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[54] **AUTOMATIC DISHWASHING
COMPOSITIONS**

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252/156; 252/539; 252/540; 252/559;
252/DIG. 10; 134/25 A**
[51] Int. Cl. **C11d 1/22; C11d 3/02; C11d 7/10**
[58] Field of Search **252/99, 539, 540, 558,
252/559, 133, 353, DIG. 10; 134/25 A**

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[57] **ABSTRACT**

Automatic dishwashing detergent compositions comprising C₁₇–C₂₂ alkylbenzene sulfonates and sodium, lithium, or ammonium sulfates effect dishwashing without potential discharge or pollutants.

7 Claims, No Drawings

AUTOMATIC DISHWASHING COMPOSITIONS

This invention relates to nonpolluting detergent compositions particularly suitable for use in automatic dishwashing machines.

Because of the vigorous agitation and high washing temperatures encountered in automatic dishwashers the use of conventional anionic detergents in these dishwashers has not been successful. Detergents which have sufficient cleaning ability produce too much foam. Those which produce acceptable foams failed to clean properly. Consequently, almost all successful dishwashing machine detergents have comprised a large percentage of a water-softening salt such as a polyphosphate or carbonate with minor portions of various materials being added to prevent glazing and spotting of the articles washed.

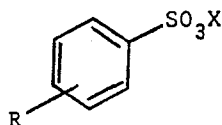
While these conventional dishwashing compositions have been satisfactory in their cleaning properties, environmental considerations make their use less than desirable because of their high concentrations of phosphates which cause eutrophication of water bodies or of carbonates and metasilicates which are corrosive and particularly dangerous to humans.

It is thus desirable to supply detergent compositions which perform effectively in automatic dishwashers and do not require the presence of large amounts of phosphates, carbonates, or silicates, etc.

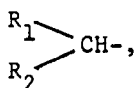
SUMMARY OF THE INVENTION

A water-soluble detergent composition suitable for use in automatic dishwashers is provided, comprising:

a. one part by weight of a linear alkylbenzene sulfonate of the formula



in which X is a water-soluble salt-forming cation, in which R is alkyl of 17 to 22 carbon atoms, and in at least 65 mol percent of said alkylbenzene sulfonate formula R is a group of the formula



R₁ and R₂ are normally attached linear alkyl groups of 2 to 19 carbon atoms, and the sum of the carbon atoms in R₁ and R₂ is 16 to 21, and

b. from 8 to 25 parts, preferably from 15 to 25 parts, by weight of a salt of the formula Y₂SO₄ in which Y is Na⁺, Li⁺, or NH₄⁺.

The water-soluble cation X in (a) may be, for example, an alkali metal or alkaline earth metal material but is preferably the same as the cation Y in (b) and is preferably sodium.

The alkylbenzene sulfonate is produced by conventional techniques, e.g. by alkylating benzene with an olefin of the proper configuration with a catalyst that will produce attachment of the chain to the ring at a

carbon atom other than the first or second carbon atoms of the olefin.

However, as noted, as much as 35 percent of the alkylbenzene sulfonates having end attachment, i.e., on the first two carbons, may be present in the detergent compositions.

The detergent composition is employed in the dishwasher in concentrations ranging from about 0.1 to 1.0 percent by weight.

The alkylbenzene precursors may be prepared by alkylating benzene with an alpha olefin in the presence of hydrogen fluoride, or may be accomplished alternatively by alkylating benzene with an olefin having a double bond internally located, preferably toward the middle of the chain.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Thus the materials are prepared by techniques known in the art, although for most detergent purposes the alkyl chain is of shorter length, i.e., 12-15 carbon atoms. As indicated, the range is from 17 to 20 carbon atoms, although this may vary slightly depending upon the source of the alkylbenzene, i.e., the point of attachment of the alkyl chain to the benzene ring. Thus the high mid-chain attached material which will usually have not more than about 10 percent of molecules in which the attachment of the ring is at the 2 carbon, a range of 17 to 20 alkyl carbon atoms gives superior performance. In the case of the materials prepared by HF alkylation of benzene the 2 attached material may reach as high as 35 percent. In the case of this material a range of 18 to 20 alkyl carbon atoms is preferred.

