

Description

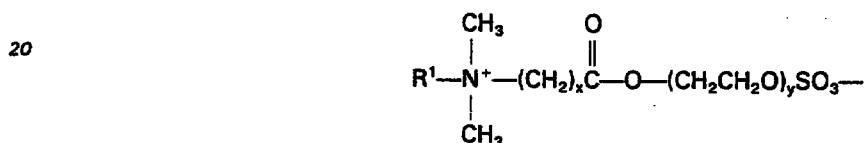
TECHNICAL FIELD

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

5 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.

10 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.

15 One class of clay-soil removal compounds which appears to work according to this model are the polyethoxylated 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:



25 wherein R¹ is a C₁₄—C₂₀ 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 polyoxyalkylene 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).

30 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 from 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.

35 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.

40 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), 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 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 surfactant.

45 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, 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.

50 European Patent Application 0112593, to J. M. Vander Meer filed December 14, 1983 and published 04.07.84, discloses detergent compositions which contain water-soluble ethoxylated amines having clay

soil removal/anti-redeposition properties. These compounds are selected from ethoxylated monoamines, ethoxylated diamines, ethoxylated polyamines, ethoxylated amine polymers and mixtures thereof.

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

5 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.

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

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

It is yet an additional object of the present invention to provide compounds useful in detergent compositions which are chlorine bleach compatible.

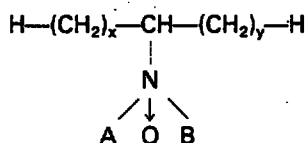
These and further objects of the present invention are hereinafter disclosed.

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BACKGROUND ART

U.S. Patent 3,457,312 to Miller et al., issued July 22, 1969, discloses alkoxyated amine oxides of secondary-alkyl and cycloalkylamines useful as detergents for dishwashing and shampooing, as surfactants, and as foam boosters. The amine oxides can have the formula:

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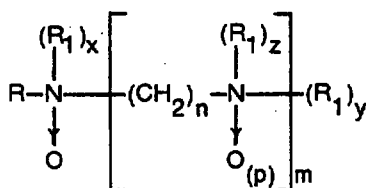


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wherein A and B are polyethylene or polypropylene oxide moieties having from 1 to 50 oxyalkylene units; and x and y are integers having a sum of from 2 to 40. The compound N,N-bis(polyethoxylated[2—100 moles])—secondary-butylamine oxide is specifically disclosed. See also U.S. Patent 3,494,962 to Miller et al., issued February 10, 1970 (aryl-substituted aliphatic amine oxides which can have polyethoxy substituents on the nitrogen atom useful as surfactants and as components of shampoos and detergent formulations); Japanese Patent Document 7213—016 to Asahi Electro Chemical Co., published April 20, 1972 (amine oxides useful as cleansing, defoaming, emulsifying, dispersing or softening agents produced by reaction of a halogenated polyoxyalkylene containing 5—90% oxyethylene units with a C₁—C₃ dialkyl substituted amine or C₁—C₃ trialkyl substituted ethylenediamine); Japanese Patent Document 7210—3013 to Asahi Electro Chemical Co., published April 20, 1972 (amine oxides useful as detergents, bactericides, defoaming agents or lubricants produced by reaction of a sulfuric acid ester of a polyoxyalkylene glycol containing 10—90% oxyethylene units with a C₁—C₃ dialkyl substituted amine).

European Patent Application 42,188 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 and from 0.1 to 1.5% by weight of an amine oxide. This amine oxide has the formula:

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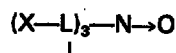
55 wherein R is C₁₀—C₂₂ alkyl or alkenyl; R₁ is C₁—C₄ alkyl, ethylene oxide or propylene oxide; n is from 1 to about 6; m is from 0 to about 6; and p is 0 or 1. Although x, y and z can each be from 1 to 10 with a total sum no greater than 25 when R₁ is ethylene oxide or propylene oxide, there is a preference that x, y or z should be no greater than 4 with a total sum of from 2 to 12. A particularly preferred class of amine oxides are those where R₁ is ethylene oxide; m is 1; n is 2 or 3; and x, y and z are each at least 1 with their sum being from 3 to 12. A preferred compound disclosed is N-hydrogenated C₁₆—C₁₈ tallow alkyl-N,N',N'-tri-(2-hydroxyethyl)-propylene-1,3-diamine oxide. See also U.S. Patent 3,412,155 to Miller et al., issued November 19, 1968 (fatty branched chain amine oxides useful as detergents, including ethoxylated amino stearyl amine dioxide); Japanese Patent Document 5137—260 to Nippon Oils and Fats, published October 25, 1980 (desizing composition containing ethylene oxide/propylene oxide condensation product of an amine oxide of a C₈—C₂₂ alkyl alkylene diamine or a C₁₀—C₃₀ trialkyl amine).

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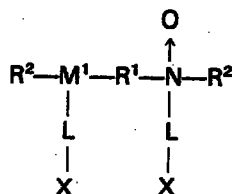
DISCLOSURE OF THE INVENTION

The present invention relates to water-soluble ethoxylated amine oxides having clay soil removal/anti-redeposition properties. These compounds are selected from the group consisting of:

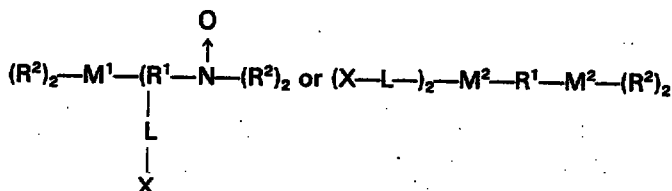
(1) ethoxylated monoamine oxides having formula I:



(2) ethoxylated amine oxides having formulas IIA, IIB or IIC:



IIA

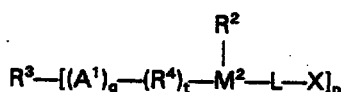


IIB

IIC

wherein M^1 is an $-\text{N} \rightarrow \text{O}$, $-\text{N}^+-\text{R}^2$ or $-\text{N}-$ group; each M^2 is an $-\text{N} \rightarrow \text{O}$, $-\text{N}^+-\text{R}^2$ or $-\text{N}-$ group, and at least one M^2 is an $-\text{N} \rightarrow \text{O}$ group;

(3) ethoxylated amine oxides having formula III:

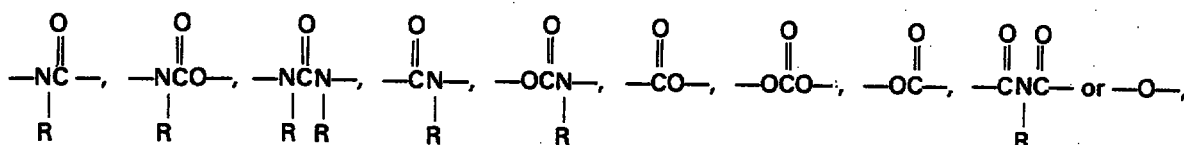


III

wherein M^2 is an $-\text{N} \rightarrow \text{O}$, $-\text{N}^+-\text{R}^2$, or $-\text{N}-$ group, and at least one M^2 is an $-\text{N} \rightarrow \text{O}$ group;

(4) ethoxylated amine oxide polymers which comprise a polymer backbone, at least 2 M^3 groups and at least one $\text{L}-\text{X}$ group, wherein M^3 is an amine oxide group attached to or integral with the backbone; and L connects groups M^3 and X , or connects group X to the polymer backbone; and

(5) mixtures thereof; wherein A^1 is



R is H or C_1-C_4 alkyl or hydroxyalkyl; R^1 is C_2-C_{12} alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene or a C_2-C_3 oxyalkylene moiety having from 2 to 20 oxyalkylene units provided that no $\text{O}-\text{N}$ bonds are formed; each R^2 is C_1-C_4 alkyl or hydroxyalkyl, the moiety $-\text{L}-\text{X}$, or two R^2 together form the moiety $-(\text{CH}_2)_r-\text{A}^2-(\text{CH}_2)_s-$, wherein A^2 is $-\text{O}-$ or $-\text{CH}_2-$, r is 1 or 2, s is 1 or 2 and $r + s$ is 3 or 4; R^3 is a substituted C_3-C_{12} alkyl, hydroxyalkyl, alkenyl, aryl or alkaryl group having p substitution sites; R^4 is C_1-C_{12} alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene, or a C_2-C_3 oxyalkylene moiety having from 2 to 20 oxyalkylene units provided that no $\text{O}-\text{N}$ bonds are formed; X is a nonionic group, or a mixture of nonionic and anionic groups; L is a hydrophilic chain which contains the polyoxyalkylene moiety $-[(\text{R}^5\text{O})_m(\text{CH}_2\text{CH}_2\text{O})_n]-$, wherein R^5 is C_3-C_4 alkylene or hydroxyalkylene, and m and n are numbers such that the moiety $-(\text{CH}_2\text{CH}_2\text{O})_n-$ comprises at least 50% by weight of said polyoxyalkylene moiety; n is at least 12 for said monoamine oxides of formula I, is at least 6 for said amine oxides of formulas IIA, IIB or IIC, and is at least 3 for said amine oxides of formula III and said amine oxide polymers; p is from 3 to 8; q is 1 or 0; t is 1 or 0, provided that t is 1 when q is 1.

The present invention further relates to detergent composition which comprise from 0.05 to 95% by weight of these amine oxides or mixtures thereof. These detergent compositions further comprise from 1

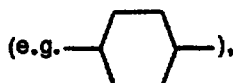
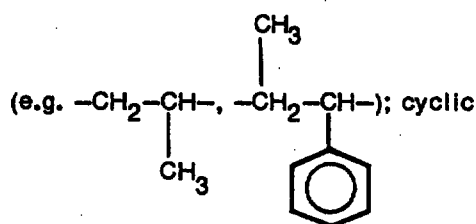
to 75% by weight of a nonionic, anionic, ampholytic, zwitterionic, or cationic detergent surfactant, or mixture thereof. In addition to these detergent surfactants, the detergent compositions can optionally comprise from 0 to 80% by weight of a detergent builder.

The amine oxides of the present invention provide clay soil removal benefits while being anionic detergent surfactant compatible. It is believed that the nitrogen atom of the amine oxide group causes adsorption of the compound onto the negatively charged layers of the clay particle. It is also believed that the hydrophilic ethoxy units attached to the compound swell the clay particle so that it loses its cohesive character and is swept away in the wash water. It is further believed that the oxidation of the nitrogen atom prevents undesirable interactions with chlorine (hypochlorite) bleach so that the compounds of the present invention are chlorine bleach compatible.

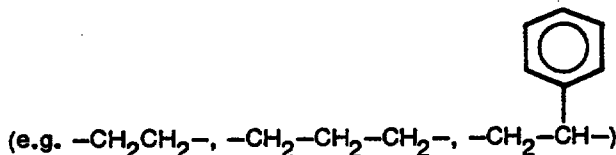
The anti-redeposition benefits provided by these amine oxides are also believed to be due to the nitrogen atom of the amine oxide group which cause it to be adsorbed onto soil suspended in the wash water. As more and more of these compounds adsorb onto the suspended soil, it becomes encased within a 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.

Amine Oxides

In the preceding formulas IIA, IIB, and IIC, R¹ can be branched



or most preferably linear



alkylene, hydroxyalkylene, alkenylene, alkarylene or oxyalkylene. R¹ is preferably C₂—C₆ alkylene. In the preceding formulas IIA, IIB, IIC and III, each R² is preferably methyl or most preferably the moiety —L—X.

In the preceding formulas I, IIA, IIB, IIC and III, X can be any compatible nonionic group, or mixture of nonionic and anionic groups. Suitable nonionic groups include C₁—C₄ alkyl or hydroxyalkyl ester or ether groups, preferably the acetate ester or methyl ether, respectively; hydrogen (H); or mixtures thereof. The particularly preferred nonionic group is H. With regard to anionic groups, COO⁻, PO₃⁻² and SO₃⁻ are suitable. The preferred anionic group is SO₃⁻. For preferred compounds, X is a nonionic group and preferably H.

In the preceding formulas I, IIA, IIB, IIC and III, hydrophilic chain L usually consists entirely of the polyoxyalkylene moiety $-(\text{R}^5\text{O})_m(\text{CH}_2\text{CH}_2\text{O})_n-$. The moieties $-(\text{R}^5\text{O})_m-$ and $-(\text{CH}_2\text{CH}_2\text{O})_n-$ of the polyoxyalkylene moiety can be mixed together or preferably form blocks of $-(\text{R}^5\text{O})_m-$ and $-(\text{CH}_2\text{CH}_2\text{O})_n-$ moieties. R⁵ is preferably C₃H₇ (propylene); m is preferably from 0 to 5 and is most preferably 0, i.e. the polyoxyalkylene moiety consists entirely of the moiety $-(\text{CH}_2\text{CH}_2\text{O})_n-$. The moiety $-(\text{CH}_2\text{CH}_2\text{O})_n-$ preferably comprises at least 85% by weight of the polyoxyalkylene moiety and most preferably 100% by weight (m is 0).

