

# UNITED STATES PATENT OFFICE

2,575,576

## ALKALI METAL SALT-ORGANIC SULFOXY DETERGENT COMPOSITIONS INHIBITED AGAINST DETERIORATION OF VITREOUS- AND CERAMIC-WARE SURFACES

Leslie R. Bacon, Wyandotte, and Joseph V. Otrhalek, Detroit, Mich., assignors to Wyandotte Chemicals Corporation, Wyandotte, Mich., a corporation of Michigan

No Drawing. Application January 13, 1950,  
Serial No. 138,518

16 Claims. (Cl. 252-138)

1

It has previously been ascertained that highly alkaline solutions, containing free caustic alkali, such as NaOH, can be inhibited against alkali attack of vitreous and ceramic surfaces (such as attack effecting actual dissolution of the vitreous or ceramic material accompanied by a scratched, scuffed, etched or worn appearance of the surface thereof) by the addition of a water-soluble zinc compound (Wegst, Bacon, and Vaughn, U. S. Pat. No. 2,447,297), a water-soluble beryllium compound (Wegst, Bacon, and Vaughn, U. S. Pat. No. 2,419,805), or a water-soluble aluminum compound (Cooper, U. S. Pat. No. 2,241,984). We have now discovered that even mildly alkaline detergent and washing compositions have a corrosive or deteriorative effect on vitreous and ceramic surfaces. That is to say, the alkali metal salts which are employed as builders for soap and synthetic detergents in compositions for washing glassware and dishes (such as laboratory glassware, overglaze decorated chinaware and earthenware), themselves possess the ability to attack glass and ceramic ware, even though their alkalinity in aqueous solutions may be on the order of 8-10 pH as compared to the greater than 12 pH alkalinity of solutions containing free caustic alkali.

The problem of compounding alkali metal salts, such as sodium-carbonates, -phosphates, -silicates and -sulfates, with a water-soluble Zn-, Be- or Al-compound, however, was found to be extremely difficult because such chemical compounds when brought together in aqueous solutions, were found to be incompatible. That is to say, it was found as a general rule, that the alkali metal builder salts when combined with the inhibiting compounds such as sodium zincate, zinc sulfate, beryllium sulfate, sodium aluminate and aluminum sulfate, produced aqueous solutions which either contained a precipitate or had a turbid or cloudy appearance. It is quite possible that the excess of free caustic alkali as present in the inhibited washing compounds of the above-mentioned U. S. Pats. Nos. 2,419,805 and 2,447,297 wherein it is disclosed that up to 40% of alkali metal carbonates, -phosphates and -silicates may be present, exerted a powerful solubilizing effect on the precipitate or turbidity-forming product which would otherwise result from the presence of the alkali metal salt and the inhibiting compound. Thus, the problem of compounding a washing composition based on an alkali metal salt or salts, a synthetic detergent selected from the group consisting of the sodium salts of alkyl sulfonates, alkyl sulfates and alkyl-

2

arylsulfonates whose alkyl group contains 10-18 carbon atoms and a Zn-, Be- or Al-inhibiting compound involved not only the discovery of those particular ingredients which would be compatible with each other, but also their proper balance and determination of the effective amount of inhibiting compound which should be present in order to overcome the corrosive and deteriorative action on glass and ceramic surfaces.

### Summary of invention

Our invention therefore resides in the discovery of the following range proportions of ingredients which are capable of producing a clear, non-turbid and precipitate-free solution when dissolved in water at customary working concentrations; and being further capable, when made into working solutions, of greatly diminishing glass dissolution, scratching, scuffing, etching, clouding and filming of glassware and the obliteration and fading of decorative effects on dishware and ceramics:

