United States Patent Office 3,523,902
Patented Aug. 11, 1970

3,523,902

CONTROLLED SUDS DETERGENT

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No Drawing. Continuation-in-part of application Ser. No. 446,432, Apr. 7, 1965. This application Aug. 3, 1967, Ser. No. 658,053

Int. Cl. C11d 3/066, 3/07

U.S. Cl. 252—137 10 Claims

ABSTRACT OF THE DISCLOSURE

The high sudsing characteristics of anionic synthetic detergents can be controlled by a synergistic combination of a water-soluble nonionic surface active agent and an alkyl phosphate ester.

This application is a continuation-in-part of patent application Ser. No. 446,432, filed Apr. 7, 1965, now abandoned.

This invention relates in one aspect to detergent compositions. In a more specific aspect, it relates to a controlled suds detergent composition.

Many of the prior art detergent compositions are high sudsing products. When high sudsing detergent products are used in front-loading, horizontal tumbler-type automatic washers, these products foam profusely and cause the tumbler to fill or overflow with dense suds. These dense suds impede the washing action by interfering with the free fall of clothes in the tumbler and may strain the working parts of the machine to cause slowing or stalling, further impeding washing action, and causing excessive wear of machine parts. The appearance of excessive suds may cause the operator to reduce the amount of the detergent used to a point where the amount is insufficient to produce the desired cleaning. It would be advantageous, therefore, to provide a detergent composition in which the foaming or sudsing can be controlled.

Therefore, an object of this invention is to provide detergent compositions in which the sudsing can be controlled.

Another object of this invention is to provide detergent compositions containing water-soluble nonionic surface active agents and anionic synthetic detergents in which the sudsing or foaming can be controlled.

In accordance with this invention, it has been discovered that the foaming or sudsing characteristics of detergents containing a high foaming anionic selected from alkyl aryl sulfonates, linear alkylate sulfonates, alcohol sulfates, alcohol ether sulfates or alpha olefin sulfonates and alkaline builders can be controlled by adding a small quantity of a synergistic mixture to the detergent formulations. The synergistic mixture is a combination of an alkyl phosphate ester and a water-soluble nonionic surface active agent. It has been further discovered that water-soluble nonionic surface active agents in detergent compositions in the absence of the alkyl phosphate ester in the compositions do not give controlled suds detergents. Detergent compositions in which the alkyl phosphate ester has been added and in which the water-soluble nonionic surface active agent has been omitted do not give controlled suds detergents. Thus, the combination of the water-soluble nonionic surface active agent and the alkyl phosphate ester synergistically controls the amount of sudsing or foaming.

The term "alkyl aryl sulfonate" is a class name for a widely used group of anionic synthetic detergents. The aryl portion is usually benzene, but not limited thereto, and the alkyl portion is often dodecyl, tridecyl, or pentadecyl. It is preferred to employ the higher alkyl aryl sulfonates such as the alkylbenzene sulfonates wherein the alkyl group has from about 9 to 18 carbon atoms. These monoalkyl benzene sulfonates are more particularly described in U.S. Pat. 2,477,383 to Lewis. Specific examples are dodecyl benzene sulfonate, pentadecyl benzene sulfonate, and octadecyl benzene sulfonate.

The term "linear alkylate sulfonate" is a class name for straight chain alkylbenzene sulfonates. These relatively new compounds are becoming more popular for use in detergent formulations by virtue of their easier biodegradability as compared to the branched chain alkyl aryl sulfonates. An example of a linear alkylate sulfonate is phenyl n-dodecane sulfonate wherein the phenyl group may be attached to any of the carbon atoms. The carbon chians in the linear alkylate sulfonates may contain from 9 to 18 carbon atoms.

The term "fatty alcohol sulfates" is a class name for a widely used group of anionic synthetic detergents derived from alcohols containing from about 8 to 18 carbon atoms. Specific examples of fatty alcohol sulfates are lauryl alcohol sulfate, coconut alcohol sulfate and tallow alcohol sulfate. The alcohol sulfates are alkali metal salts of monoesters of sulfuric acid with n-aliphatic alcohols and may be represented by the formula

$$CH_3(CH_2)_nOSO_3Me$$

where Me is an alkali metal and n is from about 7 to 17.

Alcohol ether sulfates are sulfated and neutralized ethylene oxide adducts of straight chain alcohols and may be represented by the formula

$$CH_3(CH_2)_nO—(C_2H_4O)_mSO_3Me$$

where Me is an alkali metal, n is from about 7 to 17 and m is from about 1 to 12.

Alpha olefin sulfonates are made by the sulfonation of linear alpha olefins with SO_3 and neutralization with sodium hydroxide. These sulfonates may be represented by the formula

$$RCH{=}CHCH_2SO_3Na$$

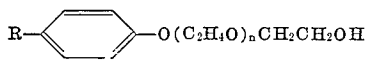
where R is a monovalent alkyl radical containing from about 6 to 15 carbon atoms.

