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DETERGENT COMPOSITIONS

Willard M. Bright, Ridgewood, N.J., assignor to Lever Brothers Company, New York, N.Y., a corporation of Maine

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The present invention relates to detergent compositions and to improvements in the cleaning of hard surfaces. More particularly, it pertains to polyphosphate-aryl sulfonate compositions having synergistic cleansing properties.

Materials which aid in producing homogeneous liquids from substances which are incompatible in aqueous media are known as hydrotropes. Short chain alkyl aryl sulfonates have been used to solubilize the longer chain alkyl aryl of sulfonates and other organic detergents in the presence of complex, inorganic phosphates. However, it has not been generally recognized that these conventional hydrotropes also possess detergent properties since compositions containing polyphosphates and short chain alkyl aryl sulfonates have always contained synthetic detergents to provide suitable detergent activity to the formulations. Specifically, it has not been recognized that products containing a polyphosphate and these hydrotropic agents are particularly efficacious in cleaning hard surfaces such as tiles and other coverings for floors, walls and the like.

It is an object of this invention to provide detergent compositions having synergistic cleansing characteristics.

Another object is to take advantage of the discovery that short chain alkyl aryl sulfonates contribute significantly to the detersive properties of formulations containing complex inorganic polyphosphates.

Still another object of the invention is to provide a means for efficiently cleansing hard surfaces.

It has now been found that certain sulfonates conventionally used as hydrotropes have enhanced tolerance for condensed phosphates and that such polyphosphate-sulfonate compositions exhibit synergistic properties in cleaning hard surfaces such as painted walls, floor tile and the like.

The polyphosphate-sulfonate mixtures according to this invention contain from about 40% to about 85% of at least one water-soluble salt of a polyphosphate and from about 15% to about 60% of at least one water-soluble arylsulfonate. The proportions are based on dry mixtures of these two ingredients. The polyphosphates used in these compositions include tetrapotassium and tetrasodium pyrophosphate, sodium and potassium tripolyphosphates and mixtures of these ingredients. The sulfonates which can be used include the alkali metal and ammonium salts of benzene sulfonate, ortho-, meta-, and para-xylene sulfonate and mixtures of these isomers, toluene sulfonate, ethylbenzene sulfonate, n-propyl and isopropylbenzene sulfonate, etc. as well as various combinations of these materials.

It is within the scope of the present disclosure that such additional ingredients as fillers, colorants, perfumes, optical dyes, bleaches, and germicides may be added.

The following examples serve to illustrate the present invention, without however, limiting the same thereto.

EXAMPLE 1

Evaluations were made using 6 sulfonates to determine how well standard soled 9 inches x 9 inches asphalt floor tiles were cleaned by (1) an aqueous solution of 8.0% sulfonate and 22.5% tetrapotassium pyrophosphate; (2) 30.5% solution of the sulfonate; (3) 30.5% solution of tetrapotassium pyrophosphate. This was done by dividing a soiled tile into quarters. One of the soiled quarters was washed in a standard manner with solution (1). The second quarter was washed with solution (2). The third quarter was washed with solution (3). The fourth quarter was kept as an unwashed control. A tile was used for each series of three solutions evaluating a given sulfonate. The washed tiles were inspected visually and ranked for cleanliness by a panel of three observers. The following hydrotropes were evaluated: sodium ortho-xylenesulfonate, sodium metaxylenesulfonate, potassium paraxylenesulfonate, sodium toluenesulfonate, sodium ethylbenzenesulfonate, and sodium isopropylbenzenesulfonate.

Details of the test

The details of soiling, washing and ranking follow:

Soiling.—The floor tiles used were 9 inches x 9 inches Armstrong Asphalt Tile, factory finished, Pattern D–900 Ivory Marble, ⅛ inch gage. A layer of vacuum cleaner dust (screened through 80 mesh to remove larger particles) was rubbed evenly over the surface with a cloth. Any excess loose dust was shaken from the tile, and the area now soiled with adhering dust was covered with three successive layers of liquid floor wax (this operation simulated waxing a normally solid floor). Each layer of wax was allowed to dry in air before the next layer was applied.