Ingredients	Per Cent by Weight	
	Operable Range	Preferred Range
Carbonate:		
Sodium bicarbonate (NaHCO <sub>3</sub> )	20-30	23-26
Modified soda <sup>1</sup>		
Sodium carbonate (Na <sub>2</sub> CO <sub>3</sub> )		
Phosphate:		
Sodium tripolyphosphate (Na <sub>5</sub> P <sub>3</sub> O <sub>10</sub> )	10-40	15-22
Sodium tetraphosphate (Na <sub>4</sub> P <sub>4</sub> O <sub>13</sub> )		
Sodium hexametaphosphate (Na <sub>6</sub> P <sub>6</sub> O <sub>18</sub> )		
Synthetic Detergent:		
Sodium alkylarylsulfonate	40-70	49-55
Sodium lauryl sulfate		
Sodium alkyl-sulfonate		
Inhibitor:		
Sodium zincate	3-10	4-6
ZnO-NaOH-H <sub>2</sub> O reaction product		
Zinc sulfate		
Sodium aluminate		
Aluminum sulfate		
Beryllium sulfate		
BeO-NaOH-H <sub>2</sub> O reaction product		

<sup>1</sup> A mixture of sodium carbonate and sodium bicarbonate having a total alkalinity as Na<sub>2</sub>O of 39-43%. See American Society for Testing Materials standard specification, ASTM designation: D457-39.

The synthetic detergent compounds, as above listed, are commercially available products which are chemically, more precisely identified as follows:

Sodium alkyl aryl sulfonate, wherein the alkyl group is derived from a petroleum hydrocarbon and contains 10-18 carbon atoms. Such compounds are synthesized according to the processes as disclosed in U. S. Pats. Nos. 1,992,160 and

2,220,099. They are commercially available under the product names "Kreelon," "Nacconol," "Santomerse" and "Oronite."

Sodium lauryl sulfate is the sodium salt of sulfated fatty alcohols such as are derived from coconut oil. This compound may be synthesized according to the process as disclosed in U. S. Pat. No. 1,968,797 and is commercially available under the product names of "Duponol ME" and "Dreft."

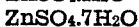
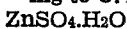
Sodium alkyl sulfonate is derived from petroleum hydrocarbons or synthetic hydrocarbons, the alkyl group containing 10-16 carbon atoms. It is made by a process such as disclosed in U. S. Pat. No. 2,197,800. A commercially available form is sold under the product name "M. P. 189."

Such compounds are usually commercially available and customarily used in their "salt-built" form, i. e. containing a certain percentage of active agent and the balance usually being the inorganic salt, Na<sub>2</sub>SO<sub>4</sub>. In the compositions of our invention, such synthetic detergents are present in their at least 35% active agent form.

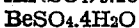
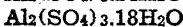
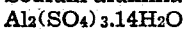
The water-soluble Zn-, Be- or Al- salts are preferably derived from the following commercially available forms:

**Sodium zincate**

ZnO-NaOH-H<sub>2</sub>O reaction product made according to U. S. Pat. No. 2,403,157



**Sodium aluminat**



Beryl-NaOH reaction product made according to U. S. Pat. No. 2,474,392 or Example 2 of U. S. Pat. No. 2,419,805.

*Solution compatibility*

In our efforts to discover a possible combination or combinations of alkali metal salts and Zn-, Be- and Al- compounds which might possibly solve the problem of producing a clear and compatible aqueous solution, preliminary formulations were made up consisting of 90% by weight of several different sodium carbonates, -silicates, -phosphates, -borate compounds and 10% of inhibiting compound. In the case of the BeSO<sub>4</sub>.4H<sub>2</sub>O inhibitor compound, this proportion was changed to 99.7% alkaline sodium salt and 0.3% inhibitor. Such prepared formulations were then dissolved in distilled water at 120-130° F. in an amount corresponding to 10% by weight solids content. The resultant solutions, by visual observation, possessed the following noted properties:

Although the foregoing test results did not seem to be too promising, they did give the clue that possibly, by a proper balance of those sodium carbonates and sodium phosphates which, individually at least, showed compatibility with an inhibitor compound, then by combination and adjustment of ingredients, proper compatibility in aqueous solution might be achieved. At the same time that the question of possible compatibility of the ingredients NaHCO<sub>3</sub>, modified soda, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>5</sub>P<sub>3</sub>O<sub>10</sub>, Na<sub>6</sub>P<sub>4</sub>O<sub>13</sub>, (NaPO<sub>3</sub>)<sub>6</sub>, and inhibitor compounds were being investigated, several different types of synthetic organic detergents and surface active agents, including anionic-, non-ionic- and cationic types, were included in the formulations. Of these synthetic detergents, it was found that those anionic compounds selected from the group consisting of the sodium salts of alkyl sulfonates, alkyl sulfates and alkylarylsulfonates whose alkyl group contains 10-18 carbon atoms were the most suitable. It was thereby found that when the following specified ingredients were maintained in the range proportions as tabulated below, that clear, compatible aqueous solutions were produced:

