

1

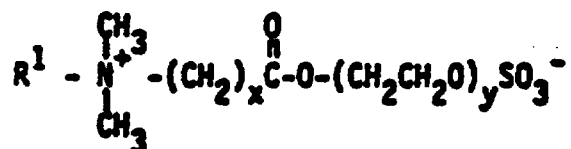
**Ethoxylated monoamines having clay-soil removal/
anti-redeposition properties**

The present application relates to ethoxylated monoamines having clay-soil removal/anti-redeposition properties when used in detergent compositions.

A particularly important property of a detergent composition is its ability to remove particulate type soils from a variety of fabrics during laundering. Perhaps the most important particulate soils are the clay-type soils. Clay soil particles generally comprise negatively charged layers of aluminosilicates and positively charged cations (e.g. calcium) which are positioned between and hold together the negatively charged layers.

A variety of models can be proposed for compounds which would have clay soil removal properties. One model requires that the compound have two distinct characteristics. The first is the ability of the compound to adsorb onto the negatively charged layers of the clay particle. The second is the ability of the compound, once adsorbed, to push apart (swell) the negatively charged layers so that the clay particle loses its cohesive force and can be removed in the wash water.

One class of clay-soil removal compounds which appears to work according to this model are the polyethoxy zwitterionic surfactants disclosed in U.S. Patent 4,301,044 to Wentler et al., issued November 17, 1981. Representative of such compounds are those having the formula:



wherein R^1 is a C_{14} - C_{20} alkyl group; x is 1 or an integer of from 3 to 5; and y is from 6 to 12. See also U.S. Patent 3,929,678 to Laughlin et al., issued December 30, 1975 (detergent composition containing polyethoxy zwitterionic surfactant plus other detergent

surfactants); U.S. Patent 3,925,262 to Laughlin et al., issued December 9, 1975 (detergent composition containing polyethoxy zwitterionic surfactants with detergent builders); U.S. Patent 4,157,277 to Gosselink et al., issued June 26, 1979 (C₄ polyoxy-alkylene zwitterionic surfactants useful in detergent compositions); U.S. Patent 4,165,334 to Gosselink et al., issued August 21, 1979 (sulfonium-type polyethoxy zwitterionic surfactants).

These polyethoxy zwitterionic surfactants are generally compatible with other detergent surfactants such as the nonionic, zwitterionic and ampholytic types. However, as indicated in the Wentler et al. patent, most anionic surfactants interfere with the particulate soil removal performance of these compounds; anionic soils such as fatty acids likewise interfere. Because anionic detergent surfactants form the most important class of such materials for use in detergent compositions, the lack of compatibility between these polyethoxy zwitterionic surfactants and anionic surfactants poses a significant handicap where particulate (clay) soil removal is desired.

In addition to clay soil removal, one of the other properties mentioned in the Laughlin et al. patents with regard to these polyethoxy zwitterionic surfactants is the ability to keep the removed soil in suspension during the laundering cycle. Soil which is removed from the fabric and suspended in the wash water can redeposit onto the surface of the fabric. This redeposited soil causes a dulling or "graying" effect which is especially noticeable on white fabrics. Because soil is normally hydrophobic, this graying effect is a particularly important problem for those fabrics made in total or in part from hydrophobic fibers, e.g. polyester.

To minimize this problem, anti-redeposition or whiteness maintenance agents can be included in the detergent composition. Besides the previously mentioned polyethoxy zwitterionic surfactants, there are a variety of other compounds which can be used as anti-redeposition agents. One class of agents are the water-soluble copolymers of acrylic or methacrylic acid with acrylic or methacrylic acid-ethylene oxide condensates disclosed in U.S.

