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3,539,519

LOW FOAMING NONIONIC DETERGENTS

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6 Claims

ABSTRACT OF THE DISCLOSURE

A high foaming monionic surfactant in the form of an alkyl polyethoxyethanol is further condensed with butylene oxide to provide a low foaming modification thereof having the general formula $R(\text{OCH}_2\text{CH}_2)_n(\text{OC}_4\text{H}_9)_x\text{OH}$.

CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of pending application entitled "Low Foaming Nonionic Detergents," U.S. Ser. No. 707,401, filed Feb. 23, 1968 by Dean R. Weimer now abandoned.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to a low foaming nonionic detergent composition consisting essentially of a mixture of surface active compounds serially containing a hydrophobic alkyl group, a hydrophilic polyoxyethylene segment and a terminal hydroxy butoxy group.

Description of the prior art

An important class of nonionic detergent is exemplified by those compositions, generally designated ethoxylates, which are obtained by condensing a hydrophobic compound having a replaceable hydrogen atom with a plurality of moles of ethylene oxide. Particularly suitable compounds providing the hydrophobic portion of such ethoxylates are either the higher aliphatic monoalcohols or an alkyl substituted phenol. These nonionic compositions are excellent detergents and are characterized as high foamers in that they are prone to result in profuse sudsing in any cleaning operation involving highly turbulent agitation conditions. In some industrial and in many household cleaning applications of the aforesaid type, it is very desirable to maintain a low level of foam during the cleansing or treating operation. For example, in various household cleaning operations conducted in mechanical washers excessive foaming of the nonionic detergent is objectionable because the foam interferes with proper rinsing and in some cases impairs cleansing efficiency. Furthermore, high foaming detergents are ultimately apt to give rise to mechanical difficulties. It is well known in the syndet art that the wetting and/or detergency power of a surface active agent is not necessarily synonymous with its foaming ability. Consequently, considerable investigation has hitherto been directed toward providing modifications of high foaming nonionic detergents whereby the inherent tendency to foam is abated without significantly detracting from the detergency power exhibited by the unmodified nonionic.

The nonionics with which this invention is concerned are basically a chemostructural combination of a hydrophobic group and a segment of hydrophilic units as can be perceived from the foregoing discussion. It has been proposed to terminate the hydrophilic portion with a radical having somewhat lesser hydrophilic characteristics in order to provide a lower foaming but equally effective

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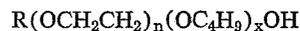
modification thereof from the standpoint of detergency. This has been generally accomplished heretofore by further condensing the ethoxylate with propylene oxide to provide a terminal polyoxypropylene segment. The disadvantage of this approach is twofold in nature. For one, the hydrophobic radical of such modified compositions must be relatively low in molecular weight thereby necessitating the use of an alcohol which does not yield optimum detergency characteristics. Secondly, if the preferred higher molecular weight alcohols or alkyl substituted phenols are utilized to prepare such modified nonionics, the terminal polyoxypropylene segment must be undesirably large. Too large a terminal segment of this type poses problems not only in regard to biodegradability but also has an adverse effect with respect to a variety of more subtle aspects.

OBJECT OF THE INVENTION

The primary objective of this invention is to provide a modified nonionic detergent composition of the alcohol ethoxylate type exhibiting low foaming characteristics in combination with good biodegradability, water solubility and physical appearance properties.

SUMMARY OF THE INVENTION

The present invention is directed to nonionic detergent compositions comprising a mixture of surface active compounds corresponding to the following general formula:



where R is a C_8 - C_{18} alkyl group, and 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 a mole of the compound providing said hydrocarbon groups, namely, a higher aliphatic monoalcohol, and x indicates a range of integers of from about 0.5 to 1.5.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The compounds having replaceable hydrogen atoms useful to prepare the base ethoxylates of this invention are the various detergent grade aliphatic mono-alcohols. The term "aliphatic monoalcohols" as used in this disclosure pertains to those monoalcohols whose carbon atoms are arranged in chains only. Such alcohols include linear and branched primary and secondary monoalcohols. However, the linear alcohols, are more biodegradable. Therefore, the preferred monoalcohols are the linear alcohols such as exemplified by the primary alcohols obtained in accordance with the Ziegler synthesis method or the secondary alcohols prepared by the OXO process. Particularly desirable alcohols are the linear primary alcohols. Broadly inclusive of the latter, as well as the linear secondary alcohols, are those containing from 8 to 18 carbon atoms. Especially useful alcohols within this range are the C_{10} - C_{14} alcohols and mixture thereof. For the purpose of making low foaming nonionic detergents for household cleaning applications, n -decanol or mixture thereof with minor amounts of dodecanol and/or tetradecanol provide surface active substances having an optimum balance of properties.

Ethoxylates of the foregoing compounds containing a replaceable hydrogen atom can be prepared by conventional methods. Either acid or base catalysis is applicable. Base catalysis, however, is preferred in effecting the condensation of ethylene oxide with the alcohol. Exemplary of suitable bases are the alkali metal hydroxides such as LiOH, KOH and NaOH. Sodium hydroxide is the preferred base catalyst for effecting condensation. Exemplary of suitable acid catalysts are SbCl_5 , SnCl_4 and BF_3 . Boron

trifluoride is the preferred acid catalyst for effecting condensation.

The general procedure for carrying out the condensation reaction involves adding the requisite amount of ethylene oxide to the alcohol together with the catalyst selected and heating the reactants to an elevated temperature under autogenous pressure. The ethoxylation or condensation reaction can be carried out in a temperature range of from about 320 to 380° F. The preferred temperature range is from about 340 to 360° F. The foregoing temperature ranges are applicable for the preferred catalyst, specifically sodium hydroxide. When using an acid catalyst, such as boron trifluoride, a lower temperature is to be observed. A range of from about 175 to 220° F. is suitable for such catalysis.

The amount of ethylene oxide to be reacted with the monoalcohol is primarily dependent upon the molecular weight of said alcohol. As the molecular weight of the hydrophobe portion increases, the use of correspondingly greater amounts of ethylene oxide is the customary practice. For the broad range of alcohols contemplated herein the corresponding amount of ethylene oxide ranges from about 3.5 to 10 moles per mole of the alcohol. An ethylene oxide range of from 3.5 to 6 moles per mole of the preferred C₁₀ to C₁₄ alcohols is applicable. However, in order to produce a nonionic low foaming composition having excellent solubility properties I prefer to employ from about 5.2 to 5.7 moles of ethylene oxide per mole of the C₁₀ to C₁₄ alcohols or blends thereof. Desirable results have also been obtained where the resultant condensate is the reaction product of a mole of a C₁₀-C₁₂ alcohol and from about 5 to 6 moles of ethylene oxide. The preferred weight ratio of ethylene oxide to any given alcohol in the resultant condensate is in the order of from 1.3 to 1.8. Especially when using a mono-

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 except as such limitations are indicated in the appended claims. All parts are parts by weight unless otherwise stated.

EXAMPLE I

A series of butylene oxide capped alcohol ethoxylates was prepared following the general procedure of reacting ethylene oxide with the alcohol at about 350-360° F. in the presence of NaOH catalyst in the amount of about 0.125 percent based on the weight of the alcohol. Capping of the resultant ethoxylates was accomplished in those runs employing base catalysis by adding the requisite amount of 1,2-butylene oxide and heating at approximately the temperature observed in effecting ethoxylation. In the run in which capping with the butylene oxide was conducted in the presence of BF₃ catalyst (about 0.1 percent based on the weight of the ethoxylate) the crude ethoxylate product was first neutralized with glacial acetic acid and then filtered. All of the capped products were then heated at from 340 to 360° F. and at about 10 mm. Hg to remove any light ends contained by the product. Following removal of the light ends, the products were neutralized and filtered. Details as to the respective compositions of these runs as well as their comparative performance in several low foam testing methods and their wetting ability as determined by the standard Draves test are given in the following Table 1. Also indicated in the table is the general resistance of the various products to biological assimilation in a standard biodegradation test.