	Ingredient	Per Cent by Weight
30	Sodium Carbonate:	20-30
	NaHCO <sub>3</sub> .....	
	Modified soda.....	
35	Sodium Phosphate:	10-40
	Na <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .....	
	Na <sub>5</sub> P <sub>3</sub> O <sub>10</sub> .....	
40	Synthetic Detergent:	40-70
	Sodium alkylarylsulfonate.....	
	Sodium lauryl sulfate.....	
45	Inhibitor Compound:	3-10
	Sodium zincate.....	
	ZnO-NaOH-H <sub>2</sub> O reaction product.....	
	Zinc sulfate.....	
	Sodium aluminat.....	
	Beryllium sulfate.....	

In further explanation of our invention, the following exemplary formulations are given as being preferred and well adapted for commercial use.

**EXAMPLE 1**

	Ingredients	Per Cent by Weight
55	Sodium kerylbenzenesulfonate <sup>1</sup> (40% active agent).....	49
	Sodium bicarbonate (NaHCO <sub>3</sub> ).....	23
	Sodium tripolyphosphate (Na <sub>5</sub> P <sub>3</sub> O <sub>10</sub> ).....	22
	Zinc sulfate (ZnSO <sub>4</sub> .7H <sub>2</sub> O).....	6

<sup>1</sup> A sodium alkylarylsulfonate whose "keryl" or alkyl group is derived from a petroleum hydrocarbon and contains 11-16 carbon atoms.

**TABLE I**

Alkaline Salt	Inhibitor Compound					
	ZnSO <sub>4</sub> (7H <sub>2</sub> O)	NaOH-ZnO-H <sub>2</sub> O <sup>1</sup>	BeSO <sub>4</sub> (4H <sub>2</sub> O)	Beryl-NaOH <sup>2</sup>	Na <sub>2</sub> Al <sub>2</sub> O <sub>4</sub>	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (18H <sub>2</sub> O)
NaHCO <sub>3</sub> .....	P	P	C	P	P	P
Modified Soda.....	P	P	C	P	P	P
Na <sub>2</sub> CO <sub>3</sub> .....	P	P	C	P	P	P
Na <sub>2</sub> SiO <sub>3</sub> .5H <sub>2</sub> O.....	P	P	C	P	P	P
Na <sub>2</sub> HPO <sub>4</sub> .....	P	P	C	P	P	P
Na <sub>2</sub> P <sub>2</sub> O <sub>7</sub> .12H <sub>2</sub> O.....	P	P	C	P	P	P
Na <sub>2</sub> F <sub>2</sub> O <sub>7</sub> .....	P	P	C	P	P	P
Na <sub>5</sub> P <sub>3</sub> O <sub>10</sub> .....	C	P	C	P	P	P
Na <sub>6</sub> P <sub>4</sub> O <sub>13</sub> .....	C	P	C	P	P	P
(NaPO <sub>3</sub> ) <sub>6</sub> .....	C	P	C	P	P	P
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> .10H <sub>2</sub> O.....	P	P	P	C	P	P

Key: P=precipitate. T=turbid or cloudy solution. C=no precipitate, clear solution (i. e., compatible).  
<sup>1</sup> Product of U. S. Pat. No. 2,403,157, 30% ZnO content.  
<sup>2</sup> Product of Example 2 of U. S. Pat. No. 2,419,805, 0.3% BeO content.