The water-soluble nonionic surface active agents which are advantageously employed in the compositions of the invention are generally the polyoxyalkylene adducts of hydrophobic bases wherein the oxygen/carbon atom ratio in the oxyalkylene portion of the molecule is at least about 0.5. Those compositions which are condensed with hydrophobic bases to provide a polyoxyalkylene portion having an oxygen/carbon atom ratio of at least 0.5 include ethylene oxide, butadiene dioxide, glycidol, and the like. Ethylene oxide, for example, is condensed with the hydrophobic base in an amount sufficient to impart water solubility and surface active properties to the molecule being prepared. The exact amount of ethylene oxide condensed with the hydroprobic base will depend upon

the chemical characteristics of the base employed and is readily apparent to those of ordinary skill in the art relating to the synthesis of oxyalkylene surfactant condensates.

Typical hydrophobic bases which can be condensed with ethylene oxide in order to prepare nonionic surface active agents include mono- and polyalkyl phenols, polyoxypropylene condensed with a base having from about 1 to 6 carbon atoms and at least one reactive hydrogen atom, fatty acids, fatty amines, fatty amides, alkyl mercaptans, and fatty alcohols. The hydrocarbon ethers such as the benzyl or lower alkyl ether of the polyoxyethylene surfactant condensates are also advantageously employed in the compositions of the invention.

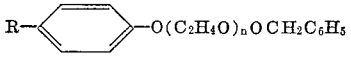
Among the suitable nonionic surfactants are the polyoxyethylene condensates of alkyl phenols having from about 6 to 20 carbon atoms in the alkyl portion and from about 5 to 30 ethenoxy groups in the polyoxyethylene radical. The alkyl substituent on the aromatic nucleus may be octyl, diamyl, polymerized propylene (such as propylene tetramer and trimer), isooctyl, nonyl, etc. The polyoxyethylene condensates of monoalkyl phenols impart good properties to the compositions of the invention, and a typical product corresponds to the formula



(1)

where R is an alkyl group and n is from about 5 to 30.

The benzyl ethers of the polyoxyethylene condensates of the alkyl phenols of Formula 1 may be used. Typical benzyl ethers correspond to the formula:



(1A)

Other suitable water-soluble nonionic surfactants are cogeneric mixtures of conjugated polyoxyalkylene compounds containing in their structure at least one hydrophobic oxyalkylene chain in which the oxygen/carbon atom ratio does not exceed about 0.33 and at least one hydrophilic oxyalkylene chain in which the oxygen/carbon atom ratio is not less than about 0.5. Propylene oxide, butylene oxide, amylene oxide, and styrene oxide are illustrative of oxyalkylene compounds having an oxygen/carbon atom ratio not exceeding about 0.33; while ethylene oxide, butadiene dioxide, and glycidol (as previously pointed out) are illustrative of oxyalkylene compounds having an oxygen/carbon atom ratio of at least about 0.5. Although the hydrophobic chain has an oxygen/carbon atom ratio not exceeding about 0.33, it is often advantageous to include in this chain a small amount of ethylene oxide (i.e., up to about 15 weight percent), and likewise, in the hydrophilic chain which has an oxygen/carbon atom ratio not less than about 0.5, it is often advantageous to include a small amount of propylene oxide or butylene oxide (i.e., up to about 15 weight percent), and the oxygen/carbon atom ratios described herein and in the claims are not intended to preclude such mixtures.

Among the conjugated polyoxyalkylene compounds which can be used in the compositions of the invention are those which correspond to the formula:

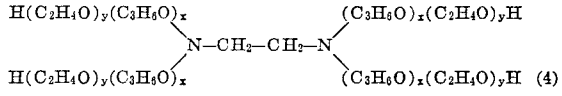
$$Y(C_3H_6O)_n(C_2H_4O)_mH \qquad (2)$$

wherein Y is the residue of an organic compound having from about 1 to 6 carbon atoms and one reactive hydrogen atom, n has an average value of at least about 6.4 as determined by hydroxyl number, and m has a value such that the oxyethylene portion constitutes about 10 to 90 weight percent of the molecule. Most of these surface active agents are more particularly described in U.S. Pat. No. 2,677,700.