In the preceding formulas IIA, IIB, IIC, and III, M¹ and each M² are preferably an



group. However, because oxidation of the



groups is sometimes not complete in the formation of the amine oxides, M¹ and M² can also be



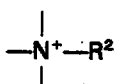
groups. For improved bleach compatibility, it is desirable to minimize the number of the unoxidized



groups. For this purpose, all or some of the



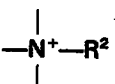
groups remaining after oxidation can be quaternized to



groups. Initially, some of the



groups can be quaternized to



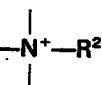
groups with the remaining unquaternized



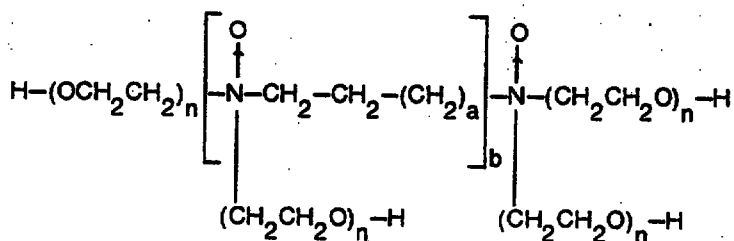
groups being oxidized to



groups. The positive charge of these



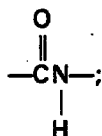
groups is offset by the appropriate number of counter anions. Suitable counter anions include Cl⁻, Br⁻, SO₃⁻², SO₄⁻², PO₄⁻², MeOSO₃⁻ and the like. Particularly preferred counter anions are Cl⁻ and Br⁻. Preferred ethoxylated mono- and diamine oxides (formulas I and IIA) have the formula I—II:



I—II

wherein n is defined as before; a is from 0 to 4 (e.g. ethylene, propylene, hexamethylene); b is 1 or 0. For preferred monoamine oxides (b = 0), n is preferably at least 15, with a typical range of from 15 to 35. For preferred diamine dioxides (b = 1), n is at least 12 with a typical range of from 12 to 42.

In the preceding formula III, R³ (linear, branched or cyclic) is preferably a substituted C₃—C₆ alkyl, hydroxyalkyl or aryl group; A¹ is preferably



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n is preferably at least 12, with a typical range of from 12 to 42; p is preferably from 3 to 6. When R³ is a substituted aryl or alkaryl group, q is preferably 1 and R⁴ is preferably C₂—C₃ alkylene. When R³ is a substituted alkyl, hydroxyalkyl, or alkenyl group, and when q is 0, R⁴ is preferably a C₂—C₃ oxyalkylene moiety; when q is 1, R⁴ is preferably C₂—C₃ alkylene.

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These ethoxylated amine oxides of formula III (preferably polyamine oxides wherein three or more M² are

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groups) can be derived from polyamino amides such as:

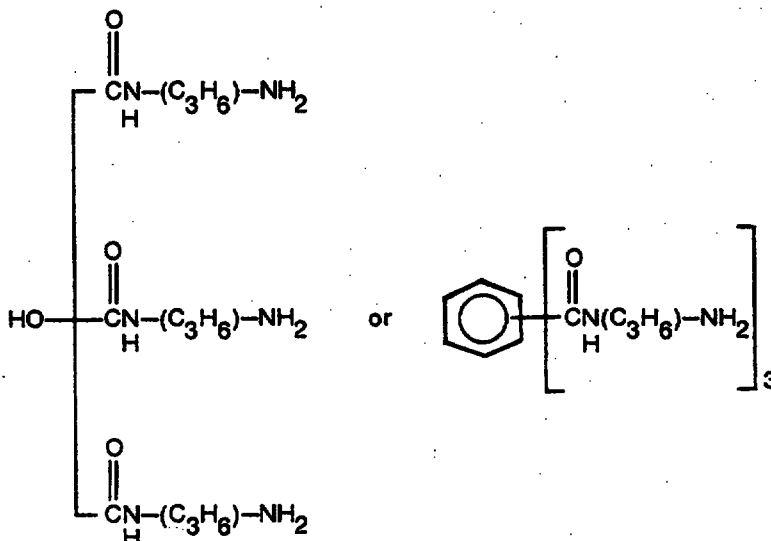
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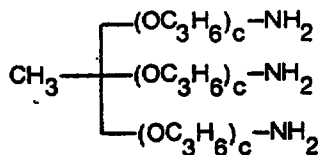
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These ethoxylated amine oxides of formula III can also be derived from polyaminopropyleneoxide derivatives such as:

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wherein each c is a number from 2 to 20.

Methods for Making Amine Oxides

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The mono-, di- and polyamine oxides of the present invention (compounds based on formulas I, IIA, IIB, IIC and III) can be prepared by standard methods for ethoxylating and oxidizing amines. There is preferably an initial step of condensing sufficient ethylene oxide to provide 2-hydroxyethyl groups at each reactive site (hydroxyethylation). This initial step can be omitted by starting with a 2-hydroxyethyl amine, e.g. triethanolamine (TEA). The appropriate amount of ethylene oxide is then condensed with these 2-hydroxyethylamines using an alkali metal (e.g., sodium, potassium), or a hydride or hydroxide thereof, as

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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 (typically 3 for the monoamines, 4 for diamines, and $2 \times p$ for polyamines) for the starting amine. The ethoxylated amine can then be oxidized with a strong oxidizing agent such as hydrogen peroxide to form the ethoxylated amine oxide.

Representative syntheses of mono- and diamine oxides of the present invention are as follows:

Example 1

Step 1: Ethoxylation

Ethylenediamine (M.W. 60, 9.02 g., 0.15 moles) which had been dried over 3Å (0.3 nm) molecular sieves was placed in a dry flask under dry argon. The flask was swept with ethylene oxide (EO) with rapid stirring. The temperature of the oil bath heating the flask was raised from 25°C to 110°C over a time period of 2.75 hrs. During this hydroxyethylation, 29.2 g. of EO was taken up for a degree of ethoxylation of 1.11.

A 40% KOH solution (2.9 g.) was added to the hydroxyethylated diamine and stirred under a vacuum for 1.25 hrs. at 110°C to remove water. A 23 g. portion of this mixture was removed and the remainder (14.2 g., 0.056 moles) reacted with additional EO swept into the flask. The flask was heated by a 103°–122°C temperature oil bath with moderately fast stirring for about 13 hrs. The resulting brown waxy solid had taken up 239.4 g. of EO for a total degree of ethoxylation of 25.3.

Step 2: Oxidation

The ethoxylated diamine from Step 1 (30.4 g., 0.0067 moles) and distilled water (30.5 ml.) were added together. This solution was adjusted to pH 8 with 1N HCl. A 33.5% H_2O_2 solution (1.6 g., 0.016 moles) was then added. The reaction mixture was then heated with stirring for 15 hrs. in a 70°C temperature water bath. More 33.5% H_2O_2 solution (0.07 g.) was then added to the reaction mixture. Stirring was continued at 65°C for 2 hrs. Six 3.2 mm alumina pellets impregnated with 0.5% platinum were added to the mixture which was permitted to stand at room temperature. See method disclosed in Swern, *Organic Peroxides*, Vol. 1, (1970), p. 501. Complete destruction of H_2O_2 was evidenced by the cessation of oxygen gas evolution. The pellets were removed and the mixture was concentrated on a rotary evaporator to 80% ethoxylated diamine oxide assuming a yield of 30.6 g (0.0067 moles). Amine oxide analysis according to method of Brooks et al., *Anal. Chem.*, Vol. 31, (1959), p. 561 indicated that 71.4% of the tertiary amine groups had been oxidized.

Example 2a

Step 1: Ethoxylation

Dried triethanolamine (TEA) (M.W. 17, 16.0 g., 0.11 moles) is catalyzed with 60% NaH in mineral oil (0.5 g., 0.013 moles). Ethylene oxide (EO) is then added under atmospheric pressure with stirring at 150°–170°C. After 23 hrs., 8.38 moles of EO is added to give a calculated total degree of ethoxylation of 26.1. The ethoxylated TEA is a light brown waxy solid.

Step 2: Oxidation

The ethoxylated TEA from step 1 (34.5 g., 0.01 moles) and distilled water (70 ml.) are placed in a flask. The solution is adjusted to pH 10 with 1N HCl. A 30% H_2O_2 solution (1.3 g., 0.011 mole equiv.) is added and the reaction mixture is then stirred at 65°C for 6 hours. A dozen 3.2 mm alumina pellets impregnated with 0.5% platinum are then added to the mixture which is permitted to stand at 65°C with occasional stirring until a very low peroxide titration is obtained. This mixture containing the ethoxylated monoamine oxide can be concentrated to an 80% solution.

Example 2b

Step 1: Ethoxylation

1,5-hexamethylenediamine (M.W. 116, 100 g., 0.86 moles) is placed in a flask and heated under argon to 85°C. Ethylene oxide (EO) is bubbled into the flask. The reaction temperature is gradually raised to 120°C over a time period of about 7.5 hours and is then raised briefly to 158°C and is cooled back to 100°C. 4 moles of EO are incorporated at this point.

Sodium spheres (1.24 g., 0.05 moles) are added and the reaction mixture is stirred overnight after which the sodium is consumed. The addition of EO is resumed and the reaction temperature is raised to 120°C. After about 3 hours, 10 moles of EO are incorporated per mole of the diamine. An additional portion of sodium spheres (3.6 g., 0.15 moles) is added and ethoxylation is continued. The temperature is allowed to rise to 125°–130°C. Ethoxylation is continued for about 22 hours. The reaction is terminated when 96 moles of EO is taken up per mole of the diamine to give a total degree of ethoxylation of 24.

Step 2: Oxidation

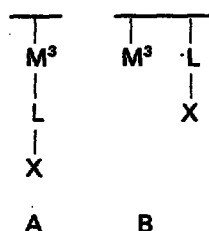
The ethoxylated diamine from step 1 (43.4 g., 0.01 moles) and distilled water (87 ml.) are placed in a flask. The solution is adjusted to pH 10 with 1N HCl. A 30% H_2O_2 solution (2.5 g., 0.022 mole equiv.) is added and the reaction mixture is then stirred at 65°C for 6 hours. A dozen 3.2 mm alumina pellets impregnated with 0.5% platinum are added to the mixture which is permitted to stand at 65°C with occasional stirring until a very low peroxide titration is obtained. This mixture containing the ethoxylated diamine oxide can be concentrated to an 80% solution.

Amine Oxide Polymers

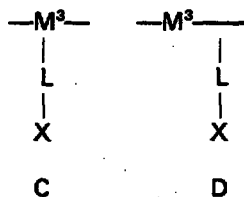
The water-soluble amine oxide polymers of the present invention comprise a polymer backbone, at least 2 M^3 groups and at least one $\text{L}-\text{X}$ group, wherein M^3 is an amine oxide group attached to or integral with the backbone; X is a nonionic group, or a mixture of nonionic and anionic groups; and L is a hydrophilic chain connecting groups M^3 and X, or connecting X to the polymer backbone.

As used herein, the term "polymer backbone" refers to the polymeric moiety to which groups M^3 and $\text{L}-\text{X}$ are attached to or integral with. Included within this term are oligomer backbones (2 to 4 units), and true polymer backbones (5 or more units).

As used herein, the term "attached to" means that the group is pendent from the polymer backbone, examples of which are represented by the following general structures A and B:

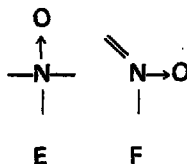


As used herein, the term "integral with" means that the group forms part of the polymer backbone, examples of which are represented by the following general structures C and D:



Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has clay soil removal/anti-redeposition properties. Suitable polymer backbones can be derived from the polyurethanes, the polyesters, the polyethers, the polyamides, the polyimides and the like, the polyacrylates, the polyacrylamides, the polyvinylethers, the polyethylenes, the polypropylenes and like polyalkylenes, the polystyrenes and the like, polyalkarylenes, the polyalkyleneamines, the polyalkyleneimines, the polyvinylamines, the polyallylamines, the polydiallylamines, the polyvinylpyridines, the polyaminotriazoles, polyvinyl alcohol, the aminopolyureylenes, and mixtures thereof.

M^3 can be any compatible amine oxide group. The amine oxide group can be represented by the following general structures E and F.



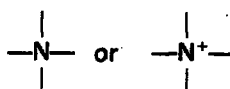
Particularly preferred M^3 groups are those represented by general structure E. The amine oxide group is preferably positioned close to or integral with the polymer backbone.