5

This formulation, when dissolved in distilled water and other waters of varying degrees of hardness, at a temperature of 120°-130° F. and at a practical working solution of 0.6% by weight total solids basis, produced clear solutions containing no precipitate, cloudiness or turbidity. When the amount of  $ZnSO_4 \cdot 7H_2O$  was varied between 5 and 10%, at the expense of the sodium kerylbenzenesulfonate- $Na_2SO_4$  present, the solution clarity or compatibility was still maintained. However, on increasing the  $ZnSO_4 \cdot 7H_2O$  content to 12%, there resulted a turbid solution having a little less than 0.5% by volume of precipitate in a standard ten grain hardness water. Thus, it was established that the tolerance of this formulation for more than 10% of inhibitor compound was quite critical.

## EXAMPLE 2

Ingredients	Per Cent by Weight
Sodium kerylbenzenesulfonate (40% active agent).....	55
Sodium bicarbonate ( $NaHCO_3$ ).....	25
Sodium tripolyphosphate ( $Na_3P_3O_{10}$ ).....	15
NaOH-ZnO- $H_2O$ reaction product (30% ZnO content).....	5

Here again, it was discovered that the tolerance of the formulation for the water-soluble zinc compound was a maximum of 10%.

## EXAMPLE 3

Ingredients	Per Cent by Weight
Sodium kerylbenzenesulfonate (40% active agent).....	55
Sodium bicarbonate ( $NaHCO_3$ ).....	25
Sodium tripolyphosphate ( $Na_3P_3O_{10}$ ).....	15
Beryllium sulfate ( $BeSO_4 \cdot 4H_2O$ ).....	5

## EXAMPLE 4

Ingredients	Per Cent by Weight
Sodium kerylbenzenesulfonate (40% active agent).....	55
Modified soda.....	25
Sodium tripolyphosphate ( $Na_3P_3O_{10}$ ).....	15
Beryllium sulfate ( $BeSO_4 \cdot 4H_2O$ ).....	5

## EXAMPLE 5

Ingredients	Per Cent by Weight
Sodium kerylbenzenesulfonate (40% active agent).....	51
Sodium bicarbonate ( $NaHCO_3$ ).....	23
Sodium tripolyphosphate ( $Na_3P_3O_{10}$ ).....	22
Aluminum sulfate ( $Al_2(SO_4)_3 \cdot 14H_2O$ ).....	4

The formulation of Example 5 likewise confirmed the 10% maximum tolerance for the aluminum sulfate inhibitor compound. When the amount of inhibitor compound was increased from 4 to 6%, at the expense of the sodium kerylbenzenesulfonate- $Na_2SO_4$  present, a very excellent composition was obtained which displayed universal solution clarity in distilled, hard and

6

soft waters, at a concentration of 0.6% solids basis and at temperatures of 120°-130° F.

*Corrosion inhibiting properties*

Formulations coming within the scope of our invention were subjected to an accelerated glass corrosion test described as follows:

Glass test tubes of a 10 x 75 mm. size, made from a borosilicate type glass, were first washed in a weak solution of sodium kerylbenzenesulfonate (60%  $Na_2SO_4$  content) in distilled water and then thoroughly rinsed in distilled water. The test tubes were then baked for 4 hours at 210° F. to drive off all surface moisture, cooled and weighed.

Test detergent formulation solutions, according to those given in Examples 1-5 inc. above, were then made up at a concentration of 0.6% total solids basis in either distilled water and/or tap water of 6 grains per gallon total hardness as  $CaCO_3$  and placed in one liter capacity stainless steel beakers, the temperature of such solutions being maintained at  $209 \pm 2^\circ F$ .

Three of the previously prepared test tubes were then placed at random on the bottom of the so-prepared test solutions and permitted to remain there for a period of 18 hours, the temperature being maintained. Thereafter, the test tubes were removed from the test solutions, brushed free of any surface deposits with a soft test tube brush, rinsed with distilled water and baked as before to drive off surface moisture, then cooled and weighed to the nearest 0.2 mg. The average weight loss of the three specimen test tubes in each test solution was found to be as follows:

TABLE II

Test Formulation	Weight Loss (mg./tube)	
	Distilled Water	Tap Water
Example 1.....	3.1	0.1
Example 2.....	4.4	0.0
Example 3.....	0.4	.....
Example 4.....	0.0	.....
Example 5.....	.....	0.0

The above results are to be compared with control tests wherein the same formulations as in the above examples, but with no inhibitor compound present were used to make up the detergent test solutions. In such control tests, the weight losses ranged from approximately 7-14 mgs. per tube in distilled water, and 4-7 mgs. per tube in tap water.

