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3,248,335
DETERGENT COMPOSITION FOR HARD SURFACES

Arthur S. Teot and Dale G. Brown, Midland, Mich., assignors to The Dow Chemical Company, Midland, Mich., a corporation of Delaware
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This application is a continuation-in-part of our copending applications Serial No. 736,001, filed May 19, 1958, now abandoned, and Serial No. 106,520, filed May 1, 1961, now abandoned.

The present invention relates to new and useful detergent compositions. More particularly the present invention relates to hard-surface detergents.

While hundreds of detergents and compositions containing the same are known to the art, very few have the properties which successfully clean hard-surface articles such as dishes and glasses. With the advent of the machine dishwasher even fewer detergents have been found with the ability to remove, adequately, food particles and to give a clean water-break under machine conditions. Several of the detergents formerly acceptable foam excessively in the machine washers because of the water pressures employed. Others lose their foam stability. Attempts to reduce the foaming with anti-foam agents and to stabilize the low foamers have not been entirely satisfactory. Therefore, it would be desirable to have a detergent useful in both machine washers and the kitchen sink which gives clean water-break, good food removal and regulated foaming. Such a detergent has been found in 2-octadecyldiphenyl oxide disulfonate. When this detergent is incorporated into the alkaline inorganic salt builders of the present day hard-surface detergents a superior detergent composition is provided. It also has been found that the substitution of as little as 10% by weight of the detergent compound of compositions containing alkylaryl sulfonate or alkylaryl polyether detergents, with the 2-octadecyldiphenyl oxide disulfonate will markedly improve the resulting composition's food removal and water-break properties and lower the foaming to a useful level for machine dishwashers.

The new compound can be prepared by reacting an aliphatic alcohol with a diphenyl oxide in the presence of aluminum chloride at temperatures of from 40° to 150° C. in the manner of U.S. Patent No. 2,555,371 and/or 2,170,989 and subsequently sulfonating the alkylated compound in the manner of U.S. Patent No. 2,584,477, issued Septembmer 30, 1958. The compound has at least one 2-octadecyl radical and between 1.8 and 2.5 sulfonate radicals per diphenyl oxide molecule.

The new compound can be successfully compounded or formulated with substantially any of the known auxiliary ingredients, i.e., builders, of hard-surface detergents.

It is to be further understood that certain of the well known detergents heretofore employed in combination with the alkaline inorganic salt builders can be markedly improved by substituting a portion from 10 to 90% by weight thereof with the active ingredient of the present invention. The two classes of detergents which show marked improvement are the alkali metal salts of the alkaryl sulfonates and the alkaryl polyethers. Representative of the first class of compounds are sodium dodecylbenzene sulfonate, potassium isopropyl-naphthalene sulfonate, sodium nonylbenzene, sulfonate and the like. Representative members of the alkaryl polyethers are nonylphenol-9 moles ethylene oxide condensate, octylphenyl condensed with 8-9 moles of ethylene oxide, dodecylphenol-10 moles ethylene oxide condensate.

Thus one can employ the alkaline inorganic salts such as sodium tripolyphosphate, chlorinated trisodium phos-

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phate, sodium carbonate, sodium metal-silicate, mixtures of the same, and the like with 2-octadecyldiphenyl oxide sodium sulfonate alone as well as with various of the alkylaryl sulfonates or the alkylaryl polyethers.

Typical formulations of hard-surface detergent compositions useful in present day machine dishwashers are set forth below. Percentages are calculated on an anhydrous basis.

	Grams	Percent by weight
I		
Na tripolyphosphate.....	14.4	64
Na metasilicate.....	7.7	34.2
Surfactant 1.....	0.44	1.8
II		
Na metasilicate.....	7.8	52
Na tripolyphosphate.....	4.8	32
Ethylenediamine tetraacetic acid tetrasodium salt.....	1.2	8
Surfactant 1.....	1.2	8
III		
Na tripolyphosphate.....	14.45	65.7
Na metasilicate.....	7.5	34.2
Surfactant.....	0.022	0.1

1 The surfactant can be employed as a binary mixture of from 10 to 90% by weight of one surfactant and the balance a second surfactant.