For the amine oxide polymers, X can be any compatible nonionic group, or mixture of nonionic and anionic groups. Suitable nonionic groups include C_1-C_4 alkyl or hydroxyalkyl ester or ether groups, preferably the acetate ester or methyl ether, respectively; hydrogen (H); or mixtures thereof. The particularly preferred nonionic group is H. With regard to anionic groups, COO^- , PO_3^{2-} and SO_3^- are suitable. The particularly preferred anionic group is SO_3^- . A mixture of from 0 to 25% anionic groups and from 75 to 100% nonionic groups provides suitable clay soil removal/anti-redeposition properties. A

mixture of from 0 to 10% anionic groups and from 90 to 100% nonionic groups provides the preferred properties. Most preferably, X is 100% nonionic groups which are preferably H.

The amine oxide polymers of the present invention normally have a ratio of amine oxide groups M^3 to groups X of 1:1. However, for example, by appropriate copolymerization of tertiary amine group containing monomers and L—X group containing monomers, and/or oxidation of the resulting polymer to form the amine oxide groups, the ratio of amine oxide groups M^3 to groups X can be varied. The ratio of groups M^3 to groups X can usually range from 2:1 to 1:10. In preferred amine oxide polymers, the ratio is from 1:1 to 1:5. The polymers formed from such copolymerization are typically random, i.e. the monomers copolymerize in a nonrepeating sequence.

The units which contain groups M^3 and groups L—X can comprise 100% of the amine oxide polymers of the present invention. However, inclusion of other units in the polymers is also permissible. Examples of other units include acrylamides, vinyl ethers, and those containing unquaternised or quaternized tertiary amine groups (M') having an



group, respectively. (The positive charge of the



groups is offset by the appropriate number of counter anions such as Cl^- , Br^- , SO_3^{-2} , SO_4^{-2} , PO_4^{-2} , $MeOSO_3^-$ and the like. For improved bleach compatibility, the number of

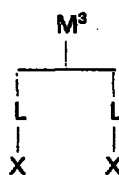


groups is desirably minimized). These other units can comprise from 0 to 90% of the polymer (from 10 to 100% of the polymer being units containing M^3 and L—X groups, including $M'-L-X$ groups). Normally, these other units comprise from 0 to 50% of the polymer (from 50 to 100% of the polymer being units containing M^3 and L—X groups).

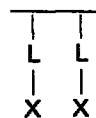
The number of groups M^3 and L—X each usually ranges from 2 to 200. Typically, the number of groups M^3 and L—X are each from 3 to 100. Preferably, the number of groups M^3 and L—X are each from 3 to 40.

Other than moieties for connecting groups M^3 and X, or for attachment to the polymer backbone, hydrophilic chain L usually consists entirely of the polyoxyalkylene moiety $[(R^5O)_m(CH_2CH_2O)_n]-$. The moieties $-(R^5O)_m-$ and $-(CH_2CH_2O)_n-$ of the polyoxyalkylene moiety can be mixed together, or preferably form blocks of $-(R^5O)_m-$ and $-(CH_2CH_2O)_n-$ moieties. R^5 is preferably C_3H_8 (propylene); m is preferably from 0 to 5, and most preferably 0, i.e. the polyoxyalkylene moiety consists entirely of the moiety $-(CH_2CH_2O)_n-$. The moiety $-(CH_2CH_2O)_n-$ preferably comprises at least 85% by weight of the polyoxyalkylene moiety, and most preferably 100% by weight (m is 0). For the moiety $-(CH_2CH_2O)_n-$, n is usually from 3 to 100. Preferably, n is from 12 to 42.

A plurality (2 or more) of moieties $-L-X$ can also be hooked together and attached to group M^3 or to the polymer backbone, examples of which are represented by the following general structures G and H:



G



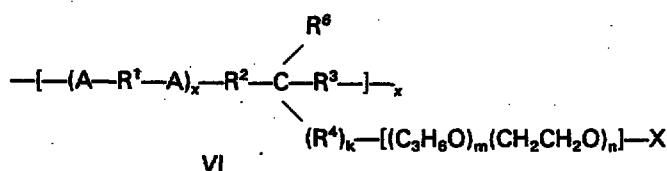
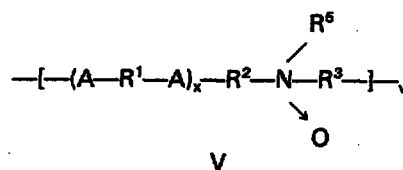
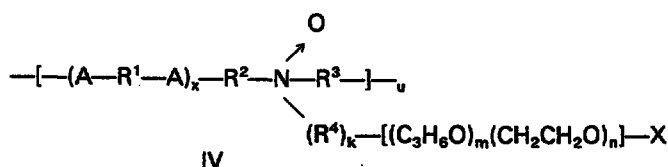
H

Structures such as G and H can be formed, for example, by reacting glycidol with group M^3 or with the polymer backbone, and ethoxylating the subsequently formed hydroxy groups.

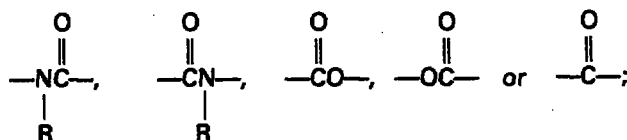
Representative classes of amine oxide polymers of the present invention are as follows:

A. Polyurethane, Polyester, Polyether, Polyamide or Like Polymers

One class of suitable amine oxide polymers are derived from polyurethanes, polyesters, polyethers, polyamides and the like. These polymers comprise units selected from those having formulas IV, V and VI:



wherein A is



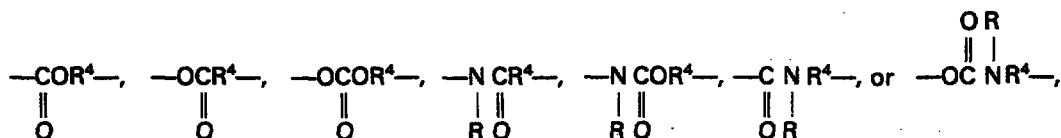
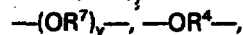
x is 0 or 1; R is H or C₁-C₄ alkyl or hydroxyalkyl; R¹ is C₂-C₁₂ alkylene, hydroxyalkylene, alkenylene, cycloalkylene, arylene or alkarylene, or a C₂-C₃ oxyalkylene moiety having from 2 to 20 oxyalkylene units provided that no O-O or O-N bonds are formed with A; when x is 1, R² is -R⁴- except when A is



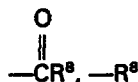
or is -(OR⁷)_y- or -OR⁴- provided that no O-O or N-O bonds are formed with A, and R³ is -R⁵- except when A is



or is (RO⁷)_y- or -OR⁴- provided that no O-O or O-N bonds are formed with A; when x is 0, R² is



and R³ is -R⁴-; R⁴ is C₁-C₁₂ alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene; R⁵ is C₁-C₄ alkyl or hydroxyalkyl; R⁶ is H, C₁-C₄ alkyl or hydroxyalkyl, or the moiety -(R⁴)_k-[(C₃H₆O)_m(CH₂CH₂O)_n]-X; R⁷ is C₂-C₃ alkylene or hydroxyalkylene; X is H,



or a mixture thereof, wherein R⁸ is C₁-C₄ alkyl or hydroxyalkyl; k is 0 or 1; m and n are numbers such that the moiety -(CH₂CH₂O)_n- comprises at least 85% by weight of the moiety -(C₃H₆O)_m(CH₂CH₂O)_n-; m is from 0 to 5; n is at least 3; y is from 2 to 20; the number of u, v and w are such that there are at least 2



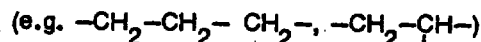
5 groups and at least 2 X groups:

In the above formulas IV, V and VI, A is preferably

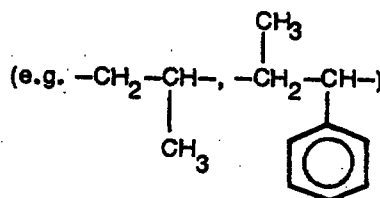


x is preferably 1; and R is preferably H.

15 R¹ can be linear



or branched



alkylene, hydroxyalkylene, alkenylene, cycloalkylene, alkarylene or oxyalkylene; when R¹ is a C₂—C₃ oxyalkylene moiety, the number of oxyalkylene units is preferably from 2 to 12; R¹ is preferably C₂—C₃ alkylene or phenylene, and most preferably C₂—C₆ alkylene (e.g. ethylene, propylene, hexamethylene). R² is preferably —OR⁴— or —(OR⁷)_y—; R³ is preferably —R⁴O— or —(R⁷O)_y—; R⁵ is preferably methyl. Like R¹, R⁴ can be linear or branched, and is preferably C₂—C₃ alkylene; R⁶ is preferably H or C₁—C₃ alkyl; R⁷ is preferably ethylene; R⁸ is preferably methyl; X is preferably H or methyl; k is preferably 0; m is preferably

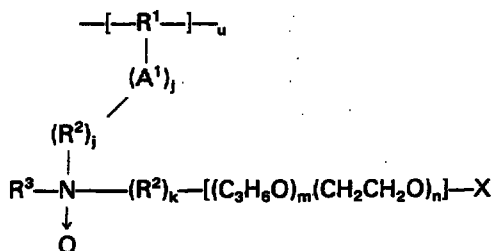
In the above formulas IV, V and VI, n is preferably at least 6 when the number of



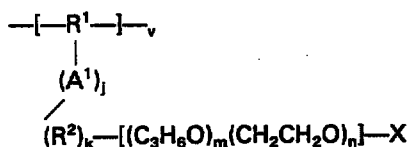
groups and X groups is 2 or 3; n is most preferably at least 12, with a typical range of from 12 to 42 for all ranges of u + v + w. For homopolymers (v and w are 0), u is preferably from 3 to 40, and is most preferably from 3 to 20. For random copolymers (u is preferably 0), v and w are each preferably from 3 to 40.

B. Polyacrylate, Polyacrylamide, Polyvinylether or Like Polymers

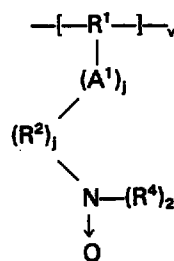
Another class of suitable amine oxide polymers are derived from polyacrylates, polyacrylamides, polyvinylethers and the like. These polymers comprise units selected from those having formulas VII, VIII and IX:



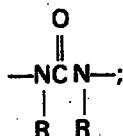
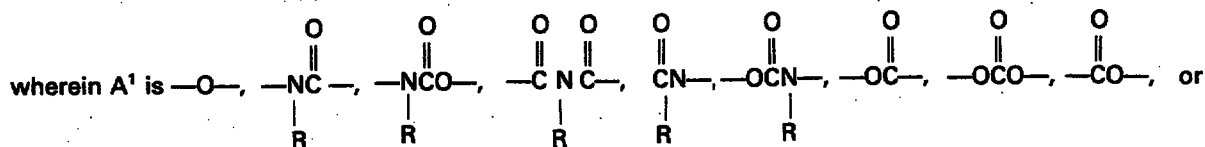
VII



VIII



IX



R is H or C₁—C₄ alkyl or hydroxyalkyl; R¹ is substituted C₂—C₁₂ alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene, or C₂—C₃ oxyalkylene; each R² is C₁—C₁₂ alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene; each R³ is C₁—C₄ alkyl or hydroxyalkyl, or the moiety $\text{---}(\text{R}^2)_k\text{---}[(\text{C}_3\text{H}_5\text{O})_m(\text{CH}_2\text{CH}_2\text{O})_n]\text{---X}$; each R⁴ is C₁—C₄ alkyl or hydroxyalkyl, or two R⁴ together form the moiety $\text{---}(\text{CH}_2)_r\text{---A}^2\text{---}(\text{CH}_2)_s\text{---}$, wherein A² is ---O--- or $\text{---CH}_2\text{---}$; X is H,

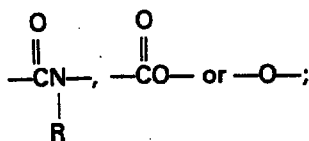


—R⁵ or a mixture thereof, wherein R⁵ is C₁—C₄ alkyl or hydroxyalkyl; j is 1 or 0; k is 1 or 0; m and n are numbers such that the moiety $\text{---}(\text{CH}_2\text{CH}_2\text{O})_n\text{---}$ comprises at least 85% by weight of the moiety $\text{---}[(\text{C}_3\text{H}_5\text{O})_m(\text{CH}_2\text{CH}_2\text{O})_n]\text{---}$; m is from 0 to 5; n is at least 3; r is 1 or 2, s is 1 or 2 and r + s is 3 or 4; the number of u, v and w are such that there are at least 2

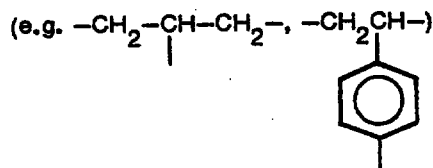


groups and at least 2 X groups.