Patent 3,719,647 to Hardy et al., issued March 6, 1973. Another class of anti-redeposition agents are the cellulose and carboxymethylcellulose derivatives disclosed in U.S. Patent 3,597,416 to Diehl, issued August 3, 1971 (ionic combination of dodecyltrimethyl phosphonium chloride and sodium carboxymethylcellulose),
5 and U.S. Patent 3,523,088 to Dean et al., issued August 4, 1970 (anti-redeposition agent consisting of alkali metal carboxymethylcellulose and hydroxypropylcellulose). A mixture of compounds has also been used to provide not only anti-redeposition, but also
10 clay soil removal properties. See U.S. Patent 4,228,044 to Cambre, issued October 14, 1980, which discloses detergent compositions having anti-redeposition and clay soil removal properties which can comprise a nonionic alkyl polyethoxy surfactant, a polyethoxy alkyl quaternary cationic surfactant and a fatty amide
15 surfactant.

These anti-redeposition agents do have a number of significant handicaps. While effective to keep soil suspended, these compounds may lack additional clay soil removal properties. Moreover, as disclosed in the Diehl and Dean et al. patents,
20 mixtures of compounds can be required to achieve the anti-redeposition benefit. To the extent that there are combined anti-redeposition/clay soil removal benefits as disclosed in the Cambre patent, mixtures of compounds are also required.

It is therefore an object of the present invention to provide
25 compounds useful in detergent compositions which provide particulate soil, in particular clay soil, removal benefits.

It is a further object of the present invention to provide compounds useful in detergent compositions which provide clay soil removal benefits and are anionic detergent surfactant compatible.

30 It is yet another object of the present invention to provide compounds useful in detergent compositions having anti-redeposition properties.

It is yet a further object of the present invention to provide compounds useful in detergent compositions which combine
35 both clay soil removal and anti-redeposition properties.

These and further objects of the present invention are hereinafter disclosed.

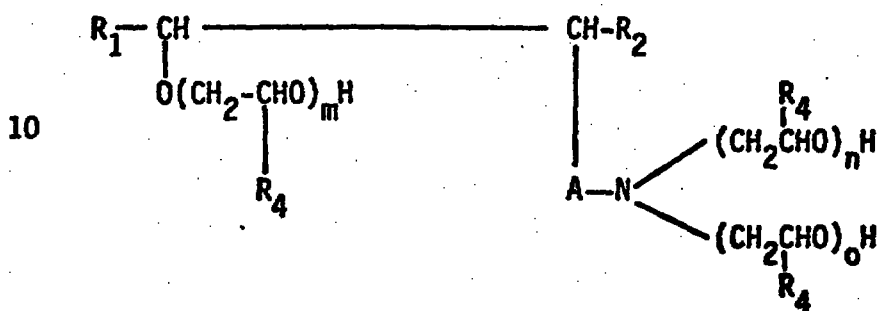
BACKGROUND ART

5 U. S. Patent 3,301,783 to Dickson, et al., issued January 31, 1967, discloses oxyalkylated, acylated, alkylated, carbonylated and olefinated derivatives of polyalkyleneimines, in particular polyethyleneimines (PEIs). For the oxyalkylated derivatives, the alkylene oxide (e.g. ethylene oxide) is reacted with the poly-
10 alkyleneimine in a mole ratio of from 1:1 to 1000:1, and preferably in a ratio of from 1:1 to 200:1. Among the ethoxylated PEIs disclosed are Examples 1-0₇ and 1-0₈ formed by condensing 105 and 200 moles, respectively, of ethylene oxide with a 900 M.W. PEI. The degree of ethoxylation calculates out to about 4.5 and about 8
15 ethoxy groups per reactive site, respectively. See also Examples 27-0₅ and 27-0₆ which disclose ethoxylated polypropyleneimines (M.W. 500) which have about 4 and about 8 ethoxy units per reactive site, respectively. Amongst the numerous disclosed uses of these polyalkyleneimine derivatives is a teaching that they are
20 useful as detergents, softening agents, and anti-static agents. Preferred uses disclosed by this patent are as chelating agents, lubricating oil additives, emulsifying agents, and cutting oils.

