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STERILIZING DETERGENT COMPOSITION
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5 Claims

#### ABSTRACT OF THE DISCLOSURE

A sterilizing detergent composition containing a long chain alkyl dimethyl benzyl ammonium saccharinate and an amphoteric surface active agent having the general formula

$$\begin{array}{c} X \\ (CH_2CHO)_nR'COOM_0 \\ R-N \\ (CH_2CHO)_mR'COOM_0 \\ X \end{array}$$

wherein R is an alkyl or alkenyl radical of  $C_8$  to  $C_{18}$ , R' 25 is an alkylene radical of  $C_1$  to  $C_2$ , X is H or a  $CH_3$  radical, Me is an alkali metal ion and n and m are integers of 0 to 5, the amount of said amphoteric surface active agent being sufficient to solubilize said saccharinate thereby in an aqueous medium.

# BACKGROUND OF THE INVENTION

#### Field of the invention

This invention relates to a new sterilizing detergent composition which may be used together with conventional washing agents consisting of anionic surface active agents and/or nonionic surface active agents without the formation of a precipitate or the reduction of either the sterilizing capability or detergency. The sterilizing detergent composition according to this invention is comprised of an alkyl dimethyl benzyl ammonium saccharinate solubilized with a specific amphoteric surface active agent as defined hereinbelow.

# Description of the prior art

Alkyl dimethyl benzyl ammonium chlorides as invert soaps, have previously been used extensively for disinfecting and sterilizing. However, if they are used together with anionic surface active agents to make a washing agent, precipitation will be caused by the ionic bond between the cationic radicals and the anionic radicals in an aqueous solution and their sterilizing effect and detergency will be remarkably reduced. Therefore, in practice they are not used together with anionic surface active agents

Further, in order to avoid such precipitation by the ionic bond, it is possible to use the alkyl dimethyl benzyl ammonium chlorides together with nonionic surface active agents as the detergent. However, in such case, due to the formation of a strong hydrated film of the nonionic surface active agent, the action of the alkyl dimethyl benzyl ammonium chloride or bacterial cell walls will be obstructed and therefore the sterilizing effect of the invert soap will be remarkably reduced. Further, an aqueous solution prepared by adding a quaternary ammonium salt to a nonionic surface active agent is generally low in detergency.

Further, the sanitizing finish of fibers is important to <sup>7</sup>

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sanitation. However, when fibers are washed with conventional invert soaps, such as alkyl dimethyl benzyl ammonium chlorides, the dye will be discolored or the fluorescent dye will lose a remarkable amount of light reflecting ability.

#### SUMMARY OF THE INVENTION

We have discovered that, when an alkyl dimethyl benzyl ammonium saccharinate is solubilized with a specific amphoteric surface active agent, that is, a compound having the formula

$$\begin{array}{c} X\\ (CH_2CHO)_nR'COOMe\\ R-N\\ (CH_2CHO)_mR'COOMe\\ X \end{array}$$

wherein R is an alkyl or alkenyl radical of C<sub>8</sub> to C<sub>18</sub>, R' is an alkylene radical of C<sub>1</sub> to C<sub>2</sub>, X is H or a CH<sub>3</sub> radical, Me is an alkali metal ion and n and m are integers of 0 to 5, a transparent or milk-white aqueous solution can be obtained and that this mixed solution is an excellent sterilizing detergent composition which does not have the above-mentioned defects of conventional invert soaps as are mentioned above.

The water-solubility of an alkyl dimethyl benzyl ammonium saccharinate is much lower than that of a conventional chloride salt, such as less than 0.1%. Therefore, said saccharinate contained in the composition according to this invention will be not only adsorbed cationically on the surface of the fibers but will also remain in the fibers due to dispersion and adsorption and will retain its sterilizing action for a long time.

An anionic surface active agent will cause a neutralizing reaction and therefore cannot be used as a solubilizer for such saccharinate. A nonionic surface active agent will greatly reduce the sterilizing strength and any amphoteric surface active agent, other than the ones which will be used in this invention, will reduce the sterilizing strength by about 20 to 30%. On the other hand, the amphoteric surface active agent having the above mentioned formula will not reduce but will rather increase the sterilizing strength. Further, the above mentioned sterilizing detergent composition, according to the present invention, can be used together with commercial washing agents, such as are mentioned hereinafter, without the formation of a precipitate or the reduction of sterilizing strength and detergency. The composition of this invention is not limited to an aqueuos solution form. If the above aqueous solution is spray-dried, then a powdered composition according to the present invention will be obtained, which can then be mixed with any conventional powdered washing agent.