The inorganic sulfate component comprises the primary portion of the composition, with practical ratios of sulfate to LAS ranging, as indicated, from 8 to 1 to 25 to 1 with a preferred range of 10 to 1 to 20 to 1. The primary function of the sulfate surprisingly is to prevent deposition of films upon plates and glassware washed through several cycles in an automatic washer. This observed function of the sulfate salt is surprising because while sulfates, particularly the alkali metal sulfates, have been employed in various detergent compositions, in general their presence was only tolerated and not observed to have any beneficial effect except as a filler which might improve the flowing and noncaking character of the compositions. The amount of sulfate used has generally been well below the amount employed in this invention, usually being present in an amount of up to about 3 or 4 times the concentration of detergent.

Unexpectedly sulfates having cations other than the claimed Na⁺, Li⁺, and NH₄⁺, for example K⁺, apparently have little or no effect upon soil deposition. Na₂SO₄ is by far the least expensive and almost as effective as lithium sulfate and is therefore preferred.

The compositions of the invention thus provide an adequate balance of low foaming and good soil removal and deposition characteristics requisite for automatic dishwasher use.

The following examples illustrate the compositions of this invention. The examples are only illustrative and are non-limiting.

EXAMPLE I

Preparation of Linear Alkylbenzene Sulfonates

In order to determine the suitability for automatic dishwashers a series of alkylbenzene sulfonates were

produced by conventional methods, i.e., alkylation of benzene with an olefin of appropriate chain length followed by sulfonation of the product with oleum. Hydrogen fluoride catalysis with alpha olefins produces a mixture having not more than about 35 percent 2-phenyl substitution on the alkyl chains. Acid catalyzed alkylation with olefin fractions having vinylene groups distributed near the center of the chain will produce alkylbenzenes having little or no 2-attachment.

High 2-phenyl content material was obtained by fractional distillation of single carbon alkylbenzenes prepared by the hydrogen fluoride route, the 2-phenyl isomer being the higher boiling constituent. Likewise, high internal attachment was obtained using the lower boiling fractions. [W. A. Sweeney and A. C. Olson, "Performance of Straight-Chain Alkylbenzene Sulfonates (LAS) in Heavy-Duty Detergents", JAOCS 41, 815 (Dec. 1964)]

Using the above described procedures three types of linear alkylbenzene sulfonates were prepared by alkylating benzene with an appropriate olefin [A. C. Olson, "Alkylation of Aromatics with 1-Alkenes", Ind. Eng. Chem. 52, 833 (Oct. 1960)].

The typical percent of attachment of the phenyl group on the chain for hexadecyl benzene is described in Table A for the three types of linear alkylbenzene sulfonates.

TABLE A

Phenyl Attachment of Alkylbenzene Sulfonates			
Phenyl Attachment	Ia	Ib	Ic
6+	—	~48	~25
5	—	~18	~10
4	Tr.	~17	~12
3	5	~15	~20
2	95	~2	~33

EXAMPLE II

Foam Screening of LAS Detergents

Various sodium alkylbenzene sulfonates prepared as described in Example I were screened in a miniaturized foam test to determine if any met the criteria for use in automatic dishwashers. The test was performed by spraying a solution of each detergent vertically, allowing the material to fall back into a beaker, and measuring the volume of foam produced. For comparison purposes a commercial automatic dishwashing composition produced a volume of 125 ml. The LAS materials tested were those of Examples Ia, b and c, i.e., various alkyl chain lengths in mixtures wherein the attachment of the phenyl group varies generally according to the distribution previously described. These data are set forth in Table I as follows:

TABLE I

MINIATURE FOAM TEST Foam Value			
Alkyl Carbons, No.	Surfactant Type		
	Ia	Ib	Ic
11	>500	>500	—
12	>500	400	—
13	>500	350	200
14	350	100	350
15	400	75	75
16	150	25	75
17	—	—	0

TABLE I-Continued

MINIATURE FOAM TEST Foam Value			
Alkyl Carbons, No.	Surfactant Type		
	Ia	Ib	Ic
18	25	—	—
19	—	0	—

These data give a primary indication that the foam level of type Ib and Ic alkylbenzene sulfonate with carbon chain lengths of 17 to 20 give a sufficiently low volume to perform satisfactorily in an automatic dishwasher. This was confirmed in tests in an automatic dishwasher.