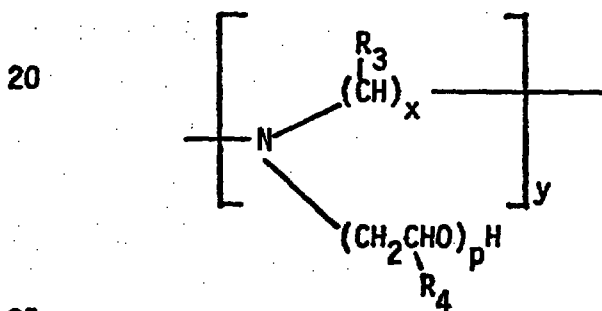
U.S. Patent 2,792,371 to Dickson, issued May 14, 1957, teaches a process for breaking petroleum emulsions with oxy-
25 alkylated tetraethylene pentaamines (TEPA). Ethoxylated TEPA's specifically disclosed include those having about 5 (Example 3aa), about 7 (Example 4aa), about 8.5 (Example 5a) and about 15.5 (Example 8c) ethoxy units per reactive site. Similarly, U.S. patent 2,792,370 to Dickson issued May 14, 1957, teaches a process
30 for breaking petroleum emulsions with oxyalkylated triethylene tetramines (TETAs) including those having about 5.5 (Example 3aa), about 7.5 (Example 4aa), about 9 (Example 5a) and about 16.5 (Example 8c) ethoxy units per reactive site. See also U. S. patent 2,792,372 to Dickson, issued May 14, 1957, (oxyalkylated
35 higher PEAs used to break petroleum emulsions); U. S. patent

2,792,369 to Dickson, issued May 14, 1957 (oxyalkylated diethylene triamines used to break petroleum emulsions).

U. S. Patent 4,171,278 to Andree et al., issued October 16, 1979, discloses cold water detergent compositions containing a detergent surfactant (e.g. anionic) and a hydroxyalkyl amine in a weight ratio of 100:1 to 1:1. The amine can have the formula:



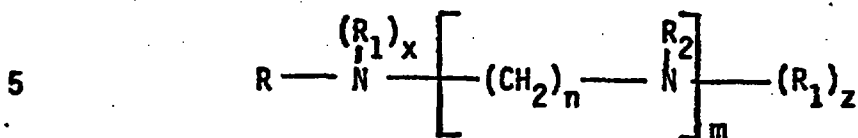
wherein R_1 is $\text{C}_1\text{-C}_{16}$ alkyl; R_2 is H or $\text{C}_1\text{-C}_{16}$ alkyl; $\text{R}_1 + \text{R}_2$ have 6-20 carbon atoms; R_4 is H or methyl; m, n, and o, are each 0 to 3 and A is bridging group such as



wherein R_3 is H or methyl; x is 2 to 6; y is 1 to 3; and p is 0 to 3; the sum of m to p being 1 to 5.5, and preferably 1 to 2. See also German Patent Document 2,165,900 to Henkel, published July 5, 1973, which discloses a washing agent for graying prevention formed by the reaction product of a PEI with an alkylglycidylether and ethylene oxide (2-hydroxyethyl moiety at each reactive site when ethoxylated).

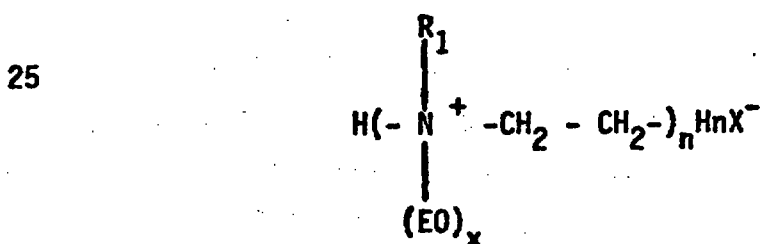
European Patent Application 42,187 to Koster, published December 23, 1981, discloses detergent compositions having enhanced soil release and cleaning properties. These compositions contain from about 2% to about 60% by weight of a detergent

surfactant (e. g. anionic) and from 0.1% to 1.2% by weight of a polyamine. This polyamine has the formula:

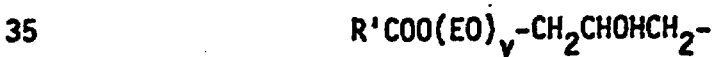


wherein R is a C₁₀ to C₂₂ alkyl or alkenyl group; R₁ is ethylene-oxide/propylene oxide; R₂ can be (R₁)_y; x, y, and z are numbers
 10 such that their sum is from 2 to about 25; n is from 1 to about 6; and m is from 1 to about 9. Preferred polyamines are those where R₁ is ethylene oxide, R₂ is ethylene oxide, n is 2 or 3, m is 1 to 3, and x, y, z, are each 1 to 4 with their sum being from 3 to 18. Examples 6 and 7 disclose ethoxylated N-hydrogenated tallow-
 15 propylene - 1,3-diamines, where the sum of x, y, and z are 7 and 12, respectively.

U. S. Patent 3,838,057 to Barnes et al., issued September 24, 1974, discloses toilet bars containing ethoxylated quaternary ammonium compounds, including ethoxylated, quaternized PEIs taught
 20 to be useful in the detergent, textile, and polymer industries, as anti-static and softening agents. These ethoxylated quaternized PEIs have the formula:



30 wherein R₁ is a compatible quaternary nitrogen substituent; n is at least 2; x is from 3 to 40; and X⁻ is a compatible anion. Preferred compounds are those where R₁ is a C₈ - C₂₂ alkyl group or the group:



where R' is a C₈-C₂₂ alkyl group and y is from 3 to 40. See also U.S. Patent 4,179,382 to Rudkin et al., issued December 18, 1979; U.S. Patent 4,152,272 to Young, issued May 1, 1979; and European Patent Application 2,085 to Rudkin et al., published May 30, 1979, which disclose ethoxylated quaternized polyamines having C₁₀ to C₂₄ alkyl or alkenyl groups attached to one of the nitrogen atoms useful as fabric softeners.

There are several patents which disclose detergent compositions, shampoo compositions and the like containing slightly ethoxylated PEIs (ethylene oxide:PEI weight ratio of 4:1 or less) to enhance the deposition and retention of particulate substances such as antimicrobials. See, for example, U.S. Patent 3,489,686 to Parran, issued January 13, 1970; U.S. Patent 3,580,853 to Parran, issued May 25, 1971; British Patent Specification 1,111,708 to Procter & Gamble published May 1, 1968; U.S. Patent 3,549,546 to Moore, issued December 22, 1970; and U.S. Patent 3,549,542 to Holderby, issued December 22, 1970.

DISCLOSURE OF THE INVENTION

The present invention relates to a water-soluble ethoxylated monoamine compound having clay soil removal/anti-redeposition properties and which has the general formula $N(L)_3$, wherein each L is $-(CH_2CH_2O)_nH$ and wherein each n is at least 12.

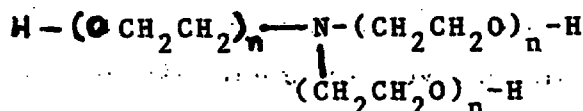
In use, the ethoxylated monoamine compounds are incorporated in detergent compositions at a level of from about 0.05 to about 95% by weight as described in GB-A-2133415.

In addition to the ethoxylated amines, the detergent compositions further comprise from about 1 to about 75% by weight of a nonionic, anionic, ampholytic, zwitterionic or cationic detergent surfactant or mixture thereof. In addition to these detergent surfactants, the detergent composition can optionally comprise from 0 to about 80% by weight of a detergent builder.

The ethoxylated amines of the present invention provide clay soil removal benefits while being anionic detergent surfactant compatible. At most wash pH's, it is believed that the nitrogen atoms of these compounds are partially protonated. The resulting positively charged centers (and remaining polar nitrogen atoms) are believed to aid in the adsorption of the compound onto the negatively charged layers of the clay particle. It is also believed that the hydrophilic ethoxy units of the compound swell the clay particle so that it loses its cohesive character and is swept away in the wash water.

