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NON-CAKING SOLID PARTICULATE DETERGENTS

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This invention relates to improvements in solid particle-form detergent compositions. More particularly, it relates to the reduction and suppression of caking tendencies of solid particulate detergent compositions which contain as their active detergent ingredients sodium salts of alkyl benzene sulfonic acids or alkyl toluene sulfonic acids having from 9 to 18 carbon atoms in the alkyl chain.

The many sulfonate and sulfate synthetic detergent compositions in current commercial use are marketed in the solid particulate form as beads, flakes, chips, scales or granules, packaged into containers such as metal drums, glass jars, wooden boxes and barrels, paper and cloth bags, and cartons. Among these various anionic sulfonate and sulfate synthetic detergent compositions, those having as their effective detergent ingredients water-soluble salts of long-chain mono-alkyl benzene sulfonic acids and long-chain alkyl toluene sulfonic acids containing from 9 to 18 carbon atoms in the alkyl chain are known to be eminently suitable for the various purposes of industrial and household use. Despite the fact that these alkyl benzene and alkyl toluene sulfonates are considered to be among the most satisfactory and efficient detergent compositions available in the trade, considerable difficulty is encountered in handling these compositions by the consumer because of the tendency of these compositions to cake upon storage, especially when exposed to warm and humid climatic conditions.

The occurrence of caking has been ascribed to a number of factors: It has been said that it is caused by the presence of the residual moisture in the dry detergent particles. Another explanation is that caking is occasioned by the penetration of the atmospheric moisture into the container even though it may appear to be perfectly well sealed. Theories have been offered to relate the phenomenon of caking to the particular physical structure or chemical nature of the detergent particles. Whatever be the true cause or causes of caking, its occurrence is highly undesirable and annoying. It interferes with the free flow of the particulate detergent material from the package; furthermore, lumps of caked material are slow to dissolve in the wash water. While presence of moisture is probably the chief factor responsible for the occurrence of caking in sulfonate detergent compositions, another important concurring factor is the pressure exerted by the weight of the mass of detergent material in the package. It contributes con-

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siderably to the occurrence of caking in large containers, barrels and bags, particularly when heavy paper or cloth bags containing detergent are stacked or piled on top of each other. Even in the presence of very small amounts of moisture in the surrounding atmosphere, the weight of the detergent material occasions undesirable caking and tackiness, which may become quite annoying at the packaging plant by clogging hoppers, and thus resulting in stoppages and waste of time.

I have found that the caking tendency of sulfonate detergent compositions can be markedly reduced and frequently completely eliminated by incorporating in the detergent composition a small quantity from about 2 to about 10% by weight, and preferably from about 3 to about 5% by weight, of boric acid based on the entire composition. The detergent composition to which the boric acid is added contains in each 100 parts by weight thereof from about 10 to about 95 parts of the aforementioned sodium salts of long-chain monoalkyl benzene sulfonic acids or long-chain monoalkyl toluene sulfonic acids, the remainder being inorganic sodium salt builders.

A convenient technique for producing solid particulate long-chain monoalkyl aryl (benzene or toluene) sulfonate detergent compositions, which can be stabilized against caking in accordance with my invention, involves alkylating benzene or toluene with a long-chain olefin or an olefin polymer containing from 9 to 18 carbon atoms, for instance, polypropylene, employing a suitable effective alkylation catalyst such as hydrofluoric acid. The resulting long-chain (C_9 to C_{18}) monoalkyl benzene or toluene product, and preferably that fraction thereof which contains from 12 to 15 carbon atoms in the long alkyl chain, is thereafter subjected to sulfonation with the aid of a suitable sulfonating agent such as concentrated sulfuric acid or oleum. Upon completion of the sulfonation reaction, the unreacted sulfuric acid may be partially separated from the sulfonic acid. Then the recovered alkyl benzene or alkyl toluene sulfonic acids are converted to sodium salts by neutralization with an aqueous solution of caustic (NaOH) or sodium carbonate. The prevailing practice is to leave all or a part of the unreacted sulfuric acid admixed with the sulfonic acids and to neutralize the sulfonic-sulfuric acid mixture to form an aqueous dispersion or slurry of the corresponding organic sodium monoalkyl benzene or toluene sulfonate detergent and inorganic sodium sulfate builder.