Other conjugated polyoxyalkylene surface active agents which are most advantageously used in the compositions of the invention correspond to the formula:

$$Y[(C_3H_6O)_n(C_2H_4O)_mH]_x \qquad (3)$$

wherein Y is the residue of an organic compound having from about 2 to 6 carbon atoms and containing x reactive hydrogen atoms in which x has a value of at least about 2, n has a value such that the molecular weight of the polyoxypropylene hydrophobic base is at least about 900, and m has a value such that the oxyethylene content of the molecule is from about 10 to 90 weight percent. Compounds falling within the scope of the definition for Y include, for example, propylene glycol, glycerine, pentaerythritol, trimethylolpropane, ethylenediamine, triethylenetetramine, triisopropanolamine, butylamine, and the like. Where Y is ethylenediamine, the compounds may be represented by the formula:



(4)

wherein x and y are integers. As already noted, the oxypropylene chains optionally but advantageously contain small amounts of ethylene oxide, and the oxyethylene chains also optionally but advantageously contain small amounts of alkylene oxides having an oxygen/carbon atom ratio of not more than about 0.33, such as propylene oxide and butylene oxide. Most of these compounds are more particularly described in U.S. Pat. Nos. 2,674,619 and 2,979,528.

Other suitable polyoxyalkylene nonionic surface active agents are the alkylene oxide adducts of higher aliphatic alcohols and thioalcohols having from about 8 to 22 carbon atoms in the aliphatic portion and about 3 to 50 oxyalkylene units in the oxyalkylene portion. Typical products are synthetic fatty alcohols, such as n-decyl, n-undecyl, n-tridecyl, n-tetradecyl, n-hexadecyl, n-octadecyl, and mixtures thereof condensed with 3 to 50 moles of ethylene oxide, a mixture of normal fatty alcohols condensed with 8 to 20 moles of ethylene oxide and capped with benzyl halide or an alkyl halide, a mixture of normal fatty alcohols condensed with 10 to 30 moles of a mixture of ethylene and propylene oxides, a mixture of several fatty alcohols condensed sequentially with 2 to 20 moles of ethylene oxide and 3 to 10 moles of propylene oxide, in either order; or a mixture of normal fatty alcohols condensed with a mixture of propylene and ethylene oxides, in which the oxygen/carbon atom ratio is less than 0.40, followed by a mixture of propylene and ethylene oxides in which the oxygen/carbon atom ratio is greater than 0.40, or a linear secondary alcohol condensed with 3 to 30 moles of ethylene oxide, or a linear secondary alcohol condensed with a mixture of propylene and ethylene oxides, or a linear secondary alcohol condensed with a mixture of ethylene, propylene, and higher alkylene oxides.

Other suitable surface active agents are the polyoxyalkylene surface active agents having heteric polyoxyethylene solubilizing chains. The polyoxyalkylene compounds conform to the following generic formula:

$$Y(—P—E—H)_x \qquad (5)$$

wherein Y is the nucleus of an organic reactive hydrogen compound containing x reactive hydrogen atoms and hav-

ing up to 6, inclusive, carbon atoms; x is an integer; P is a hydrophobic polyoxyalkylene chain having an oxygen/carbon atom ratio of not more than 0.40, the molecular weight of P and the value of x being such that the molecule, excluding E, has a molecular weight of at least about 400 to 900 and up to about 25,000; and E is a hydrophilic heteric polyoxyalkylene chain which (1) contains oxyethylene groups and at least 5% by weight of higher molecular weight oxyalkylene groups having at least 3 carbon atoms in their structure and (2) has an average oxygen/carbon atom ratio of greater than 0.40, E being present in the composition to the extent that it constitutes from 5 to 90 weight percent of the total composition. These compositions are more particularly described in U.S. Pat. No. 3,101,374.

The most common detergent builders are soda ash (sodium carbonate); phosphates, such as sodium tripolyphosphate, tetrasodium pyrophosphate; sodium silicates, such as waterglass, sodium metasilicate, sodium orthosilicate, and sodium sequisilicate; and sodium carboxymethylcellulose. Nitrilo triacetic acid or the sodium salt thereof may also be used as the detergent builder. The builders serve a number of useful purposes. They improve the detergency of the synthetic detergents. They counteract the acidity often present in soils since they are generally alkaline. They react with grease and fatty oils that may be present to form soaps, thus rendering them soluble in water. The phosphates and nitrilo triacetic acid act as water softeners by tying up the calcium and magnesium ions.

It is to be understood that minor but effective amounts of other compatible adjuvants, such as optical brighteners, dyes, perfumes, and anti-tarnishing agents, may also be included in the controlled suds detergent compositions without departing from the scope of the invention.

The phosphates that form one component of the synergistic mixture of this invention are variously called alkyl phosphates, alkyl acid phosphates, alkyl phosphate esters of alkyl acid phosphate esters. These phosphates may be prepared by the reaction of a fatty alcohol and phosphoric acid.