EXAMPLE III

Soil Deposition Tests of LAS-Sodium Sulfate

In order to determine the soil deposition characteristics of the detergent actives and compositions of the invention, in this test a Kitchen Aid dishwasher was employed. Plates are covered with 4 g. of a specially prepared soil, comprising 2 parts of margarine and 1 part of non-fat milk solids. The soil is allowed to dry overnight. The plates are then placed in the dishwasher. Two clean microscope slides are backed with black paper and the reflectance of each is measured with a Gardner reflectometer. The slides are then suspended vertically in the dishwasher. The plates are then washed at about 140°F in a conventional cycle comprising a prewash cycle of about 3.6 minutes, prerinse cycle of about 3.6 minutes, a wash cycle of about 8.4 minutes after rinse cycles of about 3.6, 3.6 and 4.8 minutes and drying cycle of about 22.8 minutes. The plates are then removed (the slides remaining in the dishwasher) and the plates are recoated with soil and allowed to dry overnight. This cycle is repeated for a total of 5 cycles (dirtying and complete washing). The slides are then removed, again backed with black paper and their reflectance measured. The increase in reflectance is a measure of the amount of material deposited upon the slides. Tests were performed using water at hardness levels of 60 ppm and 180 ppm (calculated as $\frac{1}{2}$ calcium carbonate and $\frac{1}{4}$ magnesium carbonate). In the following Table II results are shown which were obtained at a water hardness level of 60 ppm. Table III shows results with 180 ppm water. The LAS materials were of type Ib having alkyl chain lengths of 18–20 carbon atoms (Ic-1) and 19–20 carbon atoms (Ic-2), respectively, each employed at 0.025 percent concentration. Sodium sulfate was employed by itself and in combination with the LAS in the formulations at various ratios indicating its effect upon the deposition results obtained. The reflectance increase is indicated as ΔR in terms of Gardner reflectometer units.

TABLE II

FIVE CYCLE KITCHENAID DISHWASHER DEPOSITION TEST 60 ppm Hardness Water				
Test	LAS Type	Na ₂ SO ₄ Conc. %	Wt. Ratio Na ₂ SO ₄ /LAS	Reflectance Increase, ΔR
1	Water only	0	—	0.35
2	Ib-1	0	—	0.29
3	"	0.22	8.8	0.00; 0.05

TABLE II-Continued

FIVE CYCLE KITCHENAID DISHWASHER DEPOSITION TEST
60 ppm Hardness Water

Test	LAS Type	Na ₂ SO ₄ Conc. %	Wt. Ratio Na ₂ SO ₄ /LAS	Reflectance Increase, ΔR
4	"	0.26	10.4	0.08
5	"	0.5	20	0.00
6	Ib-2	0	—	0.44
7	"	0.12	4.8	0.15
8	"	0.25	10	0.10
9	"	0.5	20	0.05
10	—	0.3	—	0.2
11	—	0.5	—	0.15; 0.08

TABLE III

FIVE CYCLE KITCHENAID DISHWASHER DEPOSITION TEST
180 ppm Hardness Water

Test	LAS Type	Na ₂ SO ₄ Conc. %	Wt. Ratio Na ₂ SO ₄ /LAS	Reflectance Increase, ΔR
12	Water only	—	—	1.0
13	Ib-1	—	—	0.58
14	"	0.225	9	0.44
15	"	0.48	1.9	0.20
16	"	0.60	24	0.10; 0.15
17	"	0.75	30	0.04
18	"	0.80	32	0.00
19	Ib-2	—	—	0.68
20	"	0.25	10	0.28
21	"	0.50	20	0.08
22	"	0.80	32	0.04
23	—	0.25	—	0.40
24	—	0.30	—	0.36
25	—	0.60	—	0.20; 0.4

These data indicate that the combination of the particular types of LAS materials of the invention produces an extremely low and entirely satisfactory deposition rate in automatic dishwasher. The improvement (i.e., the decrease) in deposition is particularly noticeable in hard water. Tests performed in pure water (0 hardness) show that deposition is no problem even in the absence of a detergent.