Another technique for preparing detergent sodium monoalkyl benzene or toluene sulfonates, improved or stabilized against caking in accordance with my invention, involves condensation of benzene with chlorinated C_9 to C_{18} acyclic hydrocarbons such as are contained in a chlorinated kerosene fraction of petroleum, in the presence of a suitable catalyst, ordinarily $AlCl_3$. The resulting mixture of C_9 to C_{18} monoalkyl benzenes or toluenes is then sulfonated and neutralized in a conventional manner, and the final slurry of monoalkyl benzene or toluene sulfonate and sodium sulfate is dried and reduced to the desired particle form and size. Frequently, additional amounts of builders, e. g., more sodium sulfate and other inorganic sodium salts such as sodium silicate, and particularly phosphates such as tetrasodium

pyrophosphate or sodium tripolyphosphate, may be added to the neutralized sulfonate slurry before drying this latter in accordance with the specifications for the ultimately desired detergent composition. The slurry built with these various sodium salts is converted to the desired solid form and particle size by an appropriate drying technique, for instance, by spray-drying or drum-drying.

In addition to the inorganic sodium salt builders, organic builders, in particular sodium carboxymethyl cellulose, may be added to the neutralized sulfonate slurry in order to improve its detergency characteristics.

The introduction of the caking preventive of my invention, boric acid, usually in its conventional form of crystalline flakes, into the detergent composition is preferably carried out by adding boric acid, sodium borate, or borax to the neutralizing solution of sodium hydroxide or sodium carbonate, which is then employed to neutralize the sulfonic acid mixture. The pH of the neutralized sulfonate slurry should be less than about pH=8.3 and may be as low as pH=6.0, but preferably from about pH=7.0 to about pH=8.0, in order that boric acid rather than boric acid salts be present in the final product. One may also introduce boric acid by dispersing it in the sulfonic acid mixture.

Generally, sodium salt builders and extenders, such as sodium sulfate, tetrasodium pyrophosphate, sodium polyphosphates, sodium silicates, sodium chloride, sodium carbonate, sodium carboxymethyl cellulose, do not interfere with the anti-caking effect of boric acid provided they are employed in proportions which do not occasion a too high pH of the neutralized sulfonate slurry.

If it is desired to utilize the anti-caking effect of boric acid in the manufacture of the so-called "heavy-duty" detergent compositions, which generally contain alkaline sodium salt builders giving to these compositions a final pH greater than about 8.3 and as high as 11.5, when used in aqueous solutions of 0.2% to 0.5% in concentration conventionally employed in the laundry practice and in household washing, this may be accomplished by carrying out the compounding of the detergent composition in two separate stages. The alkaline builders which would otherwise nullify the anti-caking effect because of their alkalinity are withheld, while the other ingredients of the detergent composition including the boric acid, are dried from an essentially neutral slurry formed as described hereinabove. In this way a solid, particulate, non-caking detergent intermediate composition is prepared, which can be readily handled in manufacturing equipment without tendency to stick or cake, and which can then be compounded with more alkaline builders, such as sodium tripolyphosphate or sodium carbonate, by blending the dry materials or by the use of a process such as is described in British Patent No. 584,698.

The degree of improvement in the caking characteristics obtained for each particular composition may be varied somewhat depending on the exact amount of boric acid added, the method of drying the slurry (drum-drying or spray-drying), and the proportion of the active sulfonate detergent in the slurry. A definite advantage secured by the introduction of boric acid resides in a higher moisture content which can be tolerated in the sulfonate detergent composition without the risk of excessive caking thereof in the container.

A large number of detergent compositions containing sodium monoalkyl benzene sulfonates or sodium monoalkyl toluene sulfonates with 9 to 18 carbon atoms in the alkyl chain have been tested with respect to the reduction of their caking tendency by varying amounts of boric acid ranging from about 2 to about 10% by weight based on the solid ingredients of the detergent composition. Two different series of tests, each employing a distinct testing technique, have been carried out.