The anti-redeposition benefits provided by these ethoxylated amines are also believed to be due to the formation of positively charged centers which, together with the remaining polar nitrogens, aid in its adsorption onto soil suspended in the wash water. As more and more of these compounds adsorb onto the suspended soil, it becomes encased within a hydrophilic layer provided by the attached ethoxy units. As such, the hydrophilically encased soil is prevented from redepositing on fabrics, in particular hydrophobic fabrics such as polyester, during the laundering cycle.

The ethoxylated monoamines herein have the formula



wherein n is defined as before. For preferred ethoxylated monoamines, n is at least 15, with a typical range of from 15 to 35.

The level at which the ethoxylated amine(s) can be present in the detergent compositions herein can vary depending upon the compounds used, the particular detergent formulation (liquid, granular) and the benefits desired. These compositions can be used as laundry detergents, laundry additives, and laundry pretreatments. Generally, the ethoxylated amines can be included in an amount of from about 0.05 to about 95% by weight of the composition, with the usual range being from 0.1 to about 10% by weight for the laundry detergents. In terms of benefits achieved, preferred detergent compositions can comprise from about 0.5 to about 5% by weight of the ethoxylated compounds of the present invention. Typically, these preferred compositions comprise from about 1 to about 3% by weight of these compounds. These compounds are normally present at a level that provides from about 2 ppm to about 200 ppm, preferably from about 10 ppm to about 100 ppm, of the compound in the wash solution at recommended U.S. usage levels, and normally from about 30 ppm to about 1000 ppm, preferably from about 50 ppm to about 500 ppm for European usage levels.

Methods for Making Ethoxylated Amines

The ethoxylated compounds of the present invention can be prepared by standard methods for ethoxylating amines, preferably by starting with a 2-hydroxyethyl amine such as triethanolamine (TEA). The appropriate amount of ethylene oxide is then condensed with the

2-hydroxyethylamines using an alkali metal (e.g., sodium, potassium) hydride or hydroxide as the catalyst to provide the respective ethoxylated amines. The total degree of ethoxylation per reactive site (n) can be determined according to the following formula:

$$\text{Degree of Ethoxylation} = E/(A \times R)$$

wherein E is the total number of moles of ethylene oxide condensed (including hydroxyethylation), A is the number of moles of the starting amine, and R is the number of reactive sites for the starting amine (3 for monoamines).

A representative synthesis of ethoxylated amines of the present invention is as follows:

Example 1

Dried triethanolamine (M.W. 149,89.4 g. 0.6 moles) was catalyzed with 6.32 g. (0.0451 moles) of freshly prepared 40% potassium hydroxide solution under argon. Water was removed by stirring at 110°-120°C under an aspirator vacuum for 0.5 hrs., then under vacuum pump for 0.5 hrs. Ethylene oxide (EO) was then added under atmospheric pressure with stirring at 118°-130°C. After 5.6 hrs., a total of 917 g. (20.84 moles) of EO had been added to give a calculated total degree of ethoxylation per reactive site of 12.58. The ethoxylated amine obtained was a dark amber mobile liquid.

Clay Soil Removal/Anti-Redeposition Properties of
Various Ethoxylated Amines

A. Experimental Method

1. Clay Soil Removal

Clay soil removal comparisons were conducted in a standard 1 litre Tergotometer employing water of 1.19 mmoles CaCO_3 /litre (7 grain hardness) (3:1 $\text{Ca}^{++}:\text{Mg}^{++}$) and a temperature of 37.8°C (100°F). Soiled swatches were washed in the Tergotometer for 10 minutes and rinsed twice with water (1.19 mmoles CaCO_3 /litre - 7 grain hardness) at 21.1°C (70°F) for 2 minutes.

65% polyester/35% cotton blend fabric was used for the swatches. The swatches were 12.7×12.7 cm (5 inch x 5 inch) in size and were soiled by dipping in aqueous slurry of local clay and subsequently baked to remove the water. The dipping and baking was repeated 5 times.