In the above formulas VII, VIII and IX, A¹ is preferably

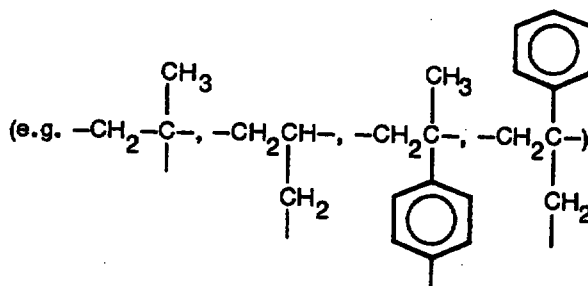


A² is preferably ---O--- ; R is preferably H. R¹ can be linear



or branched

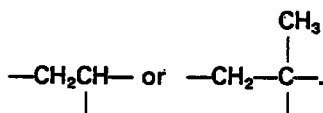
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10

substituted alkylene, hydroxyalkylene, alkenylene, alkarylene or oxyalkylene; R¹ is preferably substituted C₂—C₈ alkylene or substituted C₂—C₃ oxyalkylene, and most preferably

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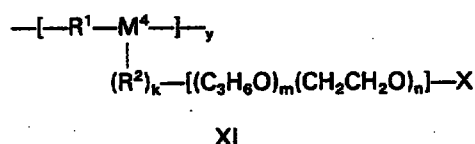
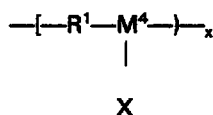


- 20 Each R² is preferably C₂—C₃ alkylene; R³ and each R⁴ are preferably methyl; R⁵ is preferably methyl; X is preferably H or methyl; j is preferably 1; k is preferably 0; m is preferably 0; r and s are each preferably 2. In the above formulas VII, VIII and IX, n, u, v and w can be varied according to the n, u, v and w for the preceding polyurethane and like polymers (formulas IV, V and VI).

25 C. Polyalkyleneamine, Polyalkyleneimine or Like Polymers

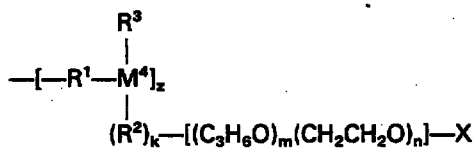
Another class of suitable amine oxide polymers are derived from polyalkyleneamines, polyalkyleneimines and the like. These polymers comprise units selected from those having formulas X, XI and XII:

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XI

35

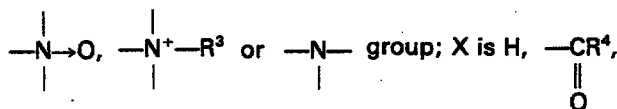


40

XII

- 45 wherein R¹ is C₂—C₁₂ alkylene, hydroxyalkylene, alkenylene, cycloalkylene, arylene or alkarylene, or a C₂—C₃ oxyalkylene moiety having from 2 to 20 oxyalkylene units provided that no O—N bonds are formed; R² is C₁—C₁₂ alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene; R³ is C₁—C₄ alkyl or hydroxyalkyl, or the moiety —(R²)_k—[(C₃H₆O)_m(CH₂CH₂O)_n—X; M⁴ is an

50



- 55 —R⁴ or a mixture thereof, wherein R⁵ is C₁—C₄ alkyl or hydroxyalkyl; k is 1 or 0; m and n are numbers such that the moiety —(CH₂CH₂O)_n— comprises at least 85% by weight of the moiety —[(C₃H₆O)_m(CH₂CH₂O)_n—; m is from 0 to 5; n is at least 3; the number of x, y and z are such that there are at least 2 M⁴ groups, at least 2

60



groups and at least 2 X groups.

- 65 In the above formulas X, XI and XII, R¹ can be varied like R¹ of the preceding polyurethane and like polymers (formulas IV, V and VI); R² is preferably C₂—C₃ alkylene; R³ is preferably methyl or the moiety

$-(R^2)_k-[(C_3H_6O)_m(CH_2CH_2O)_n]-X$; R^4 is preferably methyl; X is preferably H; k is preferably 0; m is preferably 0.

In the above formulas X, XI and XII, n is preferably at least 6 when the number of M^4 and X groups is 2 or 3; n is most preferably at least 12, with a typical range of from 12 to 42 for all ranges of $x + y + z$.

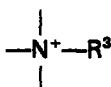
Typically, $x + y + z$ is from 2 to 40, and preferably from 2 to 20. For short chain length polymers, $x + y + z$ can range from 2 to 9 with from 2 to 9



groups and from 2 to 11 X groups. For long chain length polymers, $x + y + z$ is at least 10, with a preferred range of from 10 to 42. For the short and long chain length polymers, the M^4 groups can be a mixture of from 30 to 100%



groups, and from 0 to 70%



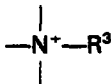
groups,



groups or mixtures thereof. Preferably, the M^4 groups comprise a mixture of from 70 to 100%



groups, and from 0 to 30%

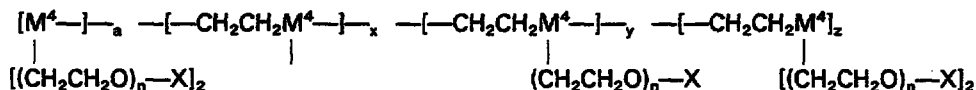


groups,



groups or mixtures thereof.

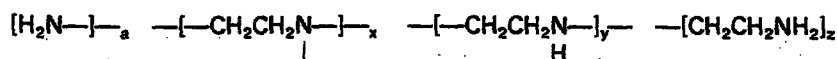
Preferred amine oxide polymers within this class are derived from the C_2-C_3 polyalkyleneamines ($x + y + z$ is from 2 to 9) and polyalkyleneimines ($x + y + z$ is at least 10, preferably from 10 to 42). Particularly preferred polyalkyleneamine oxides and polyalkyleneimine oxides are the polyethyleneamine (PEA) oxides and polyethyleneimine (PEI) oxides. These preferred amine oxide polymers have the following general formula XIII:



XIII

wherein M^4 , X , x , y , z and n are defined as before, and a is 1 or 0. Within the above formula XIII, the various units can be mixed and arranged to provide linear, branched or cyclic amine oxide polymers.

Prior to ethoxylation, the PEAs used in preparing amine oxide polymers of the present invention have the following general formula XIV:



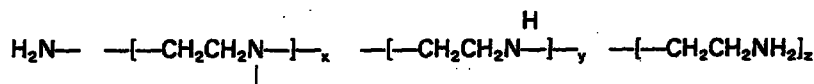
XIV

wherein $x + y + z$ is from 2 to 9, and a is 0 or 1 (molecular weight of from 100 to 400). Each hydrogen atom attached to each nitrogen atom represents an active site for subsequent ethoxylation. For preferred PEAs, $x + y + z$ is from 3 to 7 (molecular weight of from 140 to 310). These PEAs can be obtained by reactions involving ammonia and ethylene dichloride, followed by fractional distillation. The common PEAs obtained are triethylenetetramine (TETRA) and tetraethylenepentamine (TEPA). Above the pentamines, i.e., the hexamines, heptamines, octamines and possibly nonamines, the cogenerically derived mixture does not appear to separate by distillation and can include other materials such as cyclic amines and particularly piperazines; these cyclic amines can also be present in mixtures containing TETA and TEPA. There can also be present cyclic amines with side chains in which nitrogen atoms appear. See U.S. Patent 2,792,372 to

Dickson, issued May 14, 1957, which describes the preparation of PEAs.

The minimum degree of ethoxylation required for preferred clay soil removal/anti-redeposition performance can vary depending upon the number of units in the PEA. Where $y + z$ is 2 or 3, n is preferably at least 6. Where $y + z$ is from 4 to 9, suitable benefits are achieved when n is at least 3. For preferred PEA oxides, n is at least 12, with a typical range of from 12 to 42.

The PEIs used in preparing the amine oxide polymers of the present invention have a molecular weight of at least 440 prior to ethoxylation, which represents at least 10 units. Preferred PEIs used in preparing these polymers have a molecular weight of from 600 to 1800. The polymer backbone of these PEIs can be represented by the general formula XV:



XV

wherein the sum of x , y and z represents a number of sufficient magnitude to yield a polymer having the molecular weights previously specified. Although linear polymer backbones are possible, branch chains can also occur. The relative proportions of primary, secondary and tertiary amine groups present in the polymer can vary, depending on the manner of preparation. The distribution of amine groups is typically as follows:

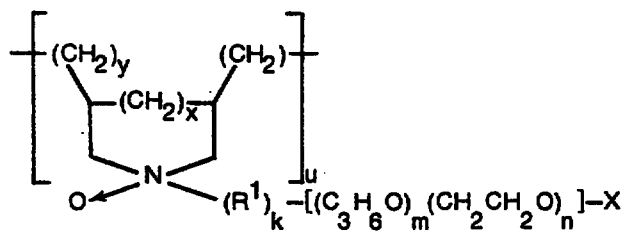
$-\text{CH}_2\text{CH}_2-\text{NH}_2$	30%
$-\text{CH}_2\text{CH}_2-\text{NH}-$	40%
$-\text{CH}_2\text{CH}_2-\text{N}-$	30%

Each hydrogen atom attached to each nitrogen atom of the PEI represents an active site for subsequent ethoxylation. These PEIs can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific methods for preparing PEIs are disclosed in U.S. Patent 2,182,306 to Ulrich et al., issued December 5, 1939; U.S. Patent 3,033,746 to Mayle et al., issued May 8, 1962; U.S. Patent 2,208,095 to Esselmann et al., issued July 16, 1940; U.S. Patent 2,806,839 to Crowther, issued September 17, 1957; and U.S. Patent 2,553,696 to Wilson, issued May 21, 1951.

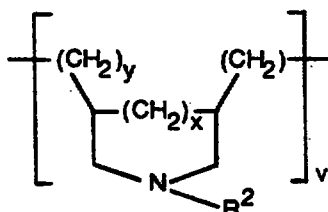
As defined in the preceding formulas, n is at least 3 for the PEI oxides. However, it should be noted that the minimum degree of ethoxylation required for suitable clay soil removal/anti-redeposition performance can increase as the molecular weight of the PEI increases, especially much beyond 1800. Also, the degree of ethoxylation for preferred polymers increases as the molecular weight of the PEI increases. For PEIs having a molecular weight of at least 600, n is preferably at least 12, with a typical range of from 12 to 42. For PEIs having a molecular weight of at least 1800, n is preferably at least 24, with a typical range of from 24 to 42.

D. Diallylamine Polymers

Another class of suitable amine oxide polymers are those derived from the diallylamines. These polymers comprise units selected from those having formulas XVI and XVII:



XVI



XVII

wherein R^1 is $\text{C}_1\text{--C}_{12}$ alkylene, hydroxyalkylene, alkylene, arylene or alkarylene; R^2 is $\text{C}_1\text{--C}_4$ alkyl or hydroxyalkyl; X is H,



---R^3 or a mixture thereof,

wherein R^3 is $\text{C}_1\text{--C}_4$ alkyl or hydroxyalkyl; k is 1 or 0; m and n are numbers such that the moiety $\text{---(CH}_2\text{CH}_2\text{O)}_n\text{---}$ comprises at least 85% by weight of the moiety $\text{[(C}_3\text{H}_6\text{O)}_m\text{(CH}_2\text{CH}_2\text{O)}_n\text{]---}$; m is from 0 to 5; n is at least 3; x is 1 or 0; y is 1 when x is 0, and 0 when x is 1; the number of u and v are such that there are at least 2



groups and at least 2 X groups.

In the above formulas XVI and XVII, R^1 is preferably $\text{C}_2\text{--C}_3$ alkylene; R^2 is preferably methyl; R^3 is preferably methyl; X is preferably H; k is preferably 0; m is preferably 0.