Washing.—The method of washing consisted of dipping a 3 inches x 4 inches swatch of new clean white terry cloth into the detergent solution, squeezing excess liquid from the fabric and rubbing each soiled area in a standard manner for 30 seconds. The loosened soil-detergent mixture was then wiped from the surface with a new clean 5 inches x 9 inches Wipette (an absorbent cellulose napkin).

Grading and ranking.—The quarters of each tile were compared for cleanliness by a panel of three observers under standard daylight lighting conditions. The cleanest quarter was ranked "1," the next cleanest "2," the next cleanest "3" and the least clean "4."

The results of tests performed on the solutions described above are tabulated below. The symbol TKPP designates tetrapotassium pyrophosphate.

Sulfonate Series	Cleanness Ranking of Quarter Washed With:			
	Sulfonate Alone	TKPP Alone	Mixture of Sulfonate and TKPP	Not Washed
Sodium ortho-xylenesulfonate	3	2	1	4
Sodium meta-xylenesulfonate	3	2	1	4
Potassium para-xylenesulfonate	2½	2½	1	4
Sodium toluenesulfonate	3	2	1	4
Sodium ethylbenzenesulfonate	2½	2½	1	4
Sodium isopropylbenzenesulfonate	3	2	1	4

NOTE 1.—A ranking of "½" is given to indicate the median when two detergents are tied for two adjacent ranks. Thus, a ranking of "2½" indicates that a tie occurred for "2" and "3" ranks and, "1½" indicates that a tie occurred for "1" and "2" ranks, i.e., "cleanest" and "next to cleanest".

It was necessary to warm the sodium ortho-xylene-sulfonate solution, and the solution of the sodium ortho-xylenesulfonate-TKPP mixture to melt crystals before use.

It was necessary also to warm the potassium para-xylenesulfonate solution to melt the crystals. However, these crystals reformed as soon as the warmed solution

was touched to the cold tile. Crystals were not removed from the mixture of potassium para-xylenesulfonate and TKPP even with warming, and when used this solution contained a small amount of crystals.

EXAMPLE 2

The following results were obtained using mixtures of tetrapotassium pyrophosphate (TKPP) and commercial sodium xylenesulfonate (SXS) for cleaning a standard soiled wall surface. Five solutions of tetrapotassium pyrophosphate of varying concentrations were each used in combination with various concentrations of the sulfonate. Various percentage concentrations of tetrapotassium pyrophosphate in water solutions, namely: 22.5%, 21.0%, 18.0% and 0% were each tested with 8.0%, 6.9%, 4.6% and 0% of sodium xylenesulfonate. For these tests, 0% of either tetrapotassium pyrophosphate or sulfonate was considered a concentration level of that component.

A panel of white Walltex, 4 feet x 2 feet, was attached with tape to a wooden table top. The surface was evenly soiled by application of a mixture of screened vacuum cleaner dust, oildag (colloidal graphite and petroleum oil) and cooking fat (bacon grease). An ordinary 9 inch paint roller was used in applying the soil evenly. The application of soil was adjusted to bring the soiled reflectance to a level of 17% on the Hunter reflectometer equipped with a green filter. The Hunter reflectometer is standardized so that the reflectance of a magnesium oxide block is 100% (green filter). For each run this test panel was divided into fifths, lengthwise, making five equal-sized rectangular test areas.

Washing of soiled areas.—The washing of the soiled area was conducted at levels of 22.5%, 21.0%, 18.0% and 0% TKPP in combination with 8.0%, 6.9%, 4.6% and 0% of SXS. Solutions of each component identified by numerals for tetrapotassium pyrophosphate and letters for sodium xylenesulfonate were prepared so that equal weight portions of each component would give the desired mixtures.

Percent Conc. of Prepared Solutions	
SXS	TKPP
a—16.0	1—45.0
b—13.8	2—42.0
c— 9.2	3—36.0
d— 0.0	4— 0.0

To illustrate.—"1a" called for equal weights of (1) 45% TKPP and (a) 16% SXS giving a resultant mixture (1a) of 22.5% TKPP and 8.0% SXS.