Next, in order to determine the effective range content of inhibitor compound in the formulations of Examples 1-5, additional test formulations were made up wherein the amount of inhibitor was varied over the range of 0-10%, at the expense of the sodium kerylbenzenesulfonate- $Na_2SO_4$  present. The test solutions were made up at concentrations of 0.6% in both distilled water and tap water except in the case of the base formulation of Example 4 where distilled water only, and of Example 5 where tap water only, were used. In general, it was noted that distilled water solutions were more corrosive than tap water solutions. Hence the former presented the more severe test conditions. The results are given in the following Table III:

7  
TABLE III

Base Formulation	Amount of Inhibitor Present (Per Cent by Weight)	Weight Loss (mg./tube)	
		Distilled Water	Tap Water
Example 1.....	ZnSO <sub>4</sub> ·7H <sub>2</sub> O:		
	0.....	14.3	-----
	4.....	7.3	-----
	5.....	4.8	-----
	6.....	3.1	0.1
Example 2.....	NaOH-ZnO-H <sub>2</sub> O:		
	0.....	9.2	-----
	2.....	7.3	3.8
	3.....	5.8	4.4
	5.....	4.4	1.3
Example 3.....	BeSO <sub>4</sub> ·4H <sub>2</sub> O:		
	0.....	6.7	3.8
	1.....	4.8	0.8
	3.....	4.2	0.0
	4.....	1.7	-----
Example 4.....	BeSO <sub>4</sub> ·4H <sub>2</sub> O:		
	0.....	6.3	-----
	2.....	5.2	-----
	3.....	2.1	-----
	4.....	1.0	-----
Example 5.....	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·14H <sub>2</sub> O:		
	0.....	6.0	0.0
	4.....	-----	7.4
	5.....	-----	0.3
	6.....	-----	0.1

Visible etching or deterioration of the glass surfaces was found to occur at above 2.0 mg./tube weight loss values. Hence, from the above corrosion test results, it will be seen that 3-6% content of inhibitor produces an effective control under conditions of normal usage, viz., in a tap water of mild hardness.

The following examples are illustrative of formulations employing synthetic detergent or sodium phosphate ingredients, other than those heretofore specified in Examples 1 to 5 inc.

EXAMPLE 6

Ingredients	Per Cent by Weight
Sodium kerylbenzenesulfonate (40% active agent).....	51
Sodium bicarbonate (NaHCO <sub>3</sub> ).....	23
Sodium tetraphosphate (Na <sub>4</sub> P <sub>4</sub> O <sub>13</sub> ).....	22
Aluminum sulfate (Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·14H <sub>2</sub> O).....	4

The above composition gave a clear solution in tap water of approximately 6 grain hardness with no precipitate and gave no precipitate in 15 grain hardness water. Such solutions were prepared at 0.3% concentration at 110-120° F. In the accelerated glass corrosion tests, this composition produced a weight loss of 0.4 mg. per tube, in distilled water.

EXAMPLE 7

Hexametaphosphate was substituted for the sodium tetraphosphate for the formulation of Example 6 with identical results in respect to solution clarity and absence of precipitate. The accelerated glass corrosion test results were slightly better however giving no weight loss in distilled water.

EXAMPLE 8

Ingredients	Per Cent by Weight
Sodium kerylbenzenesulfonate (70% active agent).....	51
Sodium bicarbonate (NaHCO <sub>3</sub> ).....	23
Sodium tripolyphosphate (Na <sub>3</sub> P <sub>3</sub> O <sub>10</sub> ).....	22
Aluminum sulfate (Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·14H <sub>2</sub> O).....	4

The composition of this example made a clear solution of 0.3% concentration in tap water of approximately 6 grains per gallon total hardness and produced no precipitate in such tap water or in water of 15 grain hardness. The accelerated glass corrosion test showed a weight loss of 0.9 mg. per tube, in distilled water.