In the above formulas XVI and XVII, n is preferably at least 6 when the number of

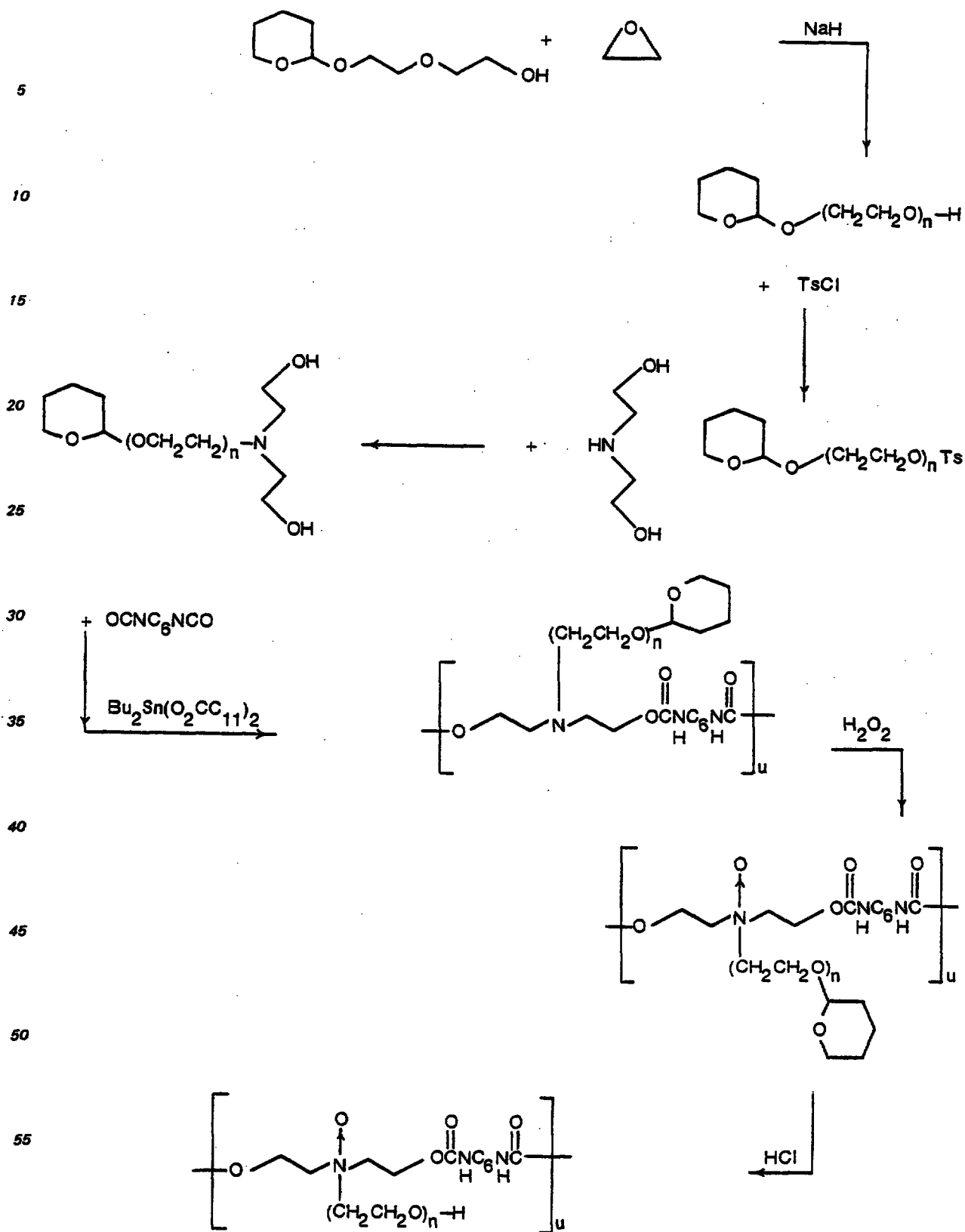


groups and X groups are each 2 or 3, n is preferably at least 12, with a typical range of from 12 to 42 for all ranges of u + v. Typically, v is 0, and u is from 2 to 40, and preferably from 2 to 20.

Methods for Making Amine Oxide Polymers

A. Polyurethane

The polyurethane versions of the present invention can be prepared according to the following general scheme.



The synthesis of one such polyurethane is described as follow:

Example 3

Step 1: Ethoxylation

- The monotetrahydropyranyl ether of diethylene glycol (1.77 moles) [Compt. Rend., 260, 1399—1401 (1965)] is ethoxylated using 5 moles % NaH to generate a catalytic amount of the corresponding alkoxide. 5 Ethoxylation is conducted at 90°—120°C until 22 moles ($n = 22$) of ethylene oxide is taken up for each mole of the starting alcohol to form the ethoxylated compound.

Step 2: Tosylation

- The ethoxylated compound from step 1 is dissolved in 1000 ml. of acetonitrile and then cooled to 10°C. 10 To this solution is added 2.7 moles of tosyl chloride dissolved in 500 ml. of acetonitrile and cooled to 10°C and then 2.9 moles of triethylamine is added. After the reaction is complete, H₂O is added to decompose the remaining tosyl chloride.

Step 3: Amination

- 15 To the reaction mixture from step 3 is added 3.4 moles of diethanolamine. After heating for 18 hrs. at 80°C, the reaction mixture is cooled and carefully acidified with HCl to a pH just above 7 and then extracted with ether. The aqueous phase is then extracted with a mixture of ether:acetonitrile (ratio of 5:2) twice. The aqueous phase is separated and then made basic with 50% NaOH. This aqueous phase is extracted with dichloromethane (2000 ml.). The lower layer is separated and then extracted 3 times with 2000 ml. portions 20 of 1/4 saturated NaCl solution while adding enough 50% NaOH solution to made the aqueous phase strongly basic (pH of about 11). The lower organic layer is stripped to give the desired aminated compound. Toluene (200 ml.) is added and the mixture is stripped again to give the desired aminated monomer.

Step 4: Polymerization

- 25 The monomer from step 3 is dissolved in chloroform free of ethanol stabilizer. The monomer is previously evacuated in a Kugelrohr at 80°—90°C under a vacuum (pressure of 1 mm. (1.33 mbar)) for at least 18 hours. The monomer in the chloroform is then dried overnight with 3Å (3×10^{-8} cm) molecular sieves and then transferred to a dry flask (equipped with mechanical stirrer) under argon. To the monomer is added dibutyltin dilaurate catalyst (0.058 mole equiv.) in chloroform under argon. To the stirred reaction 30 mixture is then added 0.7 moles of hexamethylenediisocyanate per mole of aminated monomer over a 5 minute period. The reaction mixture is stirred at room temperature for 18 hours. The chloroform is removed under a vacuum at about 70°C to give the resulting polymer.

Step 5: Oxidation and Removal of Protecting Groups

- 35 The polymer from step 5 (0.01 equivalents of titratable amino groups) and distilled water (50 ml.) are placed in a flask. The solution is then adjusted to pH 10. A 30% H₂O₂ solution (0.1 mole equiv.) is added and the reaction mixture is then stirred at 65°C for 2 hours. A dozen 3.2 mm alumina pellets impregnated with 0.5% platinum are added to the mixture which is permitted to stand at 65°C with occasional stirring until a very low peroxide titration is obtained. The pH of the mixture is then adjusted to about 4 with aqueous HCl 40 and is allowed to stand overnight to solvolyze the tetrahydropyranyl protecting group. The solution is then neutralized with NaOH and stripped to give the crude polyurethane containing amine oxide groups. This crude polyurethane is dissolved in chloroform and filtered to remove any salts. The chloroform is stripped away to give the desired, largely salt-free amine oxide polymer.

45 B. Random Copolymer of Ethoxylated Acrylate and an Amine Oxide of Methacrylamide

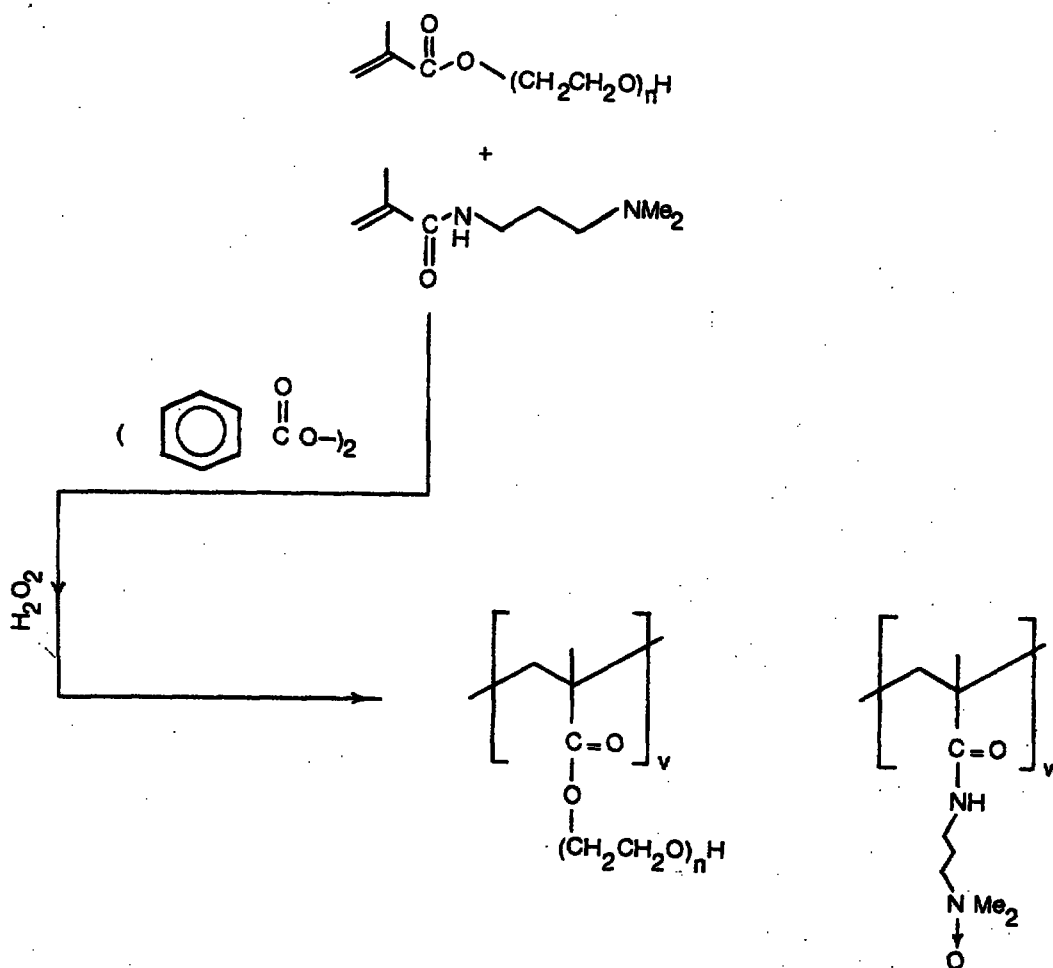
The random copolymer versions of the present invention can be prepared according to the following general scheme:

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The synthesis of one such random copolymer is described as follows:

Example 4

Decaethylene glycol monomethacrylate monomer (0.008 moles) and N-(3-dimethylaminopropyl)-methacrylamide monomer (0.011 moles) are dissolved in 40 ml. of acetonitrile. The reaction mixture is purged of oxygen by bubbling argon through it. A 0.23 g. portion of benzoyl peroxide is separately dissolved in 10 ml. of acetonitrile and similarly purged. The reaction mixture is heated to reflux and the benzoyl peroxide solution then added dropwise over 0.5 hours. Next, 0.28 g. of azobisisobutyronitrile in 5 ml. of acetonitrile is added to the reaction mixture and heating is continued overnight. The polymer obtained (0.01 equivalents of titratable amino groups) is placed with distilled water (50 ml.) in a flask. The solution pH is then maintained at pH 9. A 30% H_2O_2 solution (0.1 mole equiv.) is added and the reaction mixture is then stirred at 65°C for 2 hours. A dozen 3.2 mm (alumina pellets impregnated with 0.5% platinum) are then added to the mixture which is permitted to stand at 65°C with occasional stirring until a very low peroxide titration is obtained. The amine oxide polymer is then obtained by stripping the solvent at 50°C under a vacuum.

C. Polyethyleneamine and Polyethyleneimine Oxides

The polyethyleneamine and polyethyleneimine oxides can be prepared using standard methods for ethoxylating amines, with subsequent oxidation by H_2O_2 . Representative syntheses of such polyethyleneamine and polyethyleneimine oxides are as follows:

Example 5a

Step 1: Ethoxylation

Tetraethylenepentamine (TEPA) (M.W. 189, 94.5 g., 0.51 moles) was placed in a nominally dry flask and dried by stirring for 0.5 hrs. at 110°–120°C under vacuum (pressure less than 1 mm Hg (1.33 mbar)). The vacuum was released by drawing ethylene oxide (EO) from a prepurged trap connected to a supply tank. Once the flask was filled with EO, an outlet stopcock was carefully opened to a trap connected to an exhaust bubbler. After 10 hrs. stirring at 100–110°C, a total of 1601 g. EO was taken up to give a degree of ethoxylation of 1.04 per reactive site. In a similar apparatus, the hydroxyethylated TEPA (202.8 g., 0.41 moles) was mixed with a 40% KOH solution (10.1 g.) and stirred under a vacuum for 1 hr. at 110°C to

remove all water. The stirred reaction mixture was then swept with argon. EO was then added to the mixture as a sweep under atmospheric pressure at 110°—120°C with moderately fast stirring. After 13 hrs., 1775 g. (40.3 moles) of EO had been added to give a calculated total degree of ethoxylation of 15.1.