The weight ratio of the amphoteric surface active agent, of the above mentioned general formula to the alkyl dimethyl benzyl ammonium saccharinate is selected such that the amount of the amphoteric surface active agent is sufficient to solubilize the alkyl dimethyl benzyl ammonium saccharinate. Generally, 0.5 to 4.0 parts by weight of the amphoteric surface active agent are used per part of the alkyl dimethyl benzyl ammonium saccharinate. Preferably, 1 to 3 parts of the amphoteric surface active agent are used per part of the alkyl dimethyl benzyl ammonium saccharinate.

The alkyl radical of the long chain alkyl dimethyl benzyl ammonium saccharinate used in the present invention is the same alkyl radical of 8 to 18 carbon atoms as is used in the case of a conventional chloride salt.

However, because of the phenol coefficient of the saccharinate, an alkyl dimethyl benzyl ammonium saccharinate having an alkyl radical of 12 to 14 carbon atoms is most desirable. Accordingly, tetradecyl dimethyl benzyl ammonium saccharinate (abbreviated as TDMAS) and dimethyl benzyl laurvl ammonium saccharinate (LDMAS are suitable for the purposes of this invention. Further, the amphoteric surface active agents represented by the above formula which are suitable for the purpose of this invention include, for example, sodium 10 N-lauryl N,N-dipropionate, sodium N-lauryl N,N-bisethenoxyacetate, sodium N-octyl N,N-bis-ethenoxyacetate, sodium N-octadecyl N,N-bis-ethenoxyacetate, sodium Noctadecyl N,N-bisethenoxyacetate, sodium N-octadecyl N,N-bis-penteoxyacetate and sodium N-coconut alkyl 15 as follows: N,N-bis-ethenoxypropionate.

The sterilizing detergent composition of the present invention can be used either alone or together with anionic washing agents, such as sodium alkyl benzene sulfonates, sodium alkyl sulfates, various soaps, sodium polyoxyethylene alkyl ether sulfates and sodium polyoxyethylene alkyl ether sulfacetate, or nonionic washing agents such as polyoxyethylene alkyl ethers or polyoxyethylene alkyl phenyl ethers.

Further, inorganic builders, such as sodium sulfate, so- 25 dium tripolyphosphate, sodium pyrophosphates, sodium metasilicates and sodium orthosilicates can be used in the washing agent composition. Therefore, any conventional washing agent for washing machines can be used together with the composition of the present invention and the sterilizing effect of the composition according to the present invention can be given to the conventional washing agents without reducing their cleaning ability.

## DESCRIPTION OF THE PREFERRED **EMBODIMENTS**

The present invention shall now be explained with reference to the following examples.

# EXAMPLE 1

(1) When an aqueous solution of 10% sodium saccharinate was gradually added to an aqueous solution of 10% tetradecyl dimethyl benzyl ammonium chloride and was stirred, a white precipitate was deposited. The precipitate was filtered. The precipitate was further washed with distilled water three times. An amount of water equal to the weight of the precipitate was added to the precipitate. The precipitate was warmed to 60 to 70° C. and was dissolved. The solution was gradually cooled to reprecipitate crystals. The crystals were crushed and air-dried.

An example of the analysis of the crystals was as follows (percent): C, 68.5; H, 8.9; N, 5.4; S, 6.1; Cl, 0.03.

Purity: 90.0% (as calculated from S)

Water-solubility: not more than 0.1% (at 25° C.)

Alkyl dimethyl benzyl ammonium chlorides having, respectively, lauryl and octyl radicals as the alkyl radical were reacted to produce saccharinate salts and refined in the same manner. When their phenol coefficient against typhoid bacilli were measured, the following results were obtained:

	Con- trol 1	TDMAS2	LDMAS3	CDMAS 4	
100% effective ingredient	430	355 5 (496)	347 (496)		
10% solution	60	(68, 5)	(62, 8)	12 (116, 4)	65

Chloride salt of C<sup>14</sup>, abbreviated as "control" hereinafter.
 Saccharinate salt of C<sup>14</sup>, abbreviated as "TDMAS" hereinafter.
 Saccharinate salt of C<sup>12</sup>, abbreviated as "LDMAS" hereinafter.
 Saccharinate salt of C<sup>16</sup>, abbreviated as "CDMAS" hereinafter.
 The values in the parentheses are as converted to the same mol concentration as that of the control.