The washing scheme was as follows:

The above prepared solutions were used at room temperature in a standardized manner, 20 milliliters of solution placed in a 5 inch watch glass. A clean white piece (3 inches x 4 inches) of new terrycloth was dipped into the solution until the cloth became saturated. The fabric was removed, squeezed between the fingers to remove excess moisture, and rubbed over the rectangular soiled Walltex test area for 30 seconds. The dirt and detergent mixture left on the test area was removed by absorption with an absorbent tissue. After drying, the reflectance of the tested area was determined in four locations.

When the test washings had been completed, the test area of 9.6 inches x 2 feet was cut from the larger 2 feet x 4 feet panel of Walltex used for each run. The resultant smaller swatch was easier to handle during the reflectance determinations on the Gardner color difference meter. Each cleaned area was read four times along the longer central axis. Since there were four replicates for each

detergent, the reflectances shown in Table II are the averages of 16 readings for each detergent mixture.

TABLE II

[Average reflectance of standard soiled Walltex panels after washing]

Percent TKPP	Percent Sodium Xylenesulfonate			
	8.0	6.9	4.6	0.0
22.5	64.9	64.7	64.0	52.5
21.0	64.3	63.6	65.5	55.4
18.0	61.9	61.5	62.0	48.9
0.0	41.4	42.9	40.7	37.5

The reflectances were determined on the Rd scale of the Gardner color difference meter. The readings show the percentage whiteness compared with MgO taken as 100%.

These data indicate that the detergent solutions having tetrapotassium pyrophosphate alone and those having sulfonate alone, were inferior to solutions which were mixtures of tetrapotassium pyrophosphate and the sulfonate. A synergistic effect is shown since the sum of the reflectances from the solutions containing TKPP alone plus that from the solutions containing sulfonate alone is less than that obtained from the mixture.

EXAMPLE 3

Additional tests were conducted using the same procedure as described in Example 2 employing a 24% concentration of TKPP and a 13.8% concentration of SXS so that combining equal weights of the TKPP solution with the SXS solution gave a mixture containing 12% TKPP and 6.9% SXS. The following reflectances were observed.

TABLE III

[Average reflectance of standard soiled Walltex panels after washing]

Conc. TKPP, Percent	Conc. Sodium Xylenesulfonate	
	6.9%	0%
12.0	62.6	46.5
0	28.5	28.1

EXAMPLE 4

Additional tests were conducted with a combination of 70% tetrapotassium pyrophosphate and 30% tetrasodium pyrophosphate (TSPP) with ortho-, meta-, and para-xylene-sulfonates, and 50–50 mixtures of these isomers. The following mixtures were tested:

TABLE IV

[All percentages are by weight]

Solution Number	Percent TKPP	Percent TSPP	Percent Ortho-SXS	Percent Meta-SXS	Percent Para-SXS
1	15.75	6.75	4.0	4.0	
6	15.75	6.75	4.0		4.0
9	15.75	6.75		4.0	4.0
4	15.75	6.75	8.0		
5	15.75	6.75		8.0	
8	15.75	6.75			8.0
2	21.35	9.15			
3			15.25	15.25	
7			15.25		15.25
10				15.25	15.25

Samples 1, 4, 6, 7, 8 and 9 contained crystals. These mixtures were heated to 50° C. (122° F.) to dissolve the separated solid material and were used at this temperature; the remaining solutions were used at room temperature (80° F.).

Each soiled panel was divided into 5 test areas, as described in Example 2. The test solutions were used in a random fashion until four replicate washings had been made with each mixture. The standardized washing

method was used and the reflectances of the cleaned areas were determined as follows:

TABLE V

[Average reflectance of washed standard soiled panels]

Solution	Percent TKPP	Percent TSPP	Percent Ortho-SXS	Percent Meta-SXS	Percent Para-SXS	Unadjusted Reflectance	Adjusted Reflectance
1	15.75	6.75	4.0	4.0		54.3	36.1
6	15.75	6.75	4.0		4.0	60.8	42.6
9	15.75	6.75		4.0	4.0	62.8	44.6
4	15.75	6.75	8.0			59.5	41.3
5	15.75	6.75		8.0		58.1	39.9
8	15.75	6.75			8.0	53.4	35.2
2	21.35	9.15				31.8	13.6
3			15.25	15.25		32.6	14.4
7			15.25		15.25	39.4	21.2
10				15.25	15.25	35.5	17.3

NOTE.—The reflectances were adjusted for the water blank by subtracting the reflectance of a panel washed in water alone; thus, the adjusted figure shows the cleaning done by the solution, over and above that done by water.

