentially straight chain alkyl groups having a total of 9 to 20 carbon atoms, and X is \( \text{OSO}_3\text{Y}, -\text{SO}_3\text{Y} \text{ or } -\text{CH}_3\text{SO}_3\text{Y} \); wherein Y is an alkali metal or ammonium, which comprises uniformly dispersing throughout said detergent a small but effective amount substantially to suppress said caking tendencies of sodium sulfosuccinate or potassium sulfosuccinate.

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

3. Process according to claim 2, wherein the anticalking agent is present in an amount of about 8 to 20%, by weight, based on nonsoap detergent.

4. Process according to claim 2, wherein the anticalking agent is sodium sulfosuccinate.

5. Process according to claim 2, wherein the anticalking agent is potassium sulfosuccinate.

6. A built particulate solid detergent composition consisting essentially of straight-chain alkali metal or ammonium secondary alkyl sulfate or secondary alkyl sulfonate, in which the alkyl radical contains from 9 to 20 carbon atoms, as the nonsoap detergent component; inorganic sodium salt detergent builder component; and, as an anticalking agent component, sodium sulfosuccinate or potassium sulfosuccinate, 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 anticalking 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 anticalking 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 anticalking agent is sodium sulfosuccinate.

10. A built detergent composition according to claim 7, wherein the anticalking agent is potassium sulfosuccinate.

11. Heavy-duty particulate solid detergent composition at least about 70% by weight thereof consisting essentially of a mixture of (a) nonsoap detergent represented by the formula:

\[
\begin{align*}
R &-\text{CH}_2- \text{R'} \\
X &
\end{align*}
\]

wherein R and R' are essentially straight chain alkyl radicals having a total of 9 to 20 carbon atoms, and X is either \(-\text{OSO}_3\text{Y}\) or \(-\text{SO}_3\text{Y}\); wherein Y is an alkali metal or ammonium; and (b) inorganic sodium salt detergent builder, the weight ratio of inorganic sodium salt detergent builder to nonsoap synthetic detergent ranging from 1:1 to 10:1, and uniformly dispersed throughout the particles of said composition, as an anticalking agent, sodium sulfosuccinate or potassium sulfosuccinate, said anticalking agent being present in an amount ranging from about 2 to 25%, by weight, based on nonsoap detergent.

12. Composition according to claim 11, wherein the anticalking agent is present in an amount of about 8–20%, by weight, based on the nonsoap synthetic detergent.

13. Composition according to claim 11, wherein the anticalking agent is sodium sulfosuccinate.

14. Composition according to claim 11, wherein the anticalking agent is potassium sulfosuccinate.

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