The above table shows that saccharinates having alkyl radicals of 12 to 14 carbon atoms have strong sterilizing

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(2) When 1 part of the invert soap saccharinate salts obtained in the above (1) and 1 part of sodium N-lauryl N,N-dipropionate were mixed together with water so as to obtain an aqueous solution containing 30% solids, the former was easily solubilized by the latter and a transparent solution was obtained. In case the weight ratios of the sodium N-lauryl N,N-dipropionate relative to the saccharinate salts were further increased, clear stable aqueous solutions were always obtained.

When an aqueous solution of the TDMAS and the sodium N-lauryl N,N-dipropionate (weight ratio 1:1) was prepared and its antibacterial effect against Bacillus subtilis as Gram-positive bacteria and against Escherichia coli as Gram-negative bacteria was investigated, the results were

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The bacteria of each kind was slant-cultured at 37° C. for 24 hours in an agar medium and this culturing was repeated three times. Then, the cultured bacteria was transferred to a fresh bouillon culture medium and cultured at 37° C. for 24 hours. The bouillon cultured bacterial liquor was inoculated in an amount of a single platinum ear to a bouillon culture medium which had been prepared by adding thereto said mixed aqueous solution of TDMAS and sodium N-lauryl N,N-dipropionate of a weight ratio of 1:1 in such an amount that the TDMAS in the above bouillon culture medium might be of a predetermined concentration as shown in the following tables. These bouillon cultures were kept at 37° C. and the bacteria suppressing force of TDMAS was judged by the naked eye. That is to say, when the bacteria grows, the culture becomes turbid. This is shown as +. When the culture remains clear indicating no bacteria growth, it is shown as -.. The results are shown in the following tables.

# (A) Results with B. subtilis:

	Number of days after the inoculation					
TDMAS concentration in p.p.m.	1	2	3	4	6	
0	+	+	+	+	+	
50	_	_	· -	· <u>-</u>	<u> </u>	
100	_				-	
200	_	· =	_	_	_	
5		<del></del>				

TDMAS ganger	Nu	Number of days after the inoculation					
TDMAS concentration in p.p.m.	2	3	4	6	7		
0	. +	+	+	+	+		
20	- =	=	=		÷		
30		-	_		Ξ		
40		_		_	_		

	Nur	nber of days a he inoculation	ifte 1
	1	3	
DMAS concentr	ation in p.p.m.		
DMAS concentr	ation in p.p.m.	+	
DMAS concentre	ation in p.p.m.	<u>+</u>	

This is to say, it was found that the solution had a bacteria suppressing effect at a TDMAS concentration of 2.5 p.p.m. When TDMAS was used alone without the addition of sodium N-lauryl N,N-dipropionate, it had a bacteria suppressing force at a TDMAS concentration of 10 p.p.m.

	Number of days after the inoculation					lation	_
	1	2	. 4	5	6	7	-
TDMAS concentration	n					1.2	- 5
in p.p.m. 0	+	+	+	· +	+	+	
10	±	+	+	<u> </u>	+	<u> </u>	
30		- =	=	_	- =	= -	
50	=	=			=	=	10

It was found that the solution had a bacteria suppressing effect on E. coli at 20 p.p.m. When TDMAS was used alone without the addition of sodium N-lauryl N,N-dipropionate, it had a bacteria suppressing effect at a 15 TDMAS concentration of 35 p.p.m.

From the above results, it is observed that, when sodium N-lauryl N,N-dipropionate was used together with TDMAS, the bacterial growth suppressing effect tended to increase.

#### EXAMPLE 2

A solution consisting of 2 parts of TDMAS, 6 parts of sodium N-lauryl N,N-dipropionate, 0 to 20 parts of ethanol, 3 parts of sodium laurate, 2 parts of potassium oleate and 67 and 87 parts of water was prepared. It was a transparent liquid. The antibacterial effect of this washing solution against E. coli was sufficient even if it was diluted with by weight of water or at a concentration of 4,000 to 5,000 p.p.m. of TDMAS.

An example of the results of tests of the cleaning ability 30 was as follows:

Mixed contents	Composi- tion 1	Composi- tion 2	
TDMAS	. 0	2	35
Sodium N-lauryl N,N-dipropionate	6	6	
Sodium laurate	3	3	
Potassium oleate	2	2	
Ethanol.	20	20	
Water	69	67	
Detergency (reflectance)*	82.4	82. 5	

\*Representing the reflectance of a white cotton cloth after said white cotton cloth was stained with a carbon tetrachloride solution containing 1% of a dispersion of 0.1 part of carbon black in 10 parts of lanolin fat. The stained cloth was washed with the washing solution. No reduction of the detergency by the addition of TDMAS was observable.