The alkyl acid phosphates or alkyl acid phosphate esters which are used in the compositions of the invention are predominantly the monoalkyl phosphates which can contain, in addition thereto, minor amounts of di- and trialkyl phosphates. The alkyl, ethylenic, and acetylenic radicals have from about 12 to 18 carbon atoms, with at least 12 of the carbon atoms lying in a straight chain. In the di- and trialkyl phosphates, the radical groups can have the same or a different number of carbon atoms. Although the higher monoalkyl phosphate is preferred, it can contain up to about 50 weight percent of the dialkyl phosphate and up to about 5 weight percent of the trialkyl phosphate. Examples of saturated alkyl phosphate esters which can be used in the compositions of the invention include lauryl acid phosphate, n-tridecyl acid phosphate, myristyl acid phosphate, pentadecyl acid phosphate, cetyl acid phosphate, margaryl acid phosphate, and stearyl acid phosphate.

Ethylenic phosphate esters that may be used in the formulations include n-dodecenyl acid phosphates, n-tridecenyl acid phosphates, tetradecenyl acid phosphates, pentadecenyl acid phosphates, hexadecenyl acid phosphates, heptadecenyl acid phosphates, octadecenyl acid phosphates, and particularly oleyl acid phosphate. Acetylenic phosphate esters that can be used in the compositions of this invention include the heptadecynyl acid phosphates and the octadecynyl acid phosphates. Monostearyl acid phosphate is preferred for the compositions of this invention and may contain up to 50% by weight of the di- and tristearyl acid phosphate.

The alkyl phosphate esters available on the market are generally mixtures of mono- and dialkyl acid phosphate esters which may also contain some trialkyl phosphate. For purposes of this invention, the preferred alkyl acid phosphate ester compositions can contain, in addition to the monoalkyl acid phosphate, up to about 50 weight percent of the dialkyl acid phosphate and up to about 5 weight percent of the trialkyl phosphate. In the preferred embodiments of this invention, at least 50 weight percent of the alkyl acid phosphate is the monoalkyl acid phosphate. The preferred phosphates include lauryl acid phosphate, cetyl acid phosphate, oleyl acid phosphate, and stearyl acid phosphate. The salts and particularly the alkali metal salts of the alkyl acid phosphate esters may also be employed, as is apparent to anyone skilled in the art. Accordingly, the expressions "alkyl acid phosphate esters" and "alkyl acid phosphate" as used herein include the salts of the alkyl acid phosphate esters or alkyl acid phosphates.

The basic detergent formulation used in the composition of this invention will contain, based on the total composition, from about 2 to 20 weight percent of an alkyl aryl sulfonate or a linear alkylate sulfonate and from about 60 to 90 weight percent of the standard alkaline builders. To control the sudsing characteristics of the basic detergent formulation, a synergistic combination of a water-soluble nonionic surface active agent and an alkyl phosphate ester is added thereto. Based on the total composition, from about 2 to 20 weight percent of a water-soluble nonionic and from about 0.2 to 5.0 weight percent of an alkyl phosphate ester is added to the basic detergent formulation.

The standard detergent builders are present for exemplary purposes in the formulations of this invention in about the following amounts: sodium silicate, 8 to 12 weight percent; soda ash, 20 to 30 weight percent; sodium tripolyphosphate, 35 to 45 weight percent; and sodium carboxymethylcellulose, about 0.5 to 2.0 weight percent. Nitrilo triacetic acid or the sodium salt thereof may be substituted in whole or in part, on an equal weight basis, for the sodium tripolyphosphate. The compositions of this invention may be prepared by blending the dry ingredients together and adding the liquid ingredient, if any, last. Alternatively, all the ingredients may be dissolved in water and the homogeneous solution may be dried in a spray tower, in a revolving drum, or by any other suitable means. It is to be understood that the detergent builders named above may be substituted for, in whole or in part, by other builders without departing from the scope of the invention claimed herein.

A more comprehensive understanding of the invention can be obtained by referring to the following illustrative examples, which are not intended, however, to be unduly limitative of the invention.

EXAMPLES 1–56

The compositions shown in the table hereinafter were prepared and tested as described below. The compositions of Examples 5, 8, 9, 11, 16, 21, 24, 32 to 35, and 40 to 53 are in accordance with the present invention, while the compositions of the other examples have been included as controls. The figures in the table are given as weight percent of the total formulation.

The Bendix washing machine was charged with 2,100 grams of rags. Forty-five grams of each composition was added through the top of the washers as the wash water flowed into the machine. The wash water entered the machine at 135° to 145° F. The heights of the foam or suds of the detergent compositions were measured in a horizontally agitated Bendix washing machine in the following manner: The transparent door of the washing machine was graduated in inches, starting with zero at the bottom and going up to eight inches at the top. The machine was stopped periodically during the wash cycle (for example, after 5, 10, and 15 minutes) to record the foam height. The maximum foam height is reported in the table. Greater than eight inches means the foam came out at the top of the drum.