These results indicate that solutions containing the tetra-phosphate mixture plus sulfonate (either a single isomer or mixed isomers) are superior to the combined results of solutions containing phosphate alone, or sulfonate alone.

EXAMPLE 5

Additional tests were conducted to determine the reflectances obtained from mixtures of pyrophosphates alone, sulfonates alone, and sulfonate mixtures alone. The results are tabulated below:

TABLE VI

[Average reflectance of washed test areas]

Solution	Percent TKPP	Percent TSPP	Percent Ortho-SXS	Percent Meta-SXS	Percent Para-SXS	Unadjusted Reflectance	Adjusted Reflectance
1	15.75	6.75				31.3	11.2
2			8			24.5	4.4
3				8		24.1	4.0
4					8	21.7	1.6
5			4	4		20.5	0.4
6			4		4	21.9	1.8
7				4	4	21.9	1.8
8	(Distilled water)					20.1	0.0

Thus, by comparing the results given above with those given in Table V of Example 4, it will be seen that the values for adjusted reflectance are higher in each case for the solutions containing a mixture of pyrophosphate plus sulfonate (solutions 1, 6, 9, 4, 5 and 8 of Table V) than those values obtained by adding the adjusted reflectance for the sulfonate alone and those for the pyrophosphate alone. This clearly demonstrates the synergism of the present invention.

EXAMPLE 6

Further tests were performed on a series of mixtures to determine their effectiveness in cleaning hard surfaces. The products were evaluated as described in Example 2 by washing a Walltex board soiled in a standard manner. The reflectance of each swatch of the wall covering was measured on the Gardner color difference meter.

The mixtures received as solutions were used in the tests "as is" without dilution. All solutions were heated to about 110° F. before use. Powdered Product 6 was utilized by dissolving 32.5 grams of the mixture in 67.5 ml. of distilled water. A washing temperature of 110° F. was maintained in all tests.

TABLE VII

[Composition of products and reflectance of washed Walltex with adjustment for reflectance of water blank]

Product Number	1	2	3	4	5	6	7	8	9
Type of Product	Soln.	Soln.	Soln.	Soln.	Soln.	Powder	Soln.	Water	Soln.
Percent Penta Sodium Tripolyphosphate	15.25		11.25						
Percent Penta Potassium Tripolyphosphate	15.25		11.25						
Percent Sodium Xylene Sulfonate Comm. Grade		30.5	8.0			21.44	8.0		
Percent "Calgon"-Mainly Hexametaphosphate $(NaPO_3)_6$				18.0					
Percent Ammonium Xylene Sulfonate				8.0	12.0				
Percent Tetra Potassium Pyrophosphate					45.0	55.45	22.5		22.5
Percent Sodium Silicate Solids (SiO_2:Na_2O=2.0)					6.0				
Percent Perfumes					0.5	.46			
Percent Blue Dye ("Hastings Sky Blue")						.18			8.0
Percent Sodium Benzene Sulfonate									
Percent Fluorescent Dye [a]						.09			
Percent Potassium Dichloroisocyanurate						9.24			
Percent Sodium Metasilicate, Solids						2.77			
Percent Germicide [b]						2.77			
Percent Water	69.5	69.5	69.5	74.0	36.5	7.60	69.5	100.0	69.5
Percent Total	100.00	100.0	100.00	100.0	100.0	100.00	100.0	100.0	100.0
Average Reflectance of Washed Swatches on Gardner Color Difference Meter	26.9	30.2	48.7	31.1	57.0	48.7	54.5	18.1	51.1
Average Reflectance Minus Water Blank, or Control	8.8	12.1	30.6	13.0	38.9	30.6	36.4	0.0	

[a] 4-4'bis(4''-morphilino-6'' anilino-1'',3'',5''-triazin-2''-ylamino)-stilbene-2,2'-disulfonic acid, Na salt.
[b] Approx. equal parts by weight of 4',5-dibromo- and 3,4',5-tribromosalicylanilide.