5 Step 2: Oxidation

The ethoxylated TEPA from step 1 (103.1 g., 0.021 moles) and distilled water (240 ml.) were added together and the solution was adjusted to pH 10 with 1*N* HCl. A 33.5% H₂O₂ solution (0.117 mole equiv.) was added and the reaction mixture was then heated by a 65°—70°C temperature water bath for 6.5 hrs. During this period, the pH of the mixture slowly dropped from 10 to about 8.5 several times; each time the
10 pH reached 8.5, it was adjusted back to 10 with dilute NaOH solution. A dozen 3.2 mm alumina pellets impregnated with 0.5% platinum were added to the mixture to destroy residual H₂O₂; the mixture was also heated at 65°—70°C for 10 hrs. to aid in this destruction. The pellets were then removed and the mixture concentrated on a rotary evaporator to 80% amine oxide polymer assuming a yield of 104.4 g. (0.021 moles). Analysis indicated that 88.2% of the tertiary amine groups had been oxidized.

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Example 5b

Step 1: Ethoxylation

By a procedure similar to that of Example 5a, PEI (21.5 g., M.W. 600, 0.4 moles) was dried at 120°C under vacuum and swept with EO until hydroxyethylation was nearly complete (5 hrs.). The
20 hydroxyethylated PEI was cooled under argon and 1.0 g (0.025 moles) of 60% NaH in mineral oil was then added. The reaction mixture was heated to about 140°C and was swept for 32 hrs. with EO until a total of 603.5 g. of EO was added which gave a calculated degree of ethoxylation of 23.2.

Step 2: Oxidation

The 23.2 ethoxylated PEI from Step 1 (15 g., 0.00087 moles) and distilled water (15 ml.) were added together and the solution adjusted to pH 8.3 with 1*N* HCl. A 30% H₂O₂ solution (0.015 mole equiv.) was added and the reaction mixture was then heated in a 65°—70°C temperature water bath for 15 hrs. The pH of the mixture is adjusted when necessary to maintain the pH within the range of 8.5—10. A dozen 3.2 mm alumina pellets impregnated with 0.5% platinum were added to the reaction mixture which was allowed to
30 stand at room temperature until oxygen evolution ceased. The pellets were then removed and the mixture was concentrated to 80% amine oxide polymer. Analysis indicated that 67.7% of the tertiary amine groups had been oxidized.

D. Diallylamine Polymers

35 Diallylamine polymer versions of the present invention can be prepared according to the following general scheme:

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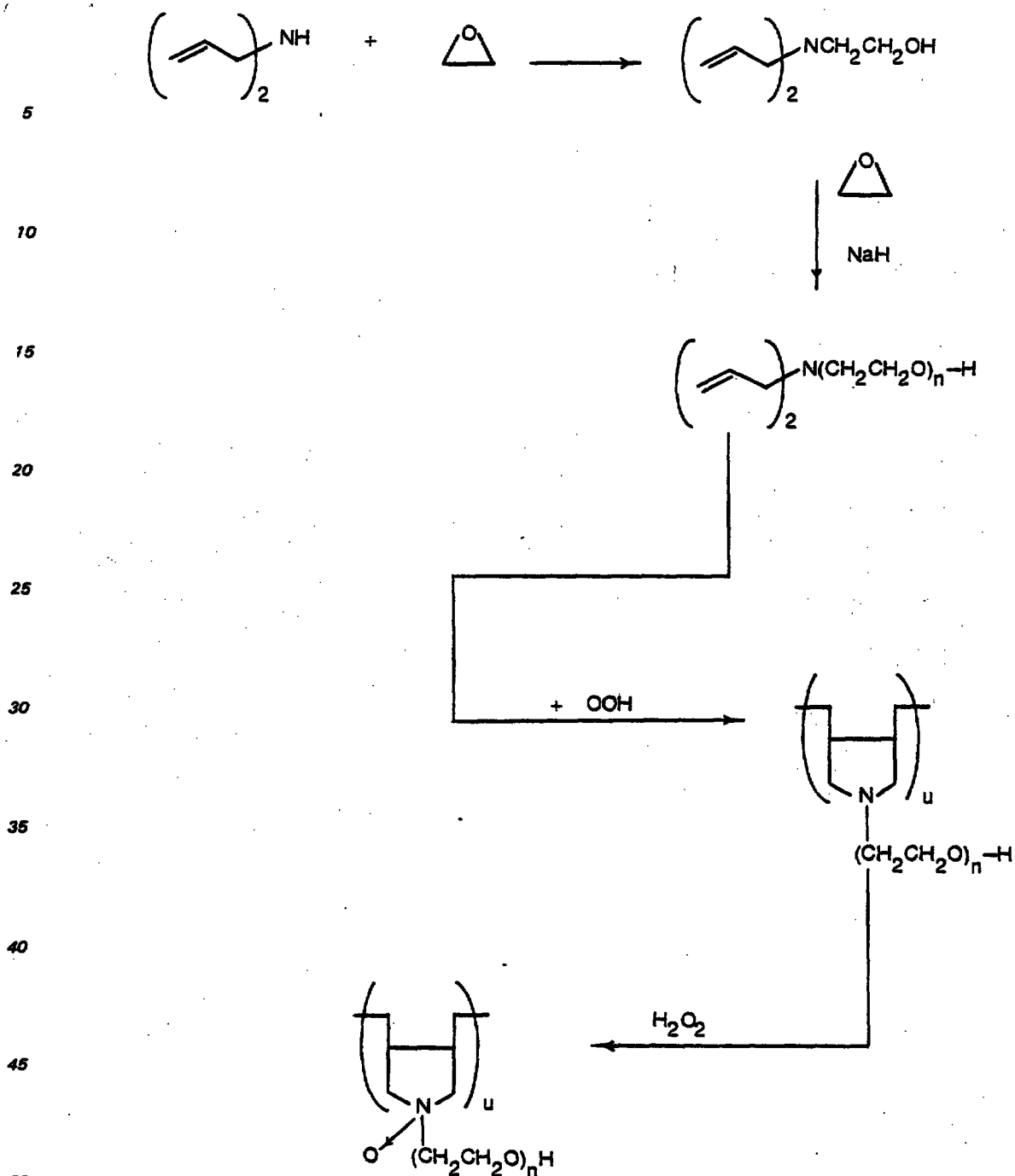
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The synthesis of one such polymer is described as follows:

Example 6

Step 1: Ethoxylation

Diallylamine (1.7 moles) is dissolved in methanol (160 ml.) under argon and then heated to 45°C. Ethylene oxide is then added for 2.5 hours. Methanol is then removed by heating the reaction mixture to 100°C *in vacuo*. To the residue is added sodium hydride in mineral oil (6.6 g., 0.17 moles) with stirring until the evolution of hydrogen has ceased. Ethylene oxide is then added until the degree of ethoxylation (n) is 7.

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Step 2: Polymerization

The ethoxylated diallylamine monomer from step 1 (20 g) is mixed with D₂O (20 ml.) and is heated to 95°C under argon for 1 hour. Tertbutylhydroperoxide (25 drops) is then added and the reaction continued at 90°C for 18 hours. Then 20 more drops of the hydroperoxide is added. After heating 3 more days, water is then removed *in vacuo* (50°—60°C at pressure of 0.1 mm (0.13 mbar)) to yield the crude polymer.

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Step 3: Oxidation

The crude diallylamine polymer from step 2 (15 g., 0.04 equivalents of titratable amino groups) and distilled water (50 ml.) are added together and the solution adjusted to pH 10 with 1N NaOH. A 30% H₂O₂ solution (0.06 mole equiv.) is added and the reaction mixture is then heated by a 65°—70°C temperature water bath for 18 hrs. The pH of the mixture is adjusted when necessary to maintain the pH within the range of 8.5—10. A dozen 3.2 min alumina pellets impregnated with 0.5% platinum are added to the reaction mixture to destroy residual H₂O₂. The pellets are then removed and the mixture is concentrated to 80% amine oxide polymer.

Detergent Compositions

The level at which the amine oxides can be present in the detergent compositions of the present invention 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. Although the detergent compositions of the present invention are normally used as is, they can also be impregnated into a suitable substrate for use. The compounds are included in an amount of from 0.05 to 95% by weight of the composition, with the usual range being from 0.1 to 10% by weight for laundry detergents. In terms of the benefits achieved, preferred detergent compositions can comprise from 0.5 to 5% by weight of the compounds of the present invention. Typically, these preferred compositions comprise from 1 to 3% by weight of these compounds. These compounds are normally present at a level that provides from 2 ppm to 200 ppm, preferably from 10 ppm to 100 ppm, of the compound in the wash solution at recommended U.S. usage levels, and normally from 30 ppm to 1000 ppm, preferably from 50 ppm to 500 ppm for European usage levels.

Detergent Surfactants

The amount of detergent surfactant included in the detergent compositions of the present invention varies from 1 to 75% by weight of the composition depending upon the detergent surfactant(s) used, the type of composition to be formulated (e.g. granular, liquid) and the effects desired. Preferably, the detergent surfactant(s) comprises from 10 to 50% by weight of the composition. The detergent surfactant can be nonionic, anionic, ampholytic, zwitterionic, cationic, or a mixture thereof:

A. Nonionic Surfactants

Suitable nonionic surfactants for use in detergent compositions of the present invention are generally disclosed in U.S. Patent 3,929,678 to Laughlin et al., issued December 30, 1975 at column 13, line 14 through column 16, line 6. Classes of nonionic surfactants included are:

1. The polyethyleneoxide condensates of alkyl phenols. These compounds include the condensation products of alkyl phenols having an alkyl group containing from 6 to 12 carbon atoms in either a straight chain or branched chain configuration with ethylene oxide, the ethylene oxide being present in an amount equal to 5 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds can be derived, for example, from polymerized propylene, diisobutylene, and the like. Examples of compounds of this type include nonyl phenol condensed with 9.5 moles of ethylene oxide per mole of nonyl phenol; dodecylphenol condensed with 12 moles of ethylene oxide per mole of phenol; dinonyl phenol condensed with 15 moles of ethylene oxide per mole of phenol; and diisooctyl phenol condensed with 15 moles of ethylene oxide per mole of phenol. Commercially available nonionic surfactants of this type include Igepal® CO-630, marketed by the GAF Corporation, and Triton® X-45, X-114, X-100, and X-102, all marketed by the Rohm & Haas Company.

2. The condensation products of aliphatic alcohols with from 1 to 25 moles of ethylene oxide. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 8 to 22 carbon atoms. Examples of such ethoxylated alcohols include the condensation product of myristyl alcohol condensed with 10 moles of ethylene oxide per mole of alcohol; and the condensation product of 9 moles of ethylene oxide with coconut alcohol (a mixture of fatty alcohols with alkyl chains varying in length from 10 to 14 carbon atoms). Examples of commercially available nonionic surfactants of this type include Tergitol® 15-S-9, marketed by Union Carbide Corporation, Neodol® 45-9, Neodol® 23-6.5, Neodol® 45-7, and Neodol® 45-4, marketed by Shell Chemical Company, and Kyro® EOB, marketed by The Procter & Gamble Company.

3. The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of these compounds has a molecular weight of from 1500 to 1800 and exhibits water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecular as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is 50% of the total weight of the condensation product, which corresponds to condensation with up to 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially available Pluronic® surfactants, marketed by Wyandotte Chemical Corporation.

4. The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, the moiety having a molecular weight of from

2500 to 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from 40% to 80% by weight of polyoxyethylene and has a molecular weight of from 5,000 to 11,000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic® compounds, marketed by Wyandotte Chemical Corporation.

5. Semi-polar nonionic detergent surfactants which include water-soluble amine oxides containing one alkyl moiety of from 10 to 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from 1 to 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from 10 to 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from 1 to 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from 10 to 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from 1 to 3 carbon atoms.

Preferred semi-polar nonionic detergent surfactants are the amine oxide detergent surfactants having the formula



- wherein R^3 is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from 8 to 22 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms or mixtures thereof; x is from 0 to 3; and each R^5 is an alkyl or hydroxyalkyl group containing from 1 to 3 carbon atoms or a polyethylene oxide group containing from one to 3 ethylene oxide groups. The R^5 groups can be attached to each other, e.g., through an oxygen or nitrogen atom to form a ring structure.

- Preferred amine oxide detergent surfactants are C_{10} — C_{18} alkyl dimethyl amine oxide and C_8 — C_{12} alkoxy ethyl dihydroxy ethyl amine oxide.

6. Alkylpolysaccharides disclosed in European Patent Application 0070074 published 19.01.1983, having a hydrophobic group containing from 6 to 30 carbon atoms, preferably from 10 to 16 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from $1\frac{1}{2}$ to 10, preferably from $1\frac{1}{2}$ to 3, most preferably from 1.6 to 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g. glucose, galactose an galactosyl moieties can be substituted for the glucosyl moieties. (Optionally the hydrophobic group is attached at the 2, 3, 4, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside.) The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6 positions on the preceding saccharide units.