EXAMPLE IV

Turbidity Measurements of Various Inorganic Sulfate Salts

In order to determine if the antideposition properties of sodium sulfate are possessed by other inorganic sulfate salts, turbidity tests were performed with LAS in a turbid aqueous solution and the degree of clarification of the solution achieved by the addition of Na₂SO₄, Li₂SO₄, (NH₄)₂SO₄, MgSO₄ and K₂SO₄ was determined. The solution contained 0.025 weight percent LAS (Ic-2) in 180 ppm hardness water. Table IV shows the degree of clarification with the various salts. A higher number indicates less turbidity.

TABLE IV

Turbidity Decrease with Sulfate Addition
to 0.25% LAS in 180 ppm Water

Salt	Salt Concentration by Weight									
	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
Na ₂ SO ₄	~20	23	38	35	66	69	71	72	72	72
K ₂ SO ₄	"	25	28	29	29	29	—	—	—	29
Li ₂ SO ₄	"	29	73	75	74	75	75	75	75	75
(NH ₄) ₂ SO ₄	"	28	36	70	71	71	68	68	68	67
MgSO ₄	"	42	40	35	36	34	35	38	38	38

These data show that while the sodium, lithium and ammonium salts effectively decrease the turbidity of the solution, magnesium and potassium salts were totally ineffective for this purpose.

EXAMPLE V

Soil Deposition Tests of LAS in Combination with Lithium and Ammonium Sulfates

Soil deposition tests as described in Example IV, Table III, were performed in 180 ppm hardness water with 0.025 percent Ic-1 LAS and 0.23 percent sodium, lithium, and ammonium sulfates. These results are set forth in the following Table V.

TABLE V

FIVE CYCLE KITCHENAID DISHWASHER DEPOSITION TEST
180 ppm Hardness Water

Test	Salt	Concentration	Ratio Salt/LAS	Reflectance Increase ΔR
27	Sodium Sulfate	0.23	9.25	0.44
28	Lithium Sulfate	"	"	0.38
29	Ammonium Sulfate	"	"	0.58

These data show, as expected from the turbidity data, that the LAS/lithium sulfate combination performs slightly better than sodium sulfate in preventing deposition and the ammonium salt is slightly less effective.

EXAMPLE VI

Soil Removal Tests with LAS/Sodium Sulfate Detergent

In the following test, the plates were soiled with three types of soil: three-minute egg yolk, chili, and spinach. About about 3 g. of each cooked food was rubbed on the plates, they were allowed to dry overnight. The amount of soil removed was determined by visual estimation. Similar results were subsequently obtained in spot checks using gravimetric methods. The data in Table VI show the percent soil removed with the LAS/Na₂SO₄ combinations. Comparison tests were made with a commercial automatic dishwasher composition which comprises about one third each of sodium tripolyphosphate, sodium carbonate, and sodium metasilicate (A). The LAS materials were prepared according to Example Ic (HF alkylation).

TABLE I

KITCHEN AID SOIL REMOVAL, % (PLATES SOILED AND DRIED OVERNIGHT - NO PREWASH)
(TAP WATER, ~60 PPM HARDNESS)

