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PHOSPHATE ESTER ADDITIVES FOR LOW FOAM NONIONICS

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2 Claims

ABSTRACT OF THE DISCLOSURE

Organic phosphate ester additives, when blended with low foam nonionic compounds, suppress foam generated by proteinaceous soil on particules being cleaned. The esters are produced by phosphorylation of C₁₆ to C₂₀ alcohols, the 1-mole ethylene oxide adduct of 16 to 20 carbon alcohols, their blends, an alcohol-1-mole ethoxylate mixture, or a blend of ethylene oxide adducts of a C₁₆ to C₂₀ alcohol wherein the 1-mole adduct is optimized.

BACKGROUND OF THE INVENTION**Field of the invention**

This invention relates to detergent compositions. In one aspect this invention relates to low foaming detergent compositions especially suitable for use in automatic dishwashing machines. In another aspect, this invention relates to organic phosphate ester additives which, when blended with a low foam nonionic compound, produce a low foam detergent composition which effectively suppresses foam generated by proteinaceous soil on articles being cleaned in automatic dishwashing machines.

Brief description of the prior art

The washing of dishes heavily loaded with proteinaceous soil in automatic dishwashing machines has been a problem facing consumers and the surfactant industry for many years. The popularity of the automatic dishwashing machine, coupled with the trend toward the use of lower water temperatures in such machines, has created problems as to excessive foaming of the detergent composition in such automatic dishwashing machines. This undesirable feature of many of the present commercial automatic dishwashing machine detergents is especially noticeable in the presence of raw egg soil. Development of excessive foam in the dishwashing machine can result in overflow of the machine. Even moderate foaming in the dishwashing machine reduces the efficiency of the automatic dishwashing machine by retarding the mechanical action of the water spray and by reducing the rate of rotation of the spray arms. Therefore, new low foaming detergent compositions and foam suppressant additives are constantly being sought for incorporation into detergent compositions and thus provide a detergent composition suitable for use in automatic dishwashing machines which does not foam excessively in the presence of proteinaceous soil, such as raw egg soil.

OBJECTS OF THE INVENTION

An object of this invention is to provide a low foaming detergent composition especially suitable for use in automatic dishwashing machines. Another object of the invention is to produce a detergent composition for use in automatic dishwashing machines which does not foam excessively in the presence of proteinaceous soil. Still another object of the invention is to provide an additive composition which, when formulated into a detergent composition suitable for use in an automatic dishwashing machine, will suppress foam generated by proteinaceous soil on articles being cleaned. These and other objects,

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advantages, and features of the present invention will become apparent to those skilled in the art from a reading of the following detailed description and appended claims.

SUMMARY OF THE INVENTION

According to the present invention I have now found that the foaming characteristics of an aqueous solution of a detergent composition containing a nonionic surface active agent which is suitable for use for automatic dishwashing machines are substantially reduced by incorporating into said detergent the ethoxylate phosphate esters produced from alcohols containing from about 16 to 20 carbon atoms, 1-mole ethoxylate blends of same, ethylene oxide adducts of 16 to 20 carbon alcohols, their blends, an alcohol-1-mole ethoxylate mixture, or a blend of ethylene oxide adducts of C₁₆ to C₂₀ alcohols wherein the 1-mole adduct is optimized. Further, I have found that in order to obtain the desirable results of producing the low foam detergent composition suitable for use in automatic dishwashing machines, the phosphate ester of said ethoxylated alcohols employed in said detergent composition is present in the amount of about 0.05 to 2 weight percent, based on the total weight of said detergent composition. Especially desirable results are obtained where the phosphate ester additive is present in the amount of about 0.06 to about 0.5 weight percent, based on the total weight of the dishwashing detergent composition, and the weight ratio of phosphate ester additive to nonionic compound is about 1:20 to 1:5.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The nonionic surface active agents which are advantageously employed in automatic dishwashing machine detergent compositions are generally the polyoxyalkylene adducts of hydrophobic bases wherein the oxygen/carbon atom ratio in the oxyalkylene portion of the molecule is greater than 0.40. Those compositions which are condensed with hydrophobic bases to provide a polyoxyalkylene portion having an oxygen/carbon atom ratio greater than 0.40 include ethylene oxide, butadiene dioxide and glycidol, mixtures of these alkylene oxides with each other and with minor amounts of propylene oxide, butylene oxide, amylene oxide, styrene oxide, and other higher molecular weight alkylene oxides. Ethylene oxide, for example, is condensed with the hydrophobic base in an amount sufficient to impart water dispersibility or solubility and surface active properties to the molecule being prepared. The exact amount of ethylene oxide condensed with the hydrophobic 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 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, n-dodecyl, polymerized propylene such as propylene tetramer and trimer, isooctyl, nonyl,