One wash employed 2000 ppm of a control liquid detergent composition containing the following surfactants:

<u>Surfactant</u>	<u>Amount (%)</u>
Sodium $\text{C}_{14}\text{-C}_{15}$ alkyl ethoxysulfate	10.8
C_{13} linear alkylbenzene sulfonic acid	7.2
$\text{C}_{12}\text{-C}_{13}$ alcohol polyethoxylate (6.5)	6.5
C_{12} alkyl trimethylammonium chloride	1.2

A second wash used the same detergent composition but also containing an ethoxylated amine at 20 ppm. Neither composition contained optical brighteners. The product washes approximated a conventional home use laundry situation. After laundering, the swatches were dried in a mini-dryer.

The swatches were graded before and after washing on a Gardner Whiteness meter reading the L, a and b coordinates. Whiteness (W) was calculated as:

$$W = \frac{7L^2 - 40Lb}{700}$$

The clay soil removal performance of each detergent composition was determined by finding the difference in whiteness (ΔW) before and after washing as:

$$\Delta W = W_{\text{after}} - W_{\text{before}}$$

The improvement in clay soil removal performance of the composition containing the ethoxylated amine was measured as the difference in W values ($\Delta^2 W$) relative to the control composition.

2. Anti-Redeposition

Anti-redeposition comparisons were conducted^t in a 5 pot Automatic Miniwasher (AMW) employing 1.19 mmoles CaCO_3 /litre (7 grain hardness) water and temperature of 35°C (95°F). Test swatches were washed for 10 minutes and rinsed twice with water (1.19 mmoles CaCO_3 /litre - 7 grain hardness) at 23.9°C (75°F) for 2 minutes.

After the AMW pots were filled with 6 litres of water each, the detergent composition to be tested (control or containing 20 ppm ethoxylated amine as in clay soil removal test) was added and agitated for 2 minutes. A background soil mixture (200 ppm artificial body soil, 100 ppm vacuum cleaner soil and 200 ppm clay soil) was then added and agitated for an additional 3 minutes. Three 12.7 cm (5 inch) square test swatches (50% polyester/50% cotton T-shirt material) were then added, along with two 80% cotton/20% polyester terry clothes and two 27.9 cm (11 inch) square swatches of 100% polyester knit fabric. The 10 minute wash cycle commenced at this point.

Following the rinse cycle, the test swatches were dried in a mini-dryer. Gardner Whiteness meter readings (L, a and b) were then determined for the three test swatches. Anti-redeposition performance (ARD) was then calculated according to the following equation:

$$ARD = \frac{7L^2 - 40Lb}{700}$$

The ARD values for the three test swatches were then averaged. The improvement in anti-redeposition performance of the composition containing the ethoxylated amine was measured as the difference in ARD values (Δ ARD) relative to the control composition.

B Test Results

The results from testing the clay-soil removal and anti-redeposition performance of ethoxylated triethanolamine (TEA) is shown in the following table:

<u>Amine Type</u>	<u>Amine M.W.</u>	<u>Degree of Ethoxylation per reactive site (n)</u>	<u>Δ^2W</u>	<u>ΔARD</u>
TEA	149	5	1.6	2.4
		12	4.6	5.0
		17	7.4	-
		26	7.6	11.8
		35	7.4	-

For comparison, PEG 6000 (polyethylene glycol having M.W. of 6000) has a Δ^2W value of 4.9 and a ΔARD value of 8.9.



CLAIMS

1. A water-soluble ethoxylated monoamine compound having clay soil removal/anti-redeposition properties and which has the general formula $N(L)_3$, wherein ~~each~~ L represents $-(CH_2CH_2O)_nH$ and wherein ~~each~~ n is at least 12.

2. A compound according to Claim 1 wherein ~~each~~ n is at least 15.

3. A compound according to Claim 2 wherein ~~each~~ n is from 15 to 35.