- Optionally, and less desirably, there can be a polyalkylene-oxide chain joining the hydrophobic moiety and the polysaccharide moiety. The preferred alkyleneoxide is ethylene oxide. Typical hydrophobic groups include alkyl groups, either saturated or unsaturated, branched or unbranched containing from 8 to 18, preferably from 10 to 16 carbon atoms. Preferably, the alkyl group is a straight chain saturated alkyl group. The alkyl group can contain up to 3 hydroxy groups and/or the polyalkyleneoxide chain can contain up to 10, preferably less than 5, most preferably 0, alkyleneoxide moieties. Suitable alkyl polysaccharides are octyl, nonyldecyl, undecyldodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl, di-, tri-, tetra-, penta-, and hexagluco-sides, galactosides, lactosides, glucoses, fructosides, fructoses, and/or galactoses. Suitable mixtures include coconut alkyl, di-, tri-, tetra-, and pentagluco-sides and tallow alkyl tetra-, penta-, and hexagluco-sides.

- The preferred alkylpolyglycosides have the formula



- wherein R^2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 10 to 18, preferably from 12 to 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to 10, preferably 0; and x is from $1\frac{1}{2}$ to 10, preferably from $1\frac{1}{2}$ to 3, most preferably from 1.6 to 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominately the 2-position.

7. Fatty acid amide detergent surfactants having the formula:



- wherein R^6 is an alkyl group containing from 7 to 21 (preferably from 9 to 17) carbon atoms and each R^7 is selected from the group consisting of hydrogen, C_1 — C_4 alkyl, C_1 — C_4 hydroxyalkyl, and $-(\text{C}_2\text{H}_4\text{O})_x\text{H}$ where x varies from 1 to 3.

Preferred amides are C_8 — C_{20} ammonia amides, monoethanolamides, diethanolamides, and isopropanol amides.

B. Anionic Surfactants

5 Anionic surfactants suitable in detergent compositions of the present invention are generally disclosed in U.S. Patent 3,929,678 to Laughlin et al., issued December 30, 1975 at column 23, line 58 through column 29, line 23.

Classes of anionic surfactants included are:

1. Ordinary alkali metal soaps such as the sodium, potassium, ammonium and alkylammonium salts
10 of higher fatty acids containing from 8 to 24 carbon atoms, preferably from 10 to 20 carbon atoms.

2. Water-soluble salts, preferably the alkali metal, ammonium and alkylammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from 10 to 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.)

15 Examples of this group of anionic surfactants are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_8 — C_{18} carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil; and the sodium and potassium alkylbenzene sulfonates in which the alkyl group contains from 9 to 15 carbon atoms, in straight chain or branched chain configuration, e.g., those of the type described in U.S. Patents 2,220,099 and 2,477,383. Especially valuable are linear straight
20 chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from 11 to 13, abbreviated as C_{11} — C_{13} LAS.

Preferred anionic surfactants of this type are the alkyl polyethoxylate sulfates, particularly those in which the alkyl group contains from 10 to 22, preferably from 12 to 18 carbon atoms, and wherein the polyethoxylate chain contains from 1 to 15 ethoxylate moieties preferably from 1 to 3 ethoxylate moieties.
25 These anionic detergent surfactants are particularly desirable for formulating heavy-duty liquid laundry detergent compositions.

Other anionic surfactants of this type include sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates containing
30 from 1 to 10 units of ethylene oxide per molecule and wherein the alkyl groups contain from 8 to 12 carbon atoms; and sodium or potassium salts of alkyl ethylene oxide ether sulfates containing 1 to 10 units of ethylene oxide per molecule and wherein the alkyl group contains from 10 to 20 carbon atoms.

Also included are water-soluble salts of esters of alphasulfonated fatty acids containing from 6 to 20 carbon atoms in the fatty acid group and from 1 to 10 carbon atoms in the ester group; water-soluble salts
35 of 2-acyloxy-alkane-1-sulfonic acids containing from 2 to 9 carbon atoms in the acyl group and from 9 to 23 carbon atoms in the alkane moiety; alkyl ether sulfates containing from 10 to 20 carbon atoms in the alkyl group and from 1 to 30 moles of ethylene oxide; water-soluble salts of olefin sulfonates containing from 12 to 24 carbon atoms; and beta-alkyloxy alkane sulfonates containing from 1 to 3 carbon atoms in the alkyl group and from 8 to 20 carbon atoms in the alkane moiety.

40 3. Anionic phosphate surfactants.

4. N-alkyl substituted succinamates.

C. Ampholytic Surfactants

Ampholytic surfactants can be broadly described as aliphatic derivatives of secondary or tertiary
45 amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight chain or branched and wherein one of the aliphatic substituents contains from 8 to 18 carbon atoms and at least one contains an anionic water-solubilizing group, e.g. carboxy, sulfonate, sulfate. See U.S. Patent 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, lines 18—35 for examples of ampholytic surfactants.

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D. Zwitterionic Surfactants

Zwitterionic surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. Patent 3,929,678 to Laughlin et al.,
55 issued December 30, 1975 at column 19, line 38 through column 22, line 48 for examples of zwitterionic surfactants.

E. Cationic Surfactants

Cationic surfactants can also be included in detergent compositions of the present invention. Suitable
60 cationic surfactants include the quaternary ammonium surfactants having the formula:



wherein R^2 is an alkyl or alkyl benzyl group having from 8 to 18 carbon atoms in the alkyl chain; each R^3 is
65 selected from the group consisting of $—CH_2CH_2—$, $—CH_2CH(CH_3)—$, $—CH_2CH(CH_2OH)—$, $—CH_2CH_2CH_2—$,

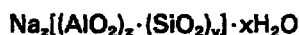
and mixtures thereof; each R^4 is selected from the group consisting of C_1 — C_4 alkyl, C_1 — C_4 hydroxyalkyl, benzyl, ring structures formed by joining the two R^4 groups, $-\text{CH}_2\text{CHOHCHOHCOR}^6\text{CHOHCH}_2\text{OH}$ wherein R^6 is any hexose or hexose polymer having a molecular weight less than 1000, and hydrogen when y is not 0; R^5 is the same as R^4 or is an alkyl chain wherein the total number of carbon atoms of R^2 plus R^5 is not more than 18; each y is from 0 to 10 and the sum of the y values is from 0 to 15; and X is any compatible anion.

Preferred of the above are the alkyl quaternary ammonium surfactants, especially the mono-long chain alkyl surfactants described in the above formula when R^5 is selected from the same groups as R^4 . The most preferred quaternary ammonium surfactants are the chloride, bromide and methylsulfate C_8 — C_{18} alkyl trimethylammonium salts, C_8 — C_{18} alkyl di(hydroxyethyl)methylammonium salts, the C_8 — C_{18} alkyl hydroxyethylmethylammonium salts, and C_8 — C_{18} alkyloxypropyl trimethylammonium salts. Of the above, decyl trimethylammonium methylsulfate, lauryl trimethylammonium chloride, myristyl trimethylammonium bromide and coconut trimethylammonium chloride and methylsulfate are particularly preferred.

Detergent Builders

Detergent compositions of the present invention can optionally comprise inorganic or organic detergent builders to assist in mineral hardness control. These builders can comprise from 0 to 80% by weight of the composition. When included, these builders typically comprise up to 60% by weight of the detergent composition. Built liquid formulations preferably comprise from 10 to 25% detergent builder while built granular formulations preferably comprise from 10 to 50% by weight detergent builder.

Suitable detergent builders include crystalline aluminosilicate ion exchange materials having the formula:



wherein z and y are at least 6, the mole ratio of z to y is from 1.0 to 0.5; and x is from 10 to 264. Amorphous hydrated aluminosilicate materials useful herein have the empirical formula

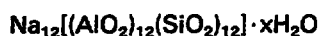


wherein M is sodium, potassium, ammonium or substituted ammonium, z is from 0.5 to 2; and y is 1; this material having a magnesium ion exchange capacity of at least 50 milligram equivalents of CaCO_3 hardness per gram of anhydrous aluminosilicate.

The aluminosilicate ion exchange builder materials are in hydrated form and contain from 10% to 28% of water by weight if crystalline, and potentially even higher amounts of water if amorphous. Highly preferred crystalline aluminosilicate ion exchange materials contain from 18% to 22% water in their crystal matrix. The preferred crystalline aluminosilicate ion exchange materials are further characterized by a particle size diameter of from 0.1 μm to 10 μm . Amorphous materials are often smaller, e.g., down to less than 0.01 μm . More preferred ion exchange materials have a particle size diameter of from 0.2 μm to 4 μm . The term "particle size diameter" represents the average particle size diameter of a given ion exchange material as determined by conventional analytical techniques such as, for example, microscopic determination utilizing a scanning electron microscope. The crystalline aluminosilicate ion exchange materials are usually further characterized by their calcium ion exchange capacity, which is at least 200 mg. of CaCO_3 water hardness/g. of aluminosilicate, calculated on an anhydrous basis, and which generally is in the range of from 300 to 352 mg CaCO_3 /g aluminosilicate ion exchange materials are still further characterized by their calcium ion exchange rate which is at least 0.034 g CaCO_3 /l/min/g of aluminosilicate (anhydrous basis), and generally lies within the range of from 0.034 g CaCO_3 /l/min/g to 0.102 g CaCO_3 /l/min/g. Optimum aluminosilicates for builder purposes exhibit a calcium ion exchange rate of at least 0.068 g CaCO_3 /l/min/g.

The amorphous aluminosilicate ion exchange materials usually have a Mg^{++} exchange capacity of at least 42 mg of MgCO_3 /g of anhydrous aluminosilicate and a Mg^{++} exchange rate of at least 0.0049g (Mg^{++})/l/min/g. Amorphous materials do not exhibit an observable diffraction pattern when examined by Cu radiation (1.54 Angstrom Units, i.e. 1.5410^{-8} cm Units).

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669 to Krummel, et al. issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula



wherein x is from 20 to 30, especially 27.

Other examples of detergency builders include the various water-soluble, alkali metal, ammonium or substituted ammonium phosphates, polyphosphates, phosphonates, polyphosphonates, carbonates, silicates, borates, polyhydroxysulfonates, polyacetates, carboxylates, and polycarboxylates. Preferred are the alkali metal, especially sodium, salts of the above.

5 Specific examples of inorganic phosphate builders are sodium and potassium triphosphate, pyrophosphate, polymeric metaphosphate having a degree of polymerization of from 6 to 21, and orthophosphate. Examples of polyphosphonate builders are the sodium and potassium salts of ethylene-1,1-diphosphonic acid, the sodium and potassium salts of ethane 1-hydroxy-1,1-diphosphonic acid and the sodium and potassium salts of ethane, 1,1,2-triphosphonic acid. Other phosphorus builder compounds are
10 disclosed in U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,422,137; 3,400,176 and 3,400,148.

Examples of nonphosphorus, inorganic builders are sodium and potassium carbonate, bicarbonate, sesquicarbonate, tetraborate decahydrate, and silicate having a mole ratio of SiO_2 to alkali metal oxide of from 0.5 to 4.0, preferably from 1.0 to 2.4.

Useful water-soluble, nonphosphorus organic builders include the various alkali metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates and polyhydroxysulfonates.
15 Examples of polyacetate and polycarboxylate builders are the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediamine tetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, and citric acid.

Highly preferred polycarboxylate builders are disclosed in U.S. Patent No. 3,308,067 to Diehl, issued
20 March 7, 1967. Such materials include the water-soluble salts of homo- and copolymers of aliphatic carboxylic acids such as maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, citraconic acid and methylenmalonic acid.

Other builders include the carboxylated carbohydrates disclosed in U.S. Patent 3,723,322 to Diehl issued March 28, 1973.

25 Other useful builders are sodium and potassium carboxymethyloxymalonate, carboxymethyloxysuccinate, cis-cyclohexanhexacarboxylate, cis-cyclopentanetetracarboxylate, phloroglucinol trisulfonate, water-soluble polyacrylates (having molecular weights of from 2,000 to 200,000 for example), and the copolymers of maleic anhydride with vinyl methyl ether or ethylene.

Other suitable polycarboxylates are the polyacetal carboxylates disclosed in U.S. Patent 4,144,226, to
30 Crutchfield et al. issued March 13, 1979, and U.S. Patent 4,246,495, to Crutchfield et al., issued March 27, 1979. These polyacetal carboxylates can be prepared by bringing together under polymerization conditions an ester of glyoxylic acid and a polymerization initiator. The resulting polyacetal carboxylate ester is then attached to chemically stable end groups to stabilize the polyacetal carboxylate against rapid depolymerization in alkaline solution, converted to the corresponding salt, and added to a surfactant.