EXAMPLE 9

Sodium lauryl sulfate (85% active agent) was substituted for the sodium kerylbenzenesulfonate ingredient of Example 5. Identical clarity and lack of precipitate, as obtained in Example 8 was produced. The accelerated glass corrosion test showed a weight loss of 0.5 mg. per tube, in distilled water.

EXAMPLE 10

Sodium alkyl sulfonate (35% active agent basis) whose alkyl group contained an average of 15 carbon atoms and was derived from a petroleum hydrocarbon, as disclosed in U. S. Pat. No. 2,197,800, was substituted for the sodium kerylbenzenesulfonate of Example 5. Similar results were obtained as in Example 9.

The concentration in aqueous solution of the detergent compositions of our invention may be varied over a range of 0.3-1.0% for effective control of glass and ceramic ware deterioration by alkaline salts. In such a range of concentration, by a further series of tests carried out on washing glass test tubes, and in the same manner as previously described, but wherein the concentration of the compositions of Examples 1, 2 and 5 were varied from 0.075% to above 2.0%, it was found that only 0.0-1.0 mg./tube weight loss was obtained in the range of 0.3-1.0% concentration of detergent composition.

The compositions of our invention are also very effective in inhibiting the deteriorative action of alkaline inorganic salts on overglaze decorated chinaware and earthenware. Ornamental effects on such ware in the form of gold striping and banding is particularly sensitive to such action. Thus, for example, two different brands or types of overglaze chinaware dinner plates, containing gold striping as well as other colored pigments, were immersed in 0.3% solutions of the compositions of Examples 1 and 5 for periods of 18 hours and 36 hours and at a constant temperature of 180° F. An uninhibited detergent composition consisting of sodium carbonate, -bicarbonate, -tripolyphosphate, tetrasodium pyrophosphate, sodium sulfate and sodium alkyl aryl sulfonate was similarly tested as a control. In each case, the gold striping was practically entirely removed from the chinaware by the uninhibited composition, whereas it remained bright and unaffected by the compositions of Examples 1 and 5.

It has also been found that the compositions of our invention are effective to inhibit depreciation of large, vitreous enamel-lined steel tanks.

It will be noted in the foregoing examples and descriptive matter that the percentage amounts of inhibitor compounds are given in terms of their actual solid weights and including combined water of hydration or of constitution. However, in order to translate such stated proportions to a more empirical basis, the following conversion table gives the Zn-, Be- and Al-

metallic oxide equivalent content of the several inhibitor compounds herein mentioned, viz:

To convert a unit of—	to its ZnO, BeO or Al <sub>2</sub> O <sub>3</sub> equivalent, Multiply by—
Sodium Zincate (Na <sub>2</sub> ZnO <sub>2</sub> ).....	.566
ZnO—NaOH—H <sub>2</sub> O reaction product.....	.300
ZnSO <sub>4</sub> ·H <sub>2</sub> O.....	.454
ZnSO <sub>4</sub> ·7H <sub>2</sub> O.....	.283
BeSO <sub>4</sub> ·4H <sub>2</sub> O.....	.141
Beryl—NaOH reaction product (Ex. 2 of U. S. 2,419,805).....	.003
Beryl—NaOH reaction product (Ex. 1 of U. S. 2,474,392).....	.020
Sodium Aluminate (Na <sub>2</sub> Al <sub>2</sub> O <sub>4</sub> ).....	.622
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·14H <sub>2</sub> O.....	.172
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·18H <sub>2</sub> O.....	.153

Thus, converting the 3-10% range proportion of inhibitor compounds to their metallic oxide content equivalent bases, it is seen that the corresponding minimum and maximum limits of water-soluble zinc compound are 0.85-5.66% ZnO content; of beryllium compound, .009-1.41% BeO content; and of aluminum compound, 0.47-6.22% Al<sub>2</sub>O<sub>3</sub> content. In the preferred 4-6% actual solid weight range of inhibitor compounds, the corresponding conversion limits are: zinc compound, 1.13-3.40% ZnO content; beryllium compound, .012-0.84% BeO content; and aluminum compound, 0.61-3.73% Al<sub>2</sub>O<sub>3</sub> content.