$$\text{C}_8\text{H}_{17}-\text{C}_6\text{H}_4-(\text{OCH}_2\text{CH}_2)_{15}\text{OCH}_2\text{C}_6\text{H}_5$$
$$\begin{array}{c} \text{R} \\ \diagup \quad \diagdown \\ \text{R}_1 \text{---} \text{C}_6\text{H}_4 \text{---} (\text{CH}_2\text{CH}_2\text{O})_n\text{H} \\ \diagdown \quad \diagup \\ \text{R}_2 \end{array}$$
$$Y(C_3H_6O)_n(C_2H_4O)_mH$$
$$Y[(C_3H_6O)_n(C_2H_4O)_mH]_x$$

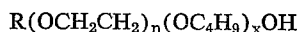
wherein Y is the residue of an organic compound having from about 2 to 6 carbon atoms and containing x reactive hydrogen atoms in which x has a value of at least about 2, n has a value such that the molecular weight of the polyoxypropylene hydrophobic base is at least about 900 and m has a value such 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, ethylene, diamine and the like. As already noted, the oxypolypropylene chain, optionally, but advantageously, contain small amounts of ethylene oxide and the oxyethylene chains also optionally, but advantageously, contain small amounts of alkylene oxides such as propylene oxide and butylene oxide. These

$$\text{P}[(\text{C}_3\text{H}_6\text{O})_n(\text{C}_2\text{H}_4\text{O})_m\text{H}]_x$$
$$\text{P}[(\text{C}_2\text{H}_4\text{O})_n(\text{C}_3\text{H}_6\text{O})_m\text{H}]_x$$

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-dodecyl, 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.

While any of the above list of nonionic surface active agents can be employed in automatic dishwashing machine detergent compositions, I have found particularly desirable results can be obtained wherein the nonionic compound is in the form of an alkyl polyethoxyethanol which is condensed with butylene oxide, thereby forming a nonionic surfactant having the general formula:



where R is a C_8 to C_{18} alkyl group, n indicates a range of integers representing the statistical distribution of oxyethylene units obtained by condensing from about 3.5 to 10 moles of ethylene oxide with 1 mole of the compound providing said hydrocarbon groups, namely a higher aliphatic mono-alcohol, and x indicates a range of integers from about 0.5 to 1.5. Especially desirable results have been obtained wherein the butylene oxide capped nonionic employed has a R value which is a mixture of C_{10} and C_{12} alkyl groups, n has an average value in the range of 5 to 6, and x has an average value in the range of 0.75 to 1.25.

The phosphate ester additive which is used as the foam depressant in the detergent composition containing any of the above listed nonionic surface active agents and which are suitable for use in automatic dishwashing machines is produced by phosphorylation of a C_{16} to C_{20} linear alcohol, the 1-mole ethoxylate of a C_{16} to C_{20} linear alcohol, blends of the ethoxylates of said alcohols, an alcohol-1-mole ethoxylate mixture or a blend of ethylene oxide adducts of a C_{16} to C_{20} alcohol wherein the 1-mole adduct is optimized. The phosphate ester can be either the acid or neutral (salt) form. When the neutral form is employed, any suitable alkali material, such as NaOH, KOH, NH_4OH , Na_2CO_3 , substituted ammonium compounds, such as mono-, di-, and tri-ethanol amines, and the like, can be used.

The 1-mole ethoxylate constituent of the C_{16} to C_{20} alcohol can be prepared by distillation of a conventional ethoxylate in order to obtain the desired 1-mole adduct, or it may be prepared by any of the known reactions, such as with sodium alcoholate or bromoethanol. Desirable results have been obtained wherein the 1-mole ethoxylate of the C_{16} to C_{20} alcohol is prepared by either base or acid catalyzed ethoxylation of a primary C_{16} to C_{20} straight chain alcohol. Especially desirable results have been obtained by employing the acid catalyzed ethoxylation of the primary C_{16} to C_{20} straight chain alcohol because the acid catalyzed ethoxylation gives a poisson distribution of adducts which contains more of the desired 1-mole adduct than does the base catalyzed ethoxylation which gives a wide distribution of adducts. However, it should be stressed that any method of obtaining the 1-mole adduct for subsequent phosphorylation to produce the desired organic phosphate esters of the present invention can be employed.