## **EXAMPLE 3**

An example of the present invention in which a sodium alkyl benzene sulfonate (ABS) was used as an anionic washing agent is shown in the following:

	Con	position	
Mixed contents	1	2	3
ABS	5	5	5
Ethanol	0	20	20
Sodium N-lauryl N.N-dipropionate	6	0	6
LDMAS	2	2	2
Aqueous solution state	(1)	(2)	(3)
Bacteria suppressing force against E. coli	_	+	_

- Milk-white transparent.
- White turbid.
  Colorless transparent.

As can be seen by comparing the properties of compo- 60 sitions 1 and 3 according to the present invention with those of composition 2 in which no sodium N-lauryl N,N-dipropionate had been mixed, when sodium Nlauryl N,N-dipropionate was used together with TDMAS, the bacteria suppressing effect was increased. The de- 65 tergencies of the compositions 1 and 3 were the same.

## EXAMPLE 4

When samples each consisting of 3 parts of a 30% aqueous solution of the hereinafter mentioned solubiliz- 70 ers and 46 parts of water with 1 part of TDMAS were prepared, clear aqueous solutions were obtained. The sterilizing effects of such solutions against E. coli at temperature of 30° C., operating time of 5 minutes and pH of 9.0 were as follows:

Village States		Kinds of			solubilizers*		
		1	2	3	4	- 5	6
TDMAS concent	ration:						
0.005			+-		+-	+	+
0.01		+	<u> </u>		-	+	+
0.02			_		_		_
0.04			_	+	-		-
0.06			-	<u> </u>	_	_	_
0.08			-		_	· — ·	_
0.16			-	_		_	_

\*Solubilizers:

1=Sodium N-lauryl N,N-dipropionate.

2=Sodium N-lauryl N,N-bis-ethenoxyacetate.

3=Polyoxyethylene nonylphenyl ether (p=9).

4=Sodium N-octyl N,N-bis-ethenoxyacetate.

5=Sodium N-octadecyl N,N-bis-ethenoxyacetate.

6=Sodium N-octadecyl N,N-bis-pentethenoxyacetate.

#### **EXAMPLE 5**

While a water-alcohol mixture containing 1 part of an N-coconut alkyl N,N-diethanol was being refluxed at 70 to 80° C., 22 parts of methyl acrylate were dropped into 20 the mixture to react with it in the presence of an alkali catalyst. Said N-coconut alkyl N,N-diethanol was obtained by reacting ethylene oxide with a reduced fatty amine having a coconut fatty acid radical. When the product was distilled, a sodium N-coconut alkyl N,N-bisethenoxypropionate was obtained. The sterilizing effects on E. coli and B. subtilis when it was used as a solubilizer for TDMAS were as follows when the mixture consisted of 3 parts of the solubilizer and 1 part of TDMAS.

	E. coli	$B.\ subtilis$
TDMAS concentration:		
0.005	+-	-
0.01	_	_
0.02		_
0.04	_	_
0.06		

# EXAMPLE 6 Ten parts of a mixture of TDMAS and sodium N-lauryl

N,N-bis-ethenoxyacetate were mixed with 90 parts of a composite washing agent consisting of 10 parts of a nonionic washing agent, 30 parts of sodium tripolyphosphate, 40 parts of sodium sulfate, 3 parts of sodium metasilicate, 10 parts of sodium carbonate and 2 parts of water. A cotton gauze was dipped in an aqueous solution of 0.3% of the resulting mixture, was washed with water at  $30^\circ$  C. and then cut into squares (2 cm. x 2 cm. under sterile conditions. The gauze was then tested. That is to say, a basic agar culture medium was made to flow on a germ free Petri dish. A bouillon cultured bacterial liquor which was cultured at 37° C, for 24 hours was mixed with an agar culture in a ratio of 2 ml. of the former with 100 ml. of the latter. Then 4 to 5 ml. of this mixed solution per Petri dish was added at 50° C. onto said basic agar culture medium and solidified in a flat plate form. The above test cloth was pasted thereon in the center of said culture and the prevention of the bacterial growth was judged with the naked eye. In this case the bacteria suppressing effect when the ratio of TDMAS/sodium N-lauryl N,N-bis-ethenoxyacetate was

Composite washing agent, (percent)	TDMAS/ solubilizer (0.03 percent)	Bacteria suppressing force
0.27 0.27 0.27 0.27	1:2	Absent. Absent. Present. Present.

varied was as follows:

At the same time, the amount of TDMAS remaining on the gauze was detected. It is evident from this detection that the amount of TDMAS remaining on the surfaces of the fibers was different depending on the ratio of TDMAS/solubilizer. It was found that the compositions consisting of 1 part of TDMAS and 1 to 3 parts of the solubilizer were excellent for sterilizing and washing 75 fibers.