TABLE

Example No	1	2	3	4	5	6	7	8	9	10	11	12	13[1]	14[1]
Formulation code	B1	B4	F2	H1	H3	H4	H5	K1	M1	Q1	M2	Q2	BA2	BA1
Max. foam height, in	>8	>8	>8	>8	3	>8	>8	3	4	>8	1	>8	5	5
Phosphates:														
High mono (80%) stearyl acid					2		2	1	1		1			
High mono (90%) stearyl acid													4	2
Surface active agents:														
Anionic 1	16	16	16	16	16	16	16	16	16	16	16	16		
Anionic 2														16
Anionic 3													11	
Soap	2	2	2	2										
Nonionic 1	[2]4	[3]4	[4]4	[5]4	[4]4	[4]4		[4]4						
Nonionic 2									4	4				
Nonionic 3											4	4		
Nonionic 8													10	
Nonionic 5														4

Example No	15[1]	16	17	18	19	20	21	22	23	24	25	26	27	28
Formulation code	BA3	M6	Q3	O1	O2	Y5	Y6	U	A15	A16	AL1	AL2	AL3	AL4
Max. foam height, in	4	2	>8	>8	>8	>8	6	>8	>8	1	>8	>8	>8	>8
Phosphates:														
High mono (80%) stearyl acid		1		1			1			0.5				
High mono (90%) stearyl acid	4													
Tributyl acid											5	2	5	2
Surface active agents:														
Anionic 1		16	16	16	16	4	4	16					18	15
Anionic 2									4	4	18	15		
Anionic 4	10													
Nonionic 1								[4]4	[4]2	[4]2				
Nonionic 6						16	16				2	5	2	5
Nonionic 7		4	4											
Nonionic 9	10													

Example No	29	30	31	32	33	34	35	36	37	38	39	40	41
Formulation code	AL5	AL6	AL7	AO1	AO2	AO5	AO6	AR1	AR3	AR5	AR7	AT1	AT5
Max. foam height, in	>8	>8	>8	2	4½	1½	1	>8	>8	>8	>8	4	2
Phosphates:													
Nonfoam 3	5	2	5										
Lauryl acid				5	2	5	2						
Monotridecyl acid								5	5				
Mono n-decyl acid										5	5		
High monolauryl acid												2	2
Surface active agents:													
Anionic 1			18						18		18		
Anionic 2	18	15		18	15	18	15	18		18		15	15
Nonionic 1				[2]2	[2]5					[2]2	[2]2		
Nonionic 3												5	
Nonionic 6								2	2				
Nonionic 7	2	5	2			2	5						5

Example No	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56[1]
Formulation code	AT7	AT8	AV3	AV5	AV6	AV7	AV8	AX1	AX2	AX3	AX4	AX5	AZ1	AZ2	BA4
Max. foam height, in	2	7	2	1	3	½	2	<½	1	1	2	3	8	8	4½
Phosphates:															
Mono (50%) stearyl acid			5	5	2	5	2						2		
High mono (90%) stearyl acid															3
High monolauryl acid	2	0.5													
Cetyl acid								2	0.5	2	0.5	2			
Surface active agents:															
Anionic 1	15	10		17	15							15			
Anionic 2		18				18	15	15	10	15	10		15	15	
Anionic 5															25
Nonionic 2				2	5	2	5			5	10				
Nonionic 4			2												
Nonionic 7	5	10						5	10			5		5	
Nonionic 9															10

[1] Detergent builders in these examples consisted essentially of: 20 to 21 weight percent sodium tripolyphosphate, 10 to 25 weight percent soda ash, 10 weight percent sodium metasilicate, 1 weight percent sodium carboxymethylcellulose 20 to 21 weight percent nitrilo triacetic acid.

[2] Approximately 39 weight percent ethylene oxide, ethylene oxide to propylene oxide ratio about 0.65.

[3] Approximately 29 weight percent ethylene oxide, ethylene oxide to propylene oxide ratio about 0.41.

[4] Approximately 80 weight percent ethylene oxide, ethylene oxide to propylene oxide ratio about 4.00.

[5] Approximately 73 weight percent ethylene oxide, ethylene oxide to propylene oxide ratio about 3.80.

NOTE.—Balance of the above formulations comprise from about 8 to 12 weight percent sodium silicate, 20 to 30 weight percent soda ash, 35 to 45 weight percent sodium tripolyphosphate, 0.5 to 2.0 weight percent sodium carboxymethylcellulose.

A brief description of the anionic and nonionic surface active agents and other materials used in the compositions of the examples of the table follows.

Anionic 1 defines alkyl benzene sodium sulfonates in which the alkyl group is derived from a propylene tetramer. Anionic 1 is a 90% active anionic, high molecular weight, high foaming detergent available in flake form.

Anionic 2 defines a biodegradable linear alkylate sulfonate having from about 9 to 18 carbon atoms in the alkyl chain.