The organic phosphate esters which are employed as the foam depressant in the detergent composition of the present invention can be prepared by any conventional phosphorylation method which is known in the art. For example, the organic phosphate ester additives of the present invention can be prepared by using 115 percent polyphosphoric acid at a mole ratio of 2:1 of the ethoxylate, the alcohol, or the alcohol-ethoxylate mixture to P_2O_5 . The acid ester thus formed is preferred, although a neutral form is also effective.

The phosphate ester additives which, when incorporated with low foam nonionics, produce a detergent composition having suppressed foam properties in the presence of proteinaceous soil, is selected from the group consisting of the phosphate esters of C_{16} to C_{20} linear primary alcohols, the 1-mole ethoxylate of the C_{16} to C_{20} alcohols, blends of the 1-mole ethoxylate of said alcohols, a C_{16} to C_{20} alcohol-1-mole ethoxylate mixture, or a blend of

ethylene oxide adducts of a C_{16} to C_{20} alcohol wherein the 1-mole adduct is optimized. Evidence establishing the criticality of the 1-mole ethoxylate adduct will be clearly indicated in the examples to follow. Further, runs similar to those in the examples were conducted wherein the phosphate ester additives were produced from a primary C_{14} straight chain alcohol. However, in the case of the 1-mole ethoxylate adducts of the C_{14} alcohol, the results were undesirable, showing that C_{14} products are not effective defoamers. However, when employing the C_{16} to C_{20} 1-mole ethoxylate adduct, desirable results were obtained. The following data will further illustrate that phosphate esters prepared from a C_{16} to C_{20} alcohol or from the 1-mole ethoxylate adduct is a good defoamer when employing the C_{16} to C_{20} range of alcohols, whereas the 2-mole ethoxylate adduct and higher of the same range of the C_{16} to C_{20} alcohols do not function as good defoamers. Especially desirable results were obtained when the phosphate esters were prepared from a linear C_{16} primary alcohol, a 1-mole ethylene oxide adduct of a linear C_{16} primary alcohol, and a blend of ethylene oxide adducts of a linear C_{16} primary alcohol wherein the 1-mole adduct is optimized.

To further illustrate the best manner contemplated for carrying out the invention, the following working examples are set forth. As indicated, the examples are primarily given by way of illustration, and accordingly any enumeration of details set forth therein are not to be interpreted as a limitation on the invention as such limitations are indicated in the appended claims. All parts are parts by weight unless otherwise stated.

Example 1.—A series of organic phosphate esters were prepared by conventional phosphorylation methods using 115% polyphosphoric acid at a mole ratio of 2:1 alcohol or ethoxylate to P_2O_5 . In the preparation of the organic phosphate esters, two (2) moles of the alcohol or ethoxylate were heated and stirred at 115° C. for 90 minutes with one (1) mole of 115% polyphosphoric acid. A nitrogen blanket was maintained on the system, while above ambient temperatures were maintained. At the end of the reaction period, a portion of each reaction product was neutralized with NaOH solution so that the products could be tested in both the acid and neutralized salt form.

Testing of the organic phosphate esters as an additive for low foam nonionics was done in an automatic dishwasher detergent formulation having the following composition:

	Percent
"ALFONIC" LF and organic phosphate ester blend	2.9
Chlorinated trisodium phosphate	51.8
Sodium metasilicate	19.9
Sodium carbonate	0.7
H ₂ O q.s.	

The "ALFONIC" LF and phosphate ester blends used were 90-95% "ALFONIC" LF and 10-5% phosphate ester in both the acid and neutralized salt form (e.g., the detergent formulations contained from about 0.29 to 0.15 weight percent phosphate ester). The "ALFONIC" LF nonionic employed is a low foam nonionic produced from a blend of C_{10} and C_{12} linear primary alcohols which have been ethoxylated with about 5.6 moles of ethylene oxide and capped with 0.95 mole of 1,2-butylene oxide.

The above described automatic dishwasher detergent formulation was then employed in a dishwasher test. The dish washing test consisted of stacking 10 clean plates in the dishwasher rack, filling the dishwasher to a measured level with 150±5° F. condensate water containing essentially zero hardness. Fifty (50) grams of well-mixed whole egg and 25.6 grams of the detergent formulation was added to the water. The machine was started and the rotor arm r.p.m.'s were visually counted through the Plexiglas window in the door. The r.p.m.'s were read for one minute each at 2, 4, 6, and 8 minutes. The values were then

averaged for the four readings, and the average value is recorded in the table below. Because foam impedes the revolution of the rotor arm, a low r.p.m. value represents poor defoaming, while a high r.p.m. value represents good defoaming.