Test No.	Washing Agent	Conc., %	Soil Type								
			3-Min. Egg Yolk			Chili			Spinach		
			1 Min.	2 Min.	10+ Rinse	1 Min.	2 Min.	10+ Rinse	1 Min.	2 Min.	10+ Rinse
1*	None	—	5	10	60				20	50	95
2	A	0.20	40	90	100	10	50	99	10	60	98
2	C ₁₈₋₂₀ LAS/Na ₂ SO ₄ (4.8/95.2)	0.525	20	60	98	10	50	100	10	50	100
3	None	—	0	10	40	10	40	98	10	50	80
4	A	0.20	50	95	100	20	50	99	30	80	98
4	C ₁₈₋₂₀ LAS/Na ₂ SO ₄ (5/95)	0.20	10	50	85	10	60	100	10	60	98
5	None	—	0	0	30	10	30	90	10	30	85
5	C ₁₈₋₂₀ LAS	0.025	0	5	80	10	20	100	10	20	100
5	C ₁₈₋₂₀ LAS/Na ₂ SO ₄ (4.8/95.2)	0.525	5	50	100	10	70	100	10	70	95
5	Na ₂ SO ₄	0.50	0	20	99	10	50	99	10	50	90
6	STP	0.20	5	50	100	5	20	99	10	60	95
6	NTA	0.20	1	80	100	2	30	95	1	50	100
6	C ₁₈₋₂₀ LAS/Na ₂ SO ₄ (5/95)	0.50	5	50	98	2	20	100	20	60	95
6	None	—	0	0	30	5	25	90	2	25	70
7	None	—	0	0	30	2	30	95	5	25	60
7	A	0.20	60	95	100	25	60	99	25	70	95
7	C ₁₈₋₂₀ LAS/Na ₂ SO ₄ (5/95)	0.20	20	70	98	10	50	100	10	40	70
7	C ₁₈₋₂₀ LAS/Na ₂ SO ₄ (5/95)	0.40	20	80	98	10	60	100	10	50	80
7	C ₁₈₋₂₀ LAS/Na ₂ SO ₄ (5/95) + 0.1% NaOH	0.40	40	95	98	20	80	100	10	50	80
8	None	—	0	0	30	5	30	98	5	30	60
8	A	0.20	70	100	100	20	60	100	30	80	98
8	C ₁₈₋₂₀ LAS/Na ₂ SO ₄ (5/95)	0.20	10	60	95	10	40	100	10	40	80
8	C ₁₈₋₂₀ LAS/Na ₂ SO ₄ (5/95) + 0.2% NaOH	0.20	20	80	95	10	40	100	10	40	85
8	C ₁₈₋₂₀ LAS/Na ₂ SO ₄ (20/80)	0.25	50	80	98	20	50	100	20	50	95
9	None	—	0	0	40	0	25	95	2	25	70
9	A	0.20	70	99	100	20	60	100	20	60	98
9	C ₁₈₋₂₀ LAS/Na ₂ SO ₄ (5/95)	0.20	10	70	98	5	30	100	5	30	75
9	C ₁₈₋₂₀ LAS/Na ₂ SO ₄ (5/95) + 0.005% Igepal CO-610	0.20	10	50	95	5	20	100	5	20	80
9	C ₁₈₋₂₀ LAS/Na ₂ SO ₄ (12.5/87.5) + 0.005% Igepal CO-610	0.20	10	70	98	5	25	100	5	25	95

*Soil drying time for this test, four hours.

These data show that the detergent compositions of this invention are excellent performers in automatic dishwashing use.

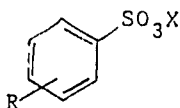
In addition to the detergent active material and the deposit reducing salts, detergent compositions designed for use in automatic dishwashers may contain other ingredients known to be useful in such compositions including but not limited to bleaching agents, pigments, dyes, perfumes, and wetting agents.

While the character of this invention has been described in detail with numerous examples, this has been done by way of illustration only and without limitation of the invention. It will be apparent to those skilled in the art that modifications and variations of the illustrative examples may be made in the practice of the invention within the scope of the following claims.

I claim:

1. A low foaming water-soluble detergent composition suitable for use in automatic dishwashing machines consisting essentially of

a. one part by weight of a linear alkylbenzene sulfonate of the formula



in which X is a water-soluble salt forming cation and R is alkyl of 17 to 22 carbon atoms, provided that in at least 65 mol percent of said sulfonates R is a group of the formula



in which R₁ and R₂ are normally attached linear alkyl groups of 2 to 19 carbon atoms and the sum of the carbon atoms in R₁ and R₂ is from 16 to 21, and

b. from 8 to 25 parts by weight of a salt of the formula Y₂SO₄ in which Y is Na⁺, Li⁺ or NH₄⁺.

2. The composition of claim 1 in which X is an alkali metal cation.

3. The composition of claim 2 in which X is Na⁺.

4. The composition of claim 1 which contains from 15 to 25 parts of (b).

5. The composition of claim 1 in which Y is Na⁺.

6. The composition of claim 1 in which Y is Li⁺.

7. A method of cleaning dishes, utensils, and the like in an automatic dishwasher which comprises contacting the articles to be cleaned with an aqueous solution containing from about 0.1 to 1 percent by weight of the composition of claim 1.

* * * * *