Anionic 3 is the sodium salt of lauryl sulfate and a 90% active powder.

Anionic 4 is the sodium salt of coconut alcohol ether sulfate containing 3 moles of ethylene oxide per mole of alcohol and is a 60% active liquid.

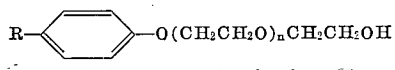
Anionic 5 is an alpha olefin sulfonate and is a 40% active bead.

Nonionic 1 defines 100% active, nonionic surface active agents which are condensates of hydrophilic ethylene oxide with hydrophobic bases formed by condensing propylene oxide with propylene glycol or diethylene glycol. These nonionic surface active agents are represented by Formulae 2 and 3 as described above in cols. 3 and 4.

Nonionic 2 defines a trimethylolpropane derived heteric surfactant with oxyethylene and oxypropylene chains. As disclosed by U.S. Pat. No. 3,101,374, the hydrophobic portion of the molecule has essentially all oxypropylene chains, while the hydrophilic portion of the molecule has at least 80% oxyethylene, with the remainder being butylene oxide or propylene oxide. The oxyethylene chains range from 40 to 80 weight percent of total compound. Formula 5 in col. 4 above represents this compound.

Nonionic 3 defines a water-soluble surfactant, 100% active nonionic liquid widely used for detergency, wetting,

and emulsification. Nonionic 3 may be represented by the general formula:



where R is an alkyl group and n is about 5 to 30.

Nonionic 4 defines a liquid straight-chain alkylphenoxypoly(ethenoxy)ethanol that is 100% active. It is a biologically soft detergent for use in industrial and household heavy-duty detergent formulations, light-duty liquid detergents, and liquid hand-dishwashing detergents.

Nonionic 5 defines a polyoxyethylene ester of tall oil, is a liquid 100% active nonionic. This low foaming nonionic is used primarily in built products for automatic washers and in applications where low foam is desired.

Nonionic 6 defines an oxyethylated straight chain alcohol, is a 100% active nonionic paste containing 60% ethylene oxide and 40% alcoholic residue of C_{12} to C_{18} straight chain alcohols. It is useful in heavy-duty liquid and solid commercial-type detergents. Nonionic 6 exhibits good detergency and moderate foaming characteristics.

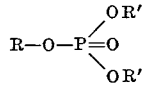
Nonionic 7 defines a series of compounds, represented by Formula 4 in col. 4 above, formed by the addition of propylene oxide to ethylene-diamine, followed by the addition of ethylene oxide. Nonionic 7 is a 100% active nonionic flake form surface active agent having a molecular weight of about 12,250 and an ethylene oxide content of about 75%.

Nonionic 8 is an alkylene oxide adduct of a mixture of long chain fatty alcohols containing 12 to 18 carbon atoms and containing a 3/1 mixture of ethylene oxide and propylene oxide, the adduct containing about 60% by weight ethylene oxide.

Nonionic 9 is a mixed alkylene oxide adduct of a mixture of long chain fatty alcohols containing about 48% ethylene oxide, 32% propylene oxide, and 20% alcoholic residue by weight, where the alcohol is a mixture of C_{12} to C_{18} alcohols.

The soap is a sodium salt of fatty acids and is a common item of commerce. The fatty acids are derived from coconut oil and tallow, thereby giving a mixture of sodium salts having carbon chains from 10 to 18, with carbon chains of 12, 16, and 18 predominating.

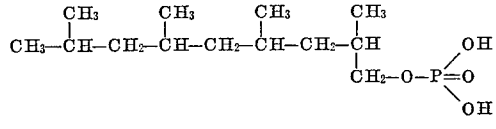
Nonfoam 3 defines an amber-colored liquid, non-foaming, nonionic wetting agent derived from phosphoric acid having the general formula:



where R is a medium chain alkyl group containing from 8 to 10 carbon atoms and R′ is a polyoxyethylene water-solubilizing group. The P_2O_5 content is about 16%.

Lauryl acid phosphate is about 50% monolauryl acid phosphate and about 50% dilauryl acid phosphate.

Monotridecyl acid phosphate, a derivative of tetrapropylene, is a branched chain compound having approximately the following structure:



High monolauryl acid phosphate contains about 70% to 75% of the monoalkyl phosphate and about 20% to 25% of the dialkyl acid phosphate.

Cetyl acid phosphate contains about 50 to 60% of the monoalkyl acid phosphate, from about 50 to 40% of the dialkyl acid phosphate, the balance of not more than 5% is trialkyl phosphate.