As used in the specification and the appended claims the phrase "NaOH, ZnO and H<sub>2</sub>O" refers to the product made by the method of U. S. Patent No. 2,403,157. Similarly the phrase "BeO—NaOH—H<sub>2</sub>O" and "beryl—NaOH" refers to the product made by the method of U. S. Patent No. 2,474,392 or Example 2 of U. S. Patent No. 2,419,805.

Other modes of applying the principle of our invention may be employed, changes being made as regards to the details described, provided the features stated in any of the following claims or the equivalent of such be employed.

We, therefore, particularly point out and distinctly claim as our invention:

1. A detergent composition inhibited against deteriorative action on vitreous and ceramic surfaces, consisting essentially of 20-30% by weight of a carbonate selected from the group consisting of sodium bicarbonate, modified soda and sodium carbonate, 10-40% of a phosphate selected from the group consisting of sodium tripolyphosphate, sodium tetraphosphate and sodium hexametaphosphate, 40-70% of a synthetic detergent selected from the group consisting of the sodium salts of alkyl sulfonates, alkyl sulfates and alkylarylsulfonates, wherein the alkyl group contains 10-18 carbon atoms, said synthetic detergent being present in at least 35% active agent form; and 3-10% of an inhibitor compound selected from the group consisting of the zincates, berylliates and aluminates of sodium and the sulfates of zinc, beryllium and aluminum compounds and corresponding to a 0.85-5.66% ZnO equivalent weight, a .009-1.41% BeO equivalent weight, and a 0.47-6.22% Al<sub>2</sub>O<sub>3</sub> equivalent weight, respectively.

2. The composition as in claim 1 wherein the inhibitor compound is zinc sulfate.

3. The composition as in claim 1 wherein the inhibitor compound is the reaction product of NaOH, ZnO and H<sub>2</sub>O of 30% ZnO content.

4. The composition as in claim 1 wherein the inhibitor compound is aluminum sulfate.

5. A detergent composition inhibited against

deteriorative action on vitreous and ceramic surfaces, consisting essentially of 23-25% by weight of a carbonate selected from the group consisting of sodium bicarbonate, modified soda and sodium carbonate, 15-22% of a phosphate selected from the group consisting of sodium tripolyphosphate, sodium tetraphosphate and sodium hexametaphosphate, 49-55% of a synthetic detergent selected from the group consisting of the sodium salts of alkyl sulfonates, alkyl sulfates and alkylarylsulfonates, wherein the alkyl group contains 10-18 carbon atoms, said synthetic detergent being present in at least 35% active agent form; and 4-6% of an inhibitor compound selected from the group consisting of the zincates, berylliates and aluminates of sodium and the sulfates of zinc, beryllium and aluminum compounds and corresponding to a 1.13-3.40% ZnO equivalent weight, a .012-0.84% BeO content, and a 0.61-3.73% Al<sub>2</sub>O<sub>3</sub> equivalent weight, respectively.

6. The composition as in claim 5 wherein the inhibitor compound is zinc sulfate.

7. The composition as in claim 5 wherein the inhibitor compound is the reaction product of NaOH, ZnO and H<sub>2</sub>O of 30% ZnO content.

8. The composition as in claim 5 wherein the inhibitor compound is aluminum sulfate.

9. A detergent composition inhibited against deteriorative action on vitreous and ceramic surfaces, consisting essentially of 20-30% by weight of a carbonate selected from the group consisting of sodium bicarbonate and modified soda, 10-40% of sodium tripolyphosphate, 40-70% of sodium kerylbenzenesulfonate whose keryl group is an alkyl group derived from petroleum hydrocarbons and contains 11-16 carbon atoms, said sodium kerylbenzenesulfonate being present in its at least 35% active agent form; and 3-10% of an inhibitor compound selected from the group consisting of the zincates, berylliates and aluminates of sodium and the sulfates of zinc, beryllium and aluminum compounds and corresponding to a 0.85-5.66% ZnO equivalent weight, a .009-1.41% BeO equivalent weight, and a 0.47-6.22% Al<sub>2</sub>O<sub>3</sub> equivalent weight respectively.