In formulations such as set forth above it has been found that the surfactant of the present invention can be employed in from 0.1 to 12% and preferably from 1 to 8% by weight of the total formulation and that it may be used to replace all or any portion of the alkylaryl sulfonates or alkylaryl polyether detergents.

The following examples illustrate the present invention but are not to be construed as limiting.

Example 1

Chinaware plates each smeared with 1/4 of a soft boiled egg per plate were allowed to stand in the air for two hours until dry. A household automatic dishwashing machine having a volume of 2 1/3 gallons' capacity, a 5-minute wash cycle, two 1-minute rinse cycles and a 23-minute drying period was employed using 22.5 grams (anhydrous basis) of formulation II above using various surfactants as the active ingredient. The incoming water was at 161° F. and had a hardness of 67 p.p.m. as CaCO3. The detergency effect of each of the surfactants is tabulated below:

A numerical rating scale was arbitrarily selected as follows:

- 5.0=all egg off; 100% clean on water-break
- 4.5=all egg off; >50% clean on water-break
- 4.0=all egg off; <50% clean on water-break
- 3.5=1 egg spot
- 3.0=2-4 egg spots
- 2.0=5-10 egg spots
- 1.0=11-20 egg spots
- 0=>20 egg spots

The following table sets forth the average of the data obtained by washing two egg-soiled plates under the above conditions. In the binary mixtures, 0.6 gram of one surfactant and 0.6 gram of a second surfactant was used. The table below shows the data obtained using the various detergent combinations. Thus A-A, the intersection of the horizontal A line over the vertical A column, is sodium dodecyl-diphenyl oxide disulfonate, A-D, is 50-50 mix-

tures of sodium dodecylphenyl oxide sulfonate and polyethylene glycol-polybutylene oxide condensate.

Detergent:	Detergent					
	A	B	C	D	E	F
A.....	2.0	-----	-----	-----	-----	-----
B.....	2.5	3.75	-----	-----	-----	-----
C.....	1.5	5.0	2.0	-----	-----	-----
D.....	2.0	2.0	3.75	1.75	-----	-----
E.....	1.0	2.5	3.75	3.5	2.0	-----
F.....	1.0	5.0	3.75	3.0	0.5	0

A=Na dodecylphenyl oxide disulfonate.
 B=Na 2-octadecylphenyl oxide disulfonate.
 C=Na dodecylbenzene sulfonate.
 D=A polyethylene glycol of molecular weight 600 to which has been added butylene oxide until the molecular weight was 1,500.
 E=A commercial formulation containing sorbitan monolaurate as the major active ingredient.
 F=A commercial formulation containing a condensate of octylphenol and 8-9 moles of ethylene oxide.

Example 2

Tests were made to compare the performance of a number of surfactants for removing dried milk from clear glass tumblers in hard water. The following formulation was used:

	Grams
Na ortho silicate	14.4
Chlorinated trisodium phosphate	2.4
Victamide (an amido-polyphosphate sequestrant made by Victor Chemical Works under U.S. 2,112,112)	2.4
Surfactant	0.8

The glasses were prepared for the washing test by emptying out homogenized whole milk rotating the glasses—purposely leaving as much milk as possible on the glasses. The four coated glasses were then placed in a convection oven at 60–85° C. After 2–3 minutes the glasses were removed, rotated to spread the milk over the sides again and replaced in the oven. This was repeated until the water had all evaporated with the maximum time being around 10 minutes. A hard water was made synthetically by adding Ca and Mg chlorides (2:1 ratio) sufficient to raise city tap water of 67 p.p.m. hardness as CaCO₃ to about 300 p.p.m. hardness. Water temperature was 160° F. The results of the washing test in a commercial home spray type dish washing machine are tabulated below. To allow statistical treatment of the data, a numerical rating system was devised.