In addition to the phosphate esters prepared from alcohols and standard base catalyzed ethoxylates, two phosphate esters were prepared from distillation cuts of a C₁₆ ethoxylate. The composition of the cuts as determined by GLC were:

	Weight percent adduct	
	C ₁₆ high 1 EO	C ₁₆ high 2 EO
C ₁₆ alcohol.....	11.6	1.1
C ₁₆ +1 EO.....	68.7	23.9
C ₁₆ +2 EO.....	19.1	75.0
C ₁₆ +3 EO.....	0.6	

Phosphate ester form.....	Average r.p.m.			
	5% acid	10% acid	5% Na salt	10% Na salt
Alkyl structure of phosphate structure:				
C ₁₆ alcohol.....	38.2	34.2	36.6	36.6
C ₁₆ +1 mole avg. EO.....	31.6	36.0	20.3	28.5
C ₁₆ +2 mole avg. EO.....	24.9	32.4	17.0	23.4
C ₁₆ +3 mole avg. EO.....	12.5	26.8	14.2	17.2
C ₁₆ high 1 mole EO.....	27.6	32.0	27.4	31.3
C ₁₆ high 2 mole EO.....	15.1	23.9	13.1	23.1
C ₁₆ alcohol.....	32.9	33.6	28.5	34.3
C ₁₆ +1 mole avg. EO.....	30.5	32.6	23.6	29.5
C ₁₆ +2 mole avg. EO.....	26.6	29.6	20.5	24.6
C ₁₆ +3 mole avg. EO.....	21.4	20.8	15.6	22.0
C ₂₀ +1 mole avg. EO.....	22.4	31.2	23.5	28.7
C ₂₀ +2 mole avg. EO.....	19.2	31.9	18.6	21.4
C ₂₀ +3 mole avg. EO.....	15.0	22.7	14.6	18.0
None.....	13.5	13.5	13.5	13.5

The above data clearly indicate the foaming properties of both the acid and Na salt form of phosphate esters formed from C₁₆-C₂₀ alcohols and the 1 mole ethylene oxide adduct of said alcohols.

Experiments were also run with similar C₁₄ products. The results of such runs were poor, indicating that the C₁₄ products are not effective defoamers.

Example 2.—A series of experiments were conducted wherein a mixture of 95% "ALFONIC" LF and 5% of a phosphate ester of the 1 mole ethylene oxide adduct of a blend of C₁₆ to C₁₈ straight chain primary alcohols were substituted for the nonionic component in five commercial automatic dishwasher detergents. In each case the formulation containing the "ALFONIC" LF and phosphate ester was better in defoaming than the corresponding commercial detergent. The experiments were conducted under the same conditions as those in Example 1, and the defoaming properties were determined in the same manner. The results of the experiments are set out below.

	A	B	C	D	E
Commercial formulation.....	26.0	26.5	26.0	11.2	13.0
95% "ALFONIC" LF, 5% C ₁₆ +1 mole EO alkyl phosphate ester sodium salt..	31.6	36.5	35.6	20.6	16.9

The above C₁₆ blend contains 65 weight percent C₁₆ constituent and 35 weight percent C₁₈ constituent. When employing such blends, the ratio of C₁₆ to C₁₈ constituents can vary. However, I prefer to maintain more than 50 weight percent C₁₆ constituent in said blends.

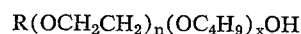
The above data in Examples 1 and 2 clearly indicate that organic phosphate esters produced from the 1-mole ethylene oxide adducts of 16 to 20 carbon alcohols, their blends, and an alcohol-ethoxylate blend containing an appreciable amount of the 1-mole ethylene oxide adduct, when blended with a low foam nonionic compound, produces a low form detergent composition which effectively suppresses foam generated by proteinaceous soil or articles being cleaned in automatic dishwashing machines.

Having thus described the invention, I claim:

1. A low foaming additive composition for use in automatic dishwashing machine detergent formulations, said additive composition consisting essentially of:

(A) an acid or neutral phosphate ester produced from the reaction of concentrated phosphoric acid and the 1-mole ethylene oxide adduct of a linear C₁₆ primary alkanol; and

(B) a butylene oxide capped nonionic surface active agent having the formula



where R is a mixture of linear C₁₀ and C₁₂ alkyl groups, n is 5 to 6 and x is 0.5 to 1.5;

the weight ratio of said (A) component to said (B) component being about 1:20 to 1:5.

2. A low foaming automatic dishwashing machine detergent composition consisting essentially of:

2.9 percent by weight of the additive composition of claim 1;

51.8 percent by weight of chlorinated trisodium phosphate;

19.9 percent by weight of sodium metasilicate;

0.7 percent by weight of sodium carbonate; and the balance water.

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