# EXAMPLE 7

When a cloth dyed with a fluorescent dye or a direct dye, such as, for example, Direct Pink B, was dipped in an aqueous solution of LDMAS, TDMAS or CDMAS used together with sodium N-lauryl N,N-bis-ethenoxyacetate (amphoteric active agent), neither light extinction or discoloration occurred. But, when a conventional invert soap was used, there was a remarkable reduction in reflected light and discoloration occurred. That is to say, the following results were obtained.

Cotton reflectance in percent (1) LDMAS/amphoteric active agent (50:50) \_\_\_ 78.9
(2) C<sub>12</sub>-chloride salt/nonionic active agent (20:80) 71.8 (3) TDMAS/amphoteric active agent (50:50) \_\_\_\_ 85.9 (4) C<sub>14</sub>-chloride salt/nonionic active agent (20:80) 78.4 (5) CDMAS/amphoteric active agent (50:50) \_\_ . 86.1 (6) C<sub>16</sub>-chloride salt/nonionic active agent (20:80) 82.7 (7) Untreated \_\_\_\_\_ 86.3

Nos. 1, 3 and 5 are compositions according to the 20 present invention. Nos. 2, 4 and 6 are compositions containing conventional invert soaps.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A sterilizing detergent composition consisting essen- 25 tially of a long chain alkyl dimethyl benzyl ammonium saccharinate and an amphoteric surface active agent having the general formula

$$\begin{array}{c} X \\ (\text{CH}_2\text{CHO})_n R' \text{COOMe} \\ R-N \\ (\text{CH}_2\text{CHO})_m R' \text{COOMe} \\ X \end{array}$$

wherein R is an alkyl or alkenyl radical of C<sub>8</sub> to C<sub>18</sub>, R' is an alkylene radical of C<sub>1</sub> to C<sub>2</sub>, X is H or a CH<sub>3</sub> radical, Me is an alkali metal ion and n and m are integers of 0 to 5, wherein said amphoteric surface active agent is mixed with said saccharinate in a ratio of 0.5 to 4.0 40 P. E. WILLIS, Assistant Examiner parts by weight of the former to 1 part by weight of the latter and wherein the alkyl of said long chain alkyl dimethyl benzyl ammonium saccharinate is an alkyl radical of  $C_{12}$  to  $C_{16}$ .

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2. The sterilizing detergent composition as defined in claim 1, wherein said ratio is 1 to 3 parts by weight of the former to 1 part by weight of the latter.

3. The sterilizing detergent composition as defined in claim 1, wherein said saccharinate is tetradecyl dimethyl

benzyl ammonium saccharinate.

4. The sterilizing detergent composition as defined in claim 1, wherein said amphoteric surface active agent is selected from the group consisting of sodium N-lauryl N,N-dipropionate, sodium N-lauryl N,N-bis-ethenoxyacetate, sodium N-octyl N,N-bis-ethenoxyacetate, sodium Noctadecyl, N,N-bis-ethenoxyacetate, sodium N-octadecyl N,N-bis-penteoxyacetate and sodium N-coconut alkyl N,N-bis-ethenoxypropionate.

5. An aqueous sterilizing detergent composition, consisting essentially of 1 part by weight of tetradecyl dimethyl benzyl ammonium saccharinate and 0.5 to 4 parts by weight of an amphoteric surface active agent selected from the group consisting of sodium N-lauryl, N,N-dipropionate, sodium N-lauryl N,N-bis-ethenoxyacetate, sodium N-octyl N,N-bis-ethenoxyacetate, sodium N-octadecyl N,N-bis-ethenoxyacetate, sodium N-octadecyl N,Nbis-penteoxyacetate and sodium N-coconut alkyl N,N-bisethenoxyproprionate, said saccharinate being solubilized in the aqueous solution by said amphoteric surface active agent.

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