DISCUSSION OF EXAMPLES

By examining various examples in the foregoing table, interesting observations may be made. For instance, the compositions of Examples 6 and 7 show maximum foam heights of greater than eight inches where the acid phosphate or nonionic 1 was used alone in the formulation. But the formulation of Example 5, having both nonionic 1 and the stearyl acid phosphate therein, resulted in a controlled maximum foam height of three inches. Examples 24, 43, and 50 show that detergent formulations containing as little as 0.5% of the alkyl acid phosphate and a nonionic will synergistically control the maximum foam height. Examples 25 to 28 and 36 to 39 teach that only selected alkyl acid phosphates exhibit the synergistic effect with the nonionic surface active agent. Examples 36 and 37 in particular show that a 13 carbon atom branched chain acid phosphate does not work. Examples 32 to 35 demonstrate that lauryl acid phosphate, a twelve carbon straight chain acid phosphate, has a synergistic effect in controlling foam heights when compounded with nonionic surface active agents. Thus, it is clearly shown it is critical that at least 12 of the carbon atoms of the alkyl acid radical lie in a straight chain. Examples 38 and 39 show that a 10 carbon atom straight chain n-alkyl acid phosphate is inoperative in the compositions of this invention. Examples 54 and 55 illustrate that the absence of either the nonionic or the alkyl acid phosphate results in uncontrolled sudsing.

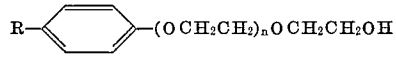
What is claimed is:

1. A controlled suds detergent composition consisting essentially of:

(A) from about 2 to 20 weight percent of an anionic synthetic detergent selected from the group of alkyl benzene sulfonates containing from about 9 to 18 carbon atoms in the alkyl group, alcohol sulfates containing from about 8 to 18 carbon atoms, alcohol ether sulfates containing from about 1 to 12 oxyethylene groups and from about 8 to 18 carbon atoms in the alkyl group, and alpha olefin sulfonates containing from about 9 to 18 carbon atoms;

(B) from about 2 to 20 weight percent of a water-soluble nonionic surface active agent selected from the group consisting of

(1)



wherein R is an alkyl group having from about 6 to 20 carbon atoms and n is an integer from about 5 to 30;

(2) a polyoxyalkylene compound corresponding to the formula

$$Y(C_3H_5O)_n(C_2H_4O)_mH$$

wherein Y is the residue of an organic compound having from about 1 to 6 carbon atoms and one reactive hydrogen atom, n has an average value of at least about 6.4, and m has a value such that the oxyethylene portion constitutes about 10 to 90 weight percent of the pound;

(3) a polyoxyalkylene surface active agent having heteric polyoxyethylene solubilizing chains and having the generic formula

$$Y(—P—E—H)_x$$

wherein Y is the nucleus of an organic reactive hydrogen compound containing x reactive hydrogen atoms and having up to 6, inclusive, carbon atoms, x is an integer, P is a hydrophobic polyoxyalkylene chain having an oxygen/carbon atom ratio of not more than 0.40,

the molecular weight of P and the value of x being such that the molecule, excluding E, has a molecular weight of at least about 400 to 900 and up to about 25,000, and E is a hydrophilic heteric polyoxyalkylene chain which (a) contains oxyethylene groups and at least 5% by weight of higher molecular weight oxyalkylene groups having at least 3 carbon atoms in their structure and (b) has an average oxygen/carbon atom ratio of greater than 0.40, E being present in the composition to the extent that it constitutes from 5 to 90 weight percent of the total composition; and

(4) a surface active agent represented by the general formula

$$Y[(C_3H_6O)_n(C_2H_4O)_mH]_x$$

wherein Y is the residue of an organic compound having from about 2 to 6 carbon atoms and containing x reactive hydrogen atoms in which x has a value of at least 2, n has a value such that the molecular weight of the polyoxypropylene hydrophobic base is at least 900, and m has a value such that the oxyethylene content of the molecule is from about 10 to 90 weight percent;

(C) from about 0.2 to 5.0 weight percent of an alkyl phosphate ester having from about 12 to 18 carbon atoms in the alkyl radical with at least 12 of the carbon atoms lying in a straight chain; and

(D) the balance of the composition consisting essentially of detergent builders.

2. The controlled suds detergent composition of claim **1** wherein the detergent builders consist essentially of:

(A) from about 8 to 12 weight percent sodium silicate;

(B) from about 20 to 30 weight percent soda ash;

(C) from about 35 to 45 weight percent of a detergent builder selected from

(1) sodium tripolyphosphate;

(2) a mixture of sodium tripolyphosphate and nitrilo triacetic acid; and

(3) nitrilo triacetic acid or the sodium salt thereof; and

(D) from about 0.5 to 2.0 weight percent sodium carboxymethyl cellulose.