10. A detergent composition inhibited against deteriorative action on vitreous and ceramic surfaces, consisting essentially of 23-25% by weight of a carbonate selected from the group consisting of sodium bicarbonate and modified soda, 15-22% of sodium tripolyphosphate, 49-55% of sodium kerylbenzenesulfonate whose keryl group is an alkyl group derived from petroleum hydrocarbons and contains 11-16 carbon atoms, said sodium kerylbenzenesulfonate being in its 40-70% active agent form; and 4-6% of an inhibitor compound selected from the group consisting of the zincates, berylliates and aluminates of sodium and the sulfates of zinc, beryllium and aluminum compounds and corresponding to a 1.13-3.40% ZnO equivalent weight, a .012-0.84% BeO equivalent weight, and a 0.61-3.73% Al<sub>2</sub>O<sub>3</sub> equivalent weight, respectively.

11. The detergent composition of the following formulation:

Ingredients	Per Cent by Weight
Sodium kerylbenzenesulfonate (40% active agent).....	49
Sodium bicarbonate (NaHCO <sub>3</sub> ).....	23
Sodium tripolyphosphate (Na <sub>5</sub> P <sub>3</sub> O <sub>10</sub> ).....	22
Zinc sulfate (ZnSO <sub>4</sub> ·7H <sub>2</sub> O).....	6

11

12. The detergent composition of the following formulation:

Ingredients	Per Cent by Weight
Sodium kerylbenzenesulfonate (40% active agent).....	55
Sodium bicarbonate (NaHCO <sub>3</sub> ).....	25
Sodium tripolyphosphate (Na <sub>5</sub> P <sub>3</sub> O <sub>10</sub> ).....	15
NaOH-ZnO-H <sub>2</sub> O reaction product (30% ZnO content).....	5

13. The detergent composition of the following formulation:

Ingredients	Per Cent by Weight
Sodium kerylbenzenesulfonate (40% active agent).....	51
Sodium bicarbonate (NaHCO <sub>3</sub> ).....	23
Sodium tripolyphosphate (Na <sub>5</sub> P <sub>3</sub> O <sub>10</sub> ).....	22
Aluminum sulfate (Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·14H <sub>2</sub> O).....	4

14. The method of washing glassware and dishware, which comprises immersing such ware in a 0.3-1.0% by weight concentration aqueous solution of the detergent composition of claim 1.

15. The method of washing glassware and dishware, which comprises immersing such ware in a 0.3-1.0% by weight concentration aqueous solution of the detergent composition of the following formula:

Ingredients	Per Cent by Weight
Sodium kerylbenzenesulfonate (40% active agent).....	49
Sodium bicarbonate (NaHCO <sub>3</sub> ).....	23
Sodium tripolyphosphate (Na <sub>5</sub> P <sub>3</sub> O <sub>10</sub> ).....	22
Zinc sulfate (ZnSO <sub>4</sub> ·7H <sub>2</sub> O).....	6

12

16. The method of washing glassware and dishware, which comprises immersing such ware in a 0.3-1.0% by weight concentration aqueous solution of the detergent composition of the following formula:

Ingredients	Per Cent by Weight
Sodium kerylbenzenesulfonate (40% active agent).....	54
Sodium bicarbonate (NaHCO <sub>3</sub> ).....	23
Sodium tripolyphosphate (Na <sub>5</sub> P <sub>3</sub> O <sub>10</sub> ).....	22
Aluminum sulfate (Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·14H <sub>2</sub> O).....	1

LESLIE R. BACON  
JOSEPH V. OTRHALEK.

## REFERENCES CITED

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

## UNITED STATES PATENTS

Number	Name	Date
2,241,984	Cooper .....	May 13, 1941
2,394,320	McGhie .....	Feb. 5, 1946
2,419,805	Wegst .....	Apr. 29, 1947
2,447,297	Wegst .....	Aug. 17, 1948