The first series of tests (humidity-cabinet tests) was

effected as follows: After incorporating boric acid into the detergent composition in accordance with the procedures described hereinabove, the neutralized slurry was dried to yield the desired particle form product. Weighed samples of the dried particulate compositions, screened through a No. 16 sieve and collected on a No. 200 sieve, were placed in small untreated sealed cardboard boxes (1½" x 2½" x 4"), and three samples of the detergent composition containing boric acid together with three samples containing no boric acid were placed in a completely random manner in a humidity cabinet, exposed to a relative humidity of about 80% at a temperature of about 90° F. After the exposure period of seven days, the boxes containing samples were re-weighed, and the extent of caking was determined by cutting away an entire side of the cardboard box and carefully transferring its contents onto a No. 4 sieve (¼" mesh) from a minimum height. The sieve was then gently swirled until all particles came into contact with the screen. The material which did not pass through the screen by this treatment was considered to be caked, and its weight vs. the weight of the original sample was designated "the percentage of material caked." The following Table I contains the results of several of these tests carried out in the humidity cabinet.

TABLE I

Effect of boric acid as a caking-preventive as shown by humidity cabinet tests

Test No.	Detergent Composition in each 100 parts by weight	Boric Acid in percent by weight	Percent Caked (Average)	Remarks
1.....	40 parts sodium monoalkyl C ₉ -C ₁₈ benzene, 60 parts Na ₂ SO ₄	0	65	Boric acid introduced into NaOH neutralizing solution.
2.....	40 parts sodium monoalkyl C ₉ -C ₁₈ benzene, 60 parts Na ₂ SO ₄	3	16	
3.....	40 parts sodium monoalkyl C ₉ -C ₁₈ benzene, 60 parts Na ₂ SO ₄	5	5	
4.....	40 parts sodium monoalkyl C ₉ -C ₁₈ benzene, 60 parts Na ₂ SO ₄	10	3	
5.....	40 parts sodium monoalkyl C ₉ -C ₁₈ benzene, 60 parts Na ₂ SO ₄	5	5	

The second series of tests (pressure-caking tests) were carried out as follows: Neutralized slurries of similarly prepared long-chain C₉-C₁₈ monoalkyl benzene and toluene sulfonate detergent compositions containing from 2 to 10% by weight of boric acid were dried and reduced to the desired form and size. The dried compositions were screened through a No. 12 sieve and collected on a No. 200 sieve, and 50 gram samples were placed into brass cylinders, 2" in diameter and 3-4" high, closed by a push piston at the top. A weight which varied from 2 to 4 kilograms was applied to the piston for 5 minutes. Then the contents of the brass cylinder were pushed out. The cylinder-shape sample was dropped from a height of 1 foot onto a No. 4 screen. The ratio of the weight of the material remaining on the screen to the weight of the original sample was taken to indicate "the percentage of material caked."

TABLE II

Effect of boric acid as a caking-preventive as shown by pressure-caking tests

Test No.	Parts by Wt. of sodium C ₉ -C ₁₈ mono- alkyl benzene sulfonate	Parts by Wt. of Builder and Extender	Percent by Wt. of boric acid added	Percent of moisture in the Detergent Composi- tion	Percent of product caked (Avg.)
	In each 100 parts of Detergent Composition				
1-----	85	15 Na ₂ SO ₄ -----	0	1.3	38.0
2-----	85	15 Na ₂ SO ₄ -----	0	2.8	98.0
3-----	85	15 Na ₂ SO ₄ -----	5	1.8	0
4-----	85	15 Na ₂ SO ₄ -----	15	2.5	0
5-----	85	15 Na ₂ SO ₄ -----	5	4.8	7.0
6-----	85	15 Na ₂ SO ₄ -----	15	7.3	17.0
7-----	70	6 Na ₂ SiO ₃ ----- 24 Na ₂ SO ₄ -----	0	2.0	47.0
8-----	70	6 Na ₂ SiO ₃ ----- 24 Na ₂ SO ₄ -----	0	3.5	99.0
9-----	70	6 Na ₂ SiO ₃ ----- 24 Na ₂ SO ₄ -----	3.3	2.0	0
10-----	70	6 Na ₂ SiO ₃ ----- 24 Na ₂ SO ₄ -----	13.3	3.2	7.0

¹ Added as borax to the neutralizing solution of NaOH.