It is seen from the above data that Product 4 containing hexametaphosphate is not within the scope of the invention since no synergistic results are obtained. However, the pH of this product was about 5 while the pH of other formulations within the scope of the invention was higher than 7, i.e., on the alkaline side. It will be recognized that the lack of synergism in Product 4 may be due to the relatively low pH and that this can be overcome by means well-known to those skilled in the art.

Moreover, it is evident from Product 6 above that compositions containing the polyphosphate and sulfonate of the invention can be marketed as dry powders and the ultimate consumer may add water before using if desired.

Additives which do not materially alter the beneficial characteristics of the mixtures of this invention may be incorporated as shown in the above table. The amount of the additives should not exceed about 45% based on the weight of the dry ingredients. Thus, up to about 3% of a germicide and 3% of sodium silicate solids can be present, as well as a maximum of about 10% of a chlorine-releasing bleaching agent. Other inert ingredients up to the 45% maximum can be added.

The term "Walltex" as used in the above examples refers to a coated cotton fabric waterproof wall covering which may be applied with paste in much the same manner as wall paper.

It will occur to those skilled in the art that there are many modifications to this invention as specifically described therein. It is intended to include all such modifications within the scope of the appended claims.

What is claimed is:

1. A composition consisting essentially of about 40% to about 85% of a water-soluble condensed, inorganic polyphosphate and from about 15% to about 60% of a water-soluble aryl sulfonate selected from the group consisting of benzenesulfonate, ortho-xylenesulfonate, meta-xylenesulfonate, para-xylenesulfonate, toluenesulfonate, ethylbenzenesulfonate, n-propylbenzenesulfonate, isopropylbenzenesulfonate and mixtures thereof, the proportions being based on the weight of the dry ingredients, said composition providing an alkaline reaction in aqueous solution.

2. A composition consisting essentially of about 40% to about 85% of a water-soluble condensed, inorganic polyphosphate, about 15% to about 60% of a water-soluble aryl sulfonate selected from the group consisting of benzenesulfonate, ortho-xylenesulfonate, meta-xylenesulfonate, para-xylene sulfonate, toluenesulfonate, ethylbenzenesulfonate, n-propylbenzenesulfonate, isopropylbenzenesulfonate and mixtures thereof, up to about 10% of a chlorine-releasing agent, up to about 3% of a germicide and up to about 3% of a sodium silicate, the proportions being based on the weight of the dry ingredients, said composition providing an alkaline reaction in aqueous solution.

3. An aqueous dispersion of the composition recited in claim 1.

4. An aqueous dispersion of the composition recited in claim 2.

5. A method which comprises cleansing a hard surface by contacting therewith a composition consisting essentially of about 40% to about 85% of a condensed inorganic water-soluble polyphosphate and from about 15% to about 60% of a water-soluble aryl sulfonate selected from the group consisting of benzenesulfonate, ortho-xylenesulfonate, meta-xylenesulfonate, para-xylenesulfonate, toluenesulfonate, ethylbenzenesulfonate, n-propylbenzenesulfonate, isopropylbenzenesulfonate and mixtures thereof, the proportions being based on the weight of the dry ingredients, said composition providing an alkaline reaction in aqueous solution.

6. A method which comprises cleansing a hard surface by contacting therewith a composition consisting essentially of about 40% to about 85% of a condensed, inorganic water-soluble polyphosphate, from about 15% to about 60% of a water-soluble aryl sulfonate selected from the group consisting of benzenesulfonate, ortho-xylenesulfonate, meta-xylenesulfonate, para-xylenesulfonate, toluenesulfonate, ethylbenzenesulfonate, n-propylbenzenesulfonate, isopropylbenzenesulfonate and mixtures thereof, up to about 10% of a chlorine-releasing agent, up to about 3% of a germicide and up to about 3% of a sodium silicate, the proportions being based on the weight of the dry ingredients, said composition providing an alkaline reaction in aqueous solution.

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LEON D. ROSDOL, *Primary Examiner.*

JULIUS GREENWALD, *Examiner.*

J. T. FEDIGAN, *Assistant Examiner.*