35 Other useful detergency builder materials are the "seeded builder" compositions disclosed in Belgian Patent No. 798,856, issued October 29, 1973. Specific examples of such seeded builder mixtures are: 3:1 wt. mixtures of sodium carbonate and calcium carbonate having 5 μm particle diameter; 2.7:1 wt. mixtures of sodium sesquicarbonate and calcium carbonate having a particle diameter of 0.5 μm ; 20:1 wt. mixtures of sodium sesquicarbonate and calcium hydroxide having a particle diameter of 0.01 μm ; and a 3:3:1 wt.
40 mixture of sodium carbonate, sodium aluminate and calcium oxide having a particle diameter of 5 μm .

Other Optional Detergent Ingredients

Other optional ingredients which can be included in detergent compositions of the present invention, in their conventional art-established levels for use (i.e., from 0 to 20%), include solvents, bleaching agents,
45 bleach activators, soil-suspending agents, corrosion inhibitors, dyes, fillers, optical brighteners, germicides, pH adjusting agents (monoethanolamine, sodium carbonate, sodium hydroxide, etc.), enzymes, enzyme-stabilizing agents, perfumes, fabric softening components, static control agents, and the like.

Detergent Formulations

50 Granular formulations embodying the detergent compositions of the present invention can be formed by conventional techniques, i.e., by slurring the individual components in water and then atomizing and spray-drying the resultant mixture, or by pan or drum granulation of the ingredients. Granular formulations preferably comprise from 10 to 30% detergent surfactant, usually anionic.

55 Liquid formulations embodying the detergent compositions can be built or unbuilt. If unbuilt, these compositions conventionally contain approximately 15 to 50% total surfactant, from 0 to 10% of an organic base such as a mono-, di-, or tri-alkanol amine, a neutralization system such as alkali metal hydroxide and a lower primary alcohol such as ethanol or isopropanol, and approximately 20 to 80% water. Such compositions are normally homogeneous single phase liquids of low viscosity (approximately 100 to 150
60 mPa·S at 21.7°C (75°F)).

Built liquid detergent compositions can be in the form of single phase liquids provided that the builder is solubilized in the mixture at its level of use. Such liquids conventionally contain 10 to 25% total surfactant, 10 to 25% builder which can be organic or inorganic, 3 to 10% of a hydrotrope system and 40 to 77% water. Liquids of this type also have a low viscosity (100 to 150 mPa·S at 21.7°C). Built liquid
65 detergents incorporating components that form heterogeneous mixtures (or levels of builder that cannot

be completely dissolved) can also comprise detergent compositions of the present invention. Such liquids conventionally employ viscosity modifiers to produce systems having plastic shear characteristics to maintain stable dispersions and to prevent phase separation or solid settlement.

5

Near Neutral Wash pH Detergent Formulations

While the detergent compositions of the present invention are operative within a wide range of wash pHs (e.g. from 5 to 12), they are particularly suitable when formulated to provide a near neutral wash pH, i.e. an initial pH of from 6.0 to 8.5 at a concentration of from 0.1 to 2% by weight in water at 20°C. Near neutral wash pH formulations are better for enzyme stability and for preventing stains from setting. In such formulations, the wash pH is preferably from 7.0 to 8.5, and more preferably from 7.5 to 8.0.

Preferred near neutral wash pH detergent formulations are disclosed in European Application 0095205 published 30.11.1983. These preferred formulations comprise:

(a) from 2 to 60% (preferably from 10 to 25%) by weight of an anionic synthetic surfactant as previously defined;

(b) from 0.25 to 12% (preferably from 1 to 4%) by weight of a cosurfactant selected from the group consisting of:

(i) quaternary ammonium surfactants having the formula:



20

wherein R^2 , each R^3 , R^4 , R^5 , X and y are as previously defined; each y is from 0 to 10 and the sum of the y values is from 0 to 15; and X is any compatible anion;

(ii) diquaternary ammonium surfactants having the formula:

25



wherein R^2 , R^3 , R^4 , y and X are as defined above; particularly preferred are the C_8 — C_{16} alkyl pentamethylethylenediamine chloride, bromide and methylsulfate salts;

(iii) amine surfactants having the formula:

30



wherein R^2 , R^3 , R^4 , R^5 and y are as defined above; particularly preferred are the C_{12} — C_{16} alkyl dimethyl amines;

(iv) diamine surfactants having the formula:



wherein R^2 , R^3 , R^4 , R^5 and y are as defined above; particularly preferred are the C_{12} — C_{16} alkyl dimethyl diamines;

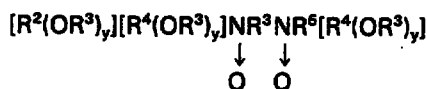
(v) amine oxide surfactants having the formula:



wherein R^2 , R^3 , R^4 , R^5 and y are as defined above; particularly preferred are the C_{12} — C_{16} alkyldimethyl amine oxides; and

(vi) di(amine oxide) surfactants having the formula:

50



wherein R^2 , R^3 , R^4 , R^5 and y are as defined above; preferred are the C_{12} — C_{16} alkyl trimethylethylene di(amine oxides) and (c) from 5% to 40% by weight (preferably 7 to 30% by weight, and most preferably from 10 to 20% by weight) of a fatty acid containing from 10 to 22 carbon atoms (preferably a C_{10} — C_{14} saturated fatty acid or mixture thereof); the mole ratio of the anionic surfactant to the cosurfactant being at least 1 and preferably from 2:1 to 20:1.

Such compositions also preferably contain from 3 to 15% by weight of an ethoxylated alcohol or ethoxylated alkyl phenol (nonionic surfactants) as previously defined. Highly preferred compositions of this type also preferably contain from 2 to 10% by weight of citric acid and minor amounts (e.g., less than 20% by weight) of neutralizing agents, buffering agents, phase regulants, hydrotropes, enzymes, enzyme stabilizing agents, polyacids, suds regulants, opacifiers, antioxidants, bactericides, dyes, perfumes and brighteners, such as those described in U.S. Patent 4,285,841 to Barrat et al., issued August 25, 1981.

65

Specific Embodiments of Detergent Compositions

According to the Present Invention

The following embodiments illustrate, but are not limiting of, detergent compositions of the present invention:

5 A granular detergent composition is as follows:

	Component	Wt. %
10	Polyurethane of Example 3	1.0
	Sodium C ₁₄ —C ₁₅ alkylethoxysulfate	10.7
	C ₁₃ linear alkyl benzene sulfonic acid	4.3
15	C ₁₂ —C ₁₄ alkylpolyethoxylate (6)	0.5
	Sodium toluene sulfonate	1.0
20	Sodium tripolyphosphate	32.9
	Sodium carbonate	20.3
	Sodium silicate	5.8
25	Minors and water	Balance to 100

The components are added together with continuous mixing to form an aqueous slurry which is then spray dried to form the composition. Instead of the polyurethane, the amine oxides of Examples 1 or 2, the random copolymer of Example 4, the PEA of Example 5a, the PEI of Example 5b or the diallylamine polymer of Example 6 can be substituted therefor.

Embodiment II

A liquid detergent composition is as follows:

	Component	Wt. %
35	Random copolymer of Example 4	1.0
	Sodium C ₁₄ —C ₁₅ alkyl polyethoxy (2.5) sulfate	8.3
40	C ₁₂ —C ₁₄ alkyl dimethyl amine oxide	3.3
	Sodium toluene sulfonate	5.0
45	Monoethanolamine	2.3
	Sodium nitrilotriacetate	18.2
50	Minors and water	Balance to 100

The components are added together with continuous mixing to form the composition. Instead of the random copolymer, the polyurethane of Example 3, the PEA of Example 5a, the PEI of Example 5b or the diallylamine polymer of Example 6 can be substituted therefor.

Embodiments III and IV

Liquid detergent compositions are as follows:

Component	Wt. %	
	III	IV
HMDA Oxide of Example 2b	1.5	1.5
C ₁₄ —C ₁₅ alkylethoxysulfuric acid	10.8	—
C ₁₄ —C ₁₅ alkylpolyethoxy (2.25) sulfuric acid	—	10.8
C ₁₃ linear alkylbenzene sulfonic acid	7.2	7.2
C ₁₂ alkyl trimethylammonium chloride	1.2	1.2
C ₁₂ —C ₁₃ alcohol polyethoxylate (6.5)	6.5	6.5
Coconut fatty acid	15.0	15.0
Citric acid monohydrate	6.9	4.0
Diethylenetriamine pentaacetic acid	0.9	0.9
Protease enzyme	0.8	0.8
Amylase enzyme	0.3	0.3
Monoethanolamine	13.6	2.0
Triethanolamine	3.0	4.0
Sodium hydroxide	—	2.0
Potassium hydroxide	—	2.8
1,2-Propanediol	5.0	5.0
Ethanol	3.0	7.0
Sodium formate	1.0	1.0
Sodium toluene sulfonate	5.0	—
Minors and water	Balance to 100	

Embodiment IV is prepared by adding the components together with continuous mixing, in the following order to produce a clear liquid: a paste premix of the alkylbenzene sulfonic acid, 0.9 parts of the sodium hydroxide, propylene glycol, and 2.3 parts of the ethanol; a paste premix of the alkylpolyethoxy-sulfuric acid, 1.1 parts of the sodium hydroxide and 3.1 parts of the ethanol; alcohol polyethoxylate; premix of monoethanolamine, triethanolamine and brighteners, 1.5 parts potassium hydroxide; balance of the ethanol; citric acid; formate; 1.4 parts potassium hydroxide; fatty acid; pentaacetic acid; alkyl trimethylammonium chloride; adjust pH to about 8.4 with potassium hydroxide, water or citric acid; enzymes; HMDa oxide (50% aqueous solution); and perfume. Embodiment III can be prepared in a similar manner. Instead of the HMDa oxide, the polyurethane of Example 3, the random copolymer of Example 4, the PEI of Example 5b or the diallylamine polymer of Example 6 can be substituted therefor.

Embodiment V

A liquid detergent composition is as follows:

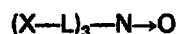
Component	Wt. %
PEA of Example 5a	1.0
Sodium C ₁₂ alkylpolyethoxy (3) sulfate	12.6
C ₁₂ —C ₁₃ alcohol polyethoxylate (6.5)	23.4
Monoethanolamine	2.0
Ethanol	9.0
Citric acid monohydrate	0.8
Minors and water	Balance to 100

The components are added together with continuous mixing to form the composition. Instead of the PEA, the amine oxides of Example 1 or 2, the polyurethane of Example 3, the random copolymer of Example 4, the PEI of Example 5b or the diallylamine polymer of Example 6 can be substituted therefor.

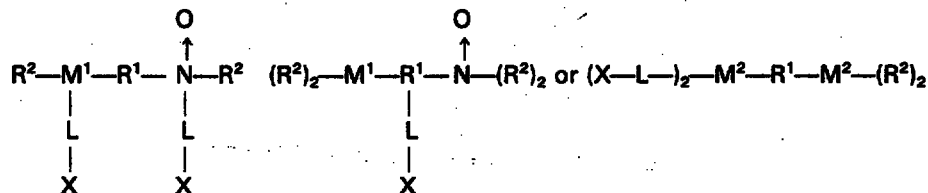
Claims

1. A water-soluble amine oxide having clay soil removal/anti-redeposition properties characterised in that it is selected from the group consisting of:

(1) ethoxylated monoamine oxides having formula I:



(2) ethoxylated amine oxides having formulas IIA, IIB or IIC;

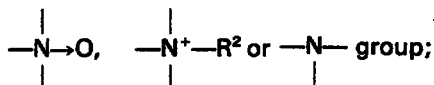


IIA

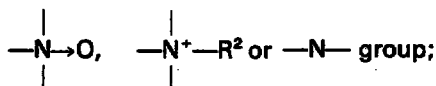
IIB

IIC

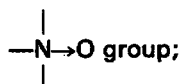
wherein M¹ is an



each M² is an



and at least one M² is an



(3) ethoxylated amine oxides having formula III:

Embodiment V

A liquid detergent composition is as follows:

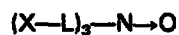
5	Component	Wt. %
	PEA of Example 5a	1.0
	Sodium C ₁₂ alkylpolyethoxy (3) sulfate	12.6
10	C ₁₂ —C ₁₃ alcohol polyethoxylate (6.5)	23.4
	Monoethanolamine	2.0
15	Ethanol	9.0
	Citric acid monohydrate	0.8
	Minors and water	Balance to 100

20 The components are added together with continuous mixing to form the composition. Instead of the PEA, the amine oxides of Example 1 or 2, the polyurethane of Example 3, the random copolymer of Example 4, the PEI of Example 5b or the diallylamine polymer of Example 6 can be substituted therefor.

25 Claims