TABLE 1

Run:	Primary alcohol or mixture	Percent EO in ethoxylate	Moles EO in ethoxylate	Moles BO per mole of ethoxylate	Low foam tests				Wetting test No. 5	Biodegradability
					Num-ber 1	Num-ber 2	Num-ber 3	Num-ber 4		
1	85% C ₁₀ -8% C ₁₂ -7% C ₁₄	58	5.2	0	2.8	2.0	0.9	1.3	6.3	Good.
2	85% C ₁₀ -8% C ₁₂ -7% C ₁₄	50	3.7	1	0.6	0.6	0.4	0.6	-----	Do.
3	85% C ₁₀ -8% C ₁₂ -7% C ₁₄	59	5.5	1	1.2	0.4	0.3	0.7	7.2	Do.
4	85% C ₁₀ -8% C ₁₂ -7% C ₁₄	60	5.7	1	1.2	0.5	0.3	0.8	7.0	Do.
5	85% C ₁₀ -8% C ₁₂ -7% C ₁₄	61	6.0	1	1.7	0.5	0.5	0.7	6.2	Do.
6	85% C ₁₀ -8% C ₁₂ -7% C ₁₄	58	5.2	1	1.6	0.4	0.3	0.8	9.2	Do.

¹ BF₃ used as catalyst for capping.

alcohol, the aforesaid range of ethylene oxide provides about the optimum balance of properties for the resultant condensate.

In accordance with this invention the ethoxylates described hereinabove are then reacted with butylene oxide in a manner whereby a substantial portion of the ethoxylated compounds are terminated with a hydroxy butoxy grouping. An applicable amount of butylene oxide for achieving such capping is from 0.5 to 1.5 moles of butylene oxide per mole of the ethoxylate. The preferred compositions are those obtained by condensing the ethoxylated product with about 0.75 to 1.25 moles of butylene oxide. Especially desirable results have been obtained wherein the ethoxylated product is condensed with about 1 mole of butylene oxide. Again, either base or acid catalysis can be used to achieve capping of the ethoxylate. A base such as sodium hydroxide is preferred from the standpoint of convenient processing. However, the use of an acid catalyst such as boron trifluoride for this purpose results in a product having somewhat better physical appearance than those capped materials prepared using base catalysis for the capping step. The respective ranges of temperatures, including the preferred ranges discussed hereinabove in connection with preparing the ethoxylate, are precisely applicable in achieving capping thereof with the butylene oxide. The various butylene oxides can be used to prepare the nonionics of this detergent. However, 1,2-butylene oxide is the preferred capping material.

A summary of the various test methods used are as follows:

Test No. 1.—0.1% surfactant in 200 ml. aqueous solution. Stirred on malt mixer at high speed at 75° F. for 3 minutes. Solution allowed to stand 2 minutes and the foam height measured in centimeters.

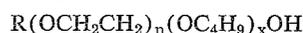
Test No. 2.—Same as No. 1 except that test is run at 140° F.

Test No. 3.—0.006% surfactants and 0.194 sodium silicate in 200 ml. aqueous solution. Stirred on malt mixer at high speed and 140° F. for 3 minutes. Solution allowed to stand 45 seconds and foam height measured in centimeters.

Test No. 4.—0.006% surfactant, 0.194% sodium silicate and 0.1% powdered milk in 200 ml. aqueous solution. Test procedure is the same as Test No. 3. Tests 3 and 4 measure the defoaming ability of the surfactant for use where proteinaceous material is present.

Test No. 5.—Measures wetting time of 0.1% solution of the surfactant at 75° F. A 5 gm. Draves cotton skein and a 3 gm. hook used.

The above data clearly indicates that a nonionic compound having the general formula



where R is a linear alkyl radical having 10 to 14 carbon atoms, *n* is an integer 3.7 to 6.0 and *x* is 1 possesses excellent cotton wetting properties and good biodegradable properties. The data further illustrates that by in-

corporating 1 mole of butylene oxide into a high foam nonionic, such as in Run No. 1, the resulting nonionic compound possesses desired low foam properties without sacrificing the above-mentioned desirable properties.