As can be seen from the data in Tables I and II, a remarkable reduction of the caking tendency is obtained by the addition of boric acid to the sulfonate detergent compositions in accordance with my invention. In a number of tests this tendency practically disappeared in the presence of boric acid. Particularly striking is the reduction of caking and tackiness in samples of long-chain C₉-C₁₈ monoalkyl toluene sulfonates heretofore considered exceptionally susceptible to caking.

The sulfonate detergent compositions, capable of being stabilized against caking by the addition of boric acid in accordance with my invention, may also contain minor amounts of additives to improve odor, sudsing, suds stability and other characteristics thereof, such as perfumes, fatty alcohols, fatty acid alkanolamides, etc. The phrase "consisting essentially" as employed in the appended claims is intended to indicate the essential components of the detergent composition claimed, but does not preclude the presence of these additives.

I claim:

1. A built detergent composition in the form of small solid particles consisting essentially of about 10 to about 95 parts by weight of a sodium salt of an alkyl aryl sulfonic acid selected from the group of alkyl benzene sulfonic and alkyl toluene sulfonic acids containing from 9 to 18 carbon atoms in the alkyl chain, sodium salt detergent builders in an amount sufficient to bring the aggregate weight of the sulfonic acid salt and the detergent builders to 100 parts by weight and so selected from the group consisting of sodium sulfate, sodium polyphosphates, sodium silicates, sodium chloride, sodium carbonate and sodium carboxymethyl cellulose that the pH of the built detergent composition is less than about 8.3, and from about 2 to about 10% by weight, based on the aggregate weight of the sulfonic acid salt and the detergent builders, of boric acid uniformly dispersed in each particle of the detergent composition.

2. A built detergent composition as defined in claim 1, wherein boric acid is present in an amount from about 3 to about 5% by weight, based on the aggregate weight of the sulfonic acid salt and the detergent builders.

3. A built detergent composition in the form of small solid particles consisting essentially of about 10 to about 95 parts by weight of a sodium salt of an alkyl aryl sulfonic acid selected from the group of alkyl benzene sul-

fonic and alkyl toluene sulfonic acids containing from 9 to 18 carbon atoms in the alkyl chain, sodium salt detergent builders, in an amount sufficient to bring the aggregate weight of the sulfonic acid salt and the detergent builders to 100 parts by weight and so selected from the group consisting of sodium sulfate, sodium polyphosphates, sodium silicates, sodium chloride, sodium carbonate and sodium carboxymethyl cellulose that the pH of the built detergent composition is in the range from about 7.0 to about 8.0, and from about 2 to about 10% by weight, based on the aggregate weight of the sulfonic acid salt and the detergent builders, of boric acid uniformly dispersed in each particle of the detergent composition.

4. In the preparation of a solid, particulate detergent composition, in which the organic detergent component is a sodium salt of an alkyl aryl sulfonic acid from the group consisting of C₉-C₁₈ alkyl benzene sulfonic and C₉-C₁₈ alkyl toluene sulfonic acids and the inorganic components are sodium salt detergent builders, said detergent composition being produced by sulfonating a mixture of alkyl aryl hydrocarbons from the group of C₉ to C₁₈ alkyl benzenes and C₉ to C₁₈ alkyl toluenes, neutralizing the resulting sulfonation product mixture and drying said mixture to solid detergent particles, a method permitting of reducing the caking tendency of said detergent composition, which comprises introducing from about 2 to about 10% of boric acid, based on the weight of the final dry detergent composition, into the neutralizing solution for the sulfonation product mixture, neutralizing said sulfonation mixture to a pH of less than about 8.3, drying the neutralized mixture to small particle size and compounding the resulting dried particles resistant to caking with sodium salt detergent builders capable of imparting a pH from about 8.3 to about 11.5 to an aqueous solution of the resulting blend, ranging from 0.2% to 0.5% in concentration.

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