- 1=Crystal clean with no more spots than one would get by washing a clean glass with distilled H₂O.
 2=Slight hint of haze.
 3=Clean with a large number of milk spots or a light hazy film covering the glass.
 4=Thick hazy film or milk streaks.

Surfactant	Drops of D-C ¹ anti-foam A to kill foam	p.p.m. Hardness	Appearance	Avg. rating of 4 replicates
None.....	0	308	All glasses clear with a large number of spots.	3
2-Octadecylphenyl oxide disulfonate.....	1	308	Three glasses were clear with 10 spots. One glass had a slight tint of haze.	1
Na dodecylbenzene sulfonate.....	4	312	Three glasses were clear with over 200 spots and the other had milk left.	3
(2)	3	281	All clear with over 100 spots.	3
(3)	6	296	Slight hint of haze with 1-2 spots.	2
(4)	4	318	Clear with high number of spots.	3
(5)	10	310	Clear glass, milk-streaked with 50 spots. Film of haze with 12 spots. Fairly clear with 100 spots.	3

¹ Silicone antifoam manufactured by Dow-Corning Corporation.

² A commercial surfactant containing as the major active ingredient a polypropylene oxide-ethylene oxide condensate.

³ A commercial surfactant containing as the major active ingredient octylphenol-ethylene oxide condensate.

⁴ A commercial surfactant containing as the major active ingredient N-octadecyl tetrasodium (1,2-dicarboxyl ethyl) sulfo succinate.

⁵ A commercial surfactant containing as a major ingredient sodium lauryl sulfate.

Example 3

In the manner described in Example 2 above using city tap water (78 p.p.m.) and four drinking glasses coated with milk (dried as described above) and cleaning formulations below additional tests were made to show the superiority of the detergent of the present invention even in amounts as small as 1%. The same rating system as employed in Example 2 was also employed in this example.

CHANGING FORMULATIONS

	Percent
Sodium tripolyphosphate	65.7
Sodium meta silicate	34.2
Surfactant	.1

15 1% α-METHYL HEPTADECYL DIPHENYL OXIDE DISULFONATE—MILK REMOVAL RATING

Glass:	
1	1
2	2
3	1
4	2
1	2
2	1
3	2
4	1

Average

30 1% SODIUM DODECYL DIPHENYL OXIDE DISULFONATE MILK REMOVAL RATING

Glass:	
1	2
2	1
3	3
4	2
1	3
2	3
3	3
4	3

Average

We claim:

1. A hard-surface detergent composition consisting essentially of alkaline inorganic salt builders and from 0.1 to 12% by weight, based on the composition, of sodium 2-octadecylphenyl oxide disulfonate.

2. A hard-surface detergent composition consisting essentially of alkaline inorganic salt builders and from 0.1 to 12% by weight of a binary detergent mixture of from 10 to 90% by weight of sodium 2-octadecylphenyl oxide disulfonate and 90 to 10% by weight of a surfactant selected from the group consisting of an alkylphenol condensed with ethylene oxide, alkali metal alkylbenzene sulfonate and alkali metal alkylnaphthalene sulfonate.

3. A hard-surface detergent composition consisting es-

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essentially of alkaline inorganic salt builders and from 1 to 12% by weight, based on the composition, of sodium 2-octadecyldiphenyl oxide disulfonate.

4. A hard-surface detergent composition consisting essentially of alkaline inorganic salt builders and from 1 to 12% by weight of a binary detergent mixture of from 10 to 90% by weight of sodium 2-octadecyldiphenyl oxide disulfonate and 90 to 10% by weight of a surfactant selected from the group consisting of an alkylphenol condensed with ethylene oxide, alkali metal alkylbenzene sulfonate and alkali metal alkylnaphthalene sulfonate.

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JULIUS GREENWALD, *Primary Examiner*.