EXAMPLE II

A series of propylene oxide capped ethoxylates was prepared following the general procedure outlined in Example I except that propylene oxide was substituted for the 1,2-butylene oxide. Details as to the respective compositions of these runs as well as their comparative performance in several low foam testing methods and their wetting ability as determined by the standard Draves test are given in the following Table 2.

TABLE 2

Run	Primary alcohol or mixture	Percent EO in ethoxylate	Moles EO in ethoxylate	Moles PO per mole of ethoxylate	Low foam tests		Wetting test No. 3	Biodegradability
					No. 1	No. 2		
6.....	45% C ₈ -55% C ₁₀	60	5	5	0.5	0	16.7	Poor.
7.....	85% C ₁₀ -8% C ₁₂ -7% C ₁₄	73	10.4	0	5.2	4.1	24.0	Good.
8.....	85% C ₁₀ -8% C ₁₂ -7% C ₁₄	73	10.4	1	4.5	2.7	19.2	Fair.
9.....	40% C ₁₂ -30% C ₁₄ -20% C ₁₆ -10% C ₁₈ ...	62.5	8.1	0	4.0	3.1	Good.
10.....	40% C ₁₂ -30% C ₁₄ -20% C ₁₆ -10% C ₁₈ ...	65	9	3.5	3.1	1.6	Poor.
11.....	40% C ₁₂ -30% C ₁₄ -20% C ₁₆ -10% C ₁₈ ...	66	9.5	7	3.3	0.6	Do.

Summary of the various test methods used are as follows:

Test No. 1.—0.1% surfactant in 200 ml. aqueous solution. Stirred on malt mixer at high speed at 75° F. for 3 minutes. Solution allowed to stand 2 minutes and the foam height measured in centimeters.

Test No. 2.—Same as No. 1 except the test is run at 140° F.

Test No. 3.—Measures wetting time of 0.1% solution of the surfactant at 75° F. A 5 gm. Draves cotton skein and a 3 gm. hook used.

Referring to the above data Run No. 8, when compared with Run No. 7, illustrates that when 1 mole of propylene oxide is employed to cap the original ethoxylate the small decrease in foam of the propylene oxide capped nonionic is not sufficient to make it a low foam nonionic. In order to get good defoaming properties the propylene oxide ratio to the ethoxylate must be relatively high. This is illustrated in Runs No. 6 and 11 where the ratio of ethylene oxide to propylene oxide is approximately 1:1. However, the nonionics containing an effective amount of propylene oxide exhibit poor biodegradability. The data also illustrates that the wetting speed of the propylene oxide capped nonionic is substantially poorer than the butylene oxide capped nonionic of Example I.

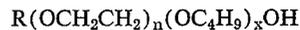
Therefore, when comparing the results of Table I and Table II, i.e., butylene oxide capped nonionic and propylene oxide capped nonionic, one can readily see that the butylene oxide capped nonionic produces superior results. Further, the butylene oxide capped nonionic has a much lower ratio of butylene oxide to ethylene oxide than the propylene oxide to ethylene oxide ratio in the propylene oxide capped nonionic.

The foregoing discussion and description has been

made in connection with preferred specific embodiments of the low foam nonionic composition of the present invention. However, it is to be understood that the discussion and description is only intended to illustrate and teach those skilled in the art how to practice the invention, and such is not to unduly limit the scope of the invention, which is to be found in the claims set forth hereinafter.

Having described the invention, I claim:

1. Biodegradable low foaming nonionic compositions consisting essentially of a mixture of compounds having the formula:



wherein R is a C₈ to C₁₈ alkyl group, n is an integer of

from about 3.5 to 10 and x is an integer from about 0.5 to 1.5.

2. The compositions of claim 1 wherein x is from 0.75 to 1.25.

3. The compositions according to claim 1 wherein x is about 1.

4. The compositions according to claim 3 wherein R is a C₁₀ to C₁₄ linear group and n is from about 3.5 to 6.

5. The compositions according to claim 4 wherein n is about 5.2 to 5.7.

6. The compositions according to claim 3 wherein R is a C₁₀ to C₁₂ linear group and n is from about 5 to 6.

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U.S. Cl. X.R.

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