3. The composition of claim **1** wherein the alkyl phosphate ester is selected from the group consisting of:

(A) monostearyl acid phosphate;

(B) a mixture of mono-, di-, and tristearyl phosphates containing at least 50% by weight monostearyl acid phosphate and not more than 5% by weight tristearyl phosphate;

(C) oleyl acid phosphate;

(D) a mixture of mono-, di-, and trioleyl phosphates containing at least 50% by weight monooleyl acid phosphate and not more than 5% by weight trioleyl phosphate;

(E) cetyl acid phosphate;

(F) a mixture of mono-, di-, and tricetyl phosphates containing at least 50% by weight monocetyl acid phosphate and not more than 5% by weight tricetyl phosphate;

(G) lauryl acid phosphate; and

(H) a mixture of mono-, di-, and trilauryl phosphates containing at least 50% by weight of monolauryl acid phosphate and not more than 5% by weight trilauryl phosphate.

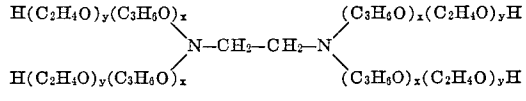
4. The composition of claim **1** wherein the alkyl phosphate ester is at least 80% monostearyl acid phosphate and the balance is distearyl acid phosphate and tristearyl phosphate.

5. The composition of claim **1** wherein the alkyl phosphate ester is at least 50% monostearyl acid phosphate and the balance is distearyl acid phosphate and tristearyl phosphate.

6. The composition of claim **1** wherein the alkyl phosphate ester is lauryl acid phosphate.

7. The composition of claim **1** wherein the alkyl phosphate ester is at least 70% to 75% monolauryl acid phosphate, at least 20% to 25% dilauryl acid phosphate, and the balance is trilauryl phosphate.

8. The composition of claim **1** wherein the surface active agent of subsection (4) has the formula:



prepared by the sequential addition of propylene and ethylene oxides to ethylene diamine, wherein x and y are integers such that the oxyethylene content of the molecule is from about 10 to 90 weight percent.

9. A controlled suds detergent composition consisting essentially of:

(A) from about 5 to 25 weight percent of an anionic synthetic detergent selected from the group of monoalkyl benzene sulfonates, containing from about 9 to 18 carbon atoms in the alkyl group, alcohol sulfates containing from about 8 to 18 carbon atoms, alcohol ether sulfates containing from about 1 to 12 oxyethylene groups and from about 8 to 18 carbon atoms in the alkyl group, and alpha olefin sulfonates containing from about 9 to 18 carbon atoms;

(B) from about 2 to 20 weight percent of an alkylene oxide adduct of higher aliphatic alcohols having from about 8 to 22 carbon atoms in the aliphatic portion and about 3 to 50 alkylene oxides in the oxyalkylene portion units;

(C) from about 0.2 to 5.0 weight percent of an alkyl phosphate ester having from 12 to 18 carbon atoms with at least 12 of the carbon atoms lying in a straight chain; and

(D) the balance of the formula comprising alkaline builders selected from the group consisting of sodium carbonate, sodium tripolyphosphate, sodium metasilicate, sodium carboxymethylcellulose, nitrilo triacetic acid, and mixtures thereof.

10. The composition of claim **9** wherein:

(A) The alkyl phosphate is selected from the group consisting of

(1) monostearyl acid phosphate;

(2) a mixture of mono-, di-, and tristearyl phosphates containing at least 50% by weight monostearyl acid phosphate and not more than 5% by weight tristearyl phosphate;

(3) cetyl acid phosphate;

(4) a mixture of mono-, di-, and tricetyl phosphates containing at least 50% by weight monocetyl acid phosphate and not more than 5% by weight tricetyl phosphate;

(5) lauryl acid phosphate; and

(6) a mixture of mono-, di-, and trilauryl acid phosphates containing at least 50% by weight of monolauryl acid phosphate and not more than 5% by weight trilauryl phosphate; and

(B) the alkylene oxide adduct of higher aliphatic alcohol is selected from the group consisting of

(1) an alkylene oxide adduct of a mixture of long chain fatty alcohols and propylene oxide and ethylene oxide containing 48% ethylene oxide, 32% propylene oxide, and 20% alcoholic residue by weight where the alcohol is a mixture of C_{12} to C_{18} alcohols;

(2) an alkylene oxide adduct of a mixture of long chain fatty alcohols containing 12 to 18 carbon atoms and a 3/1 mixture of ethylene oxide and propylene oxide, said adduct containing 60% by weight ethylene oxide; and

(3) an oxyethylated straight chain alcohol having a mixture of C_{12} to C_{18} chains and containing about 60% ethylene oxide by weight.

References Cited

UNITED STATES PATENTS

2,855,367 10/1958 Buck ---------- 252—138

3,314,891 4/1968 Schmolka et al. ------ 252—89
3,347,463 8/1967 Schmolka ---------- 252—89

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U.S. Cl. X.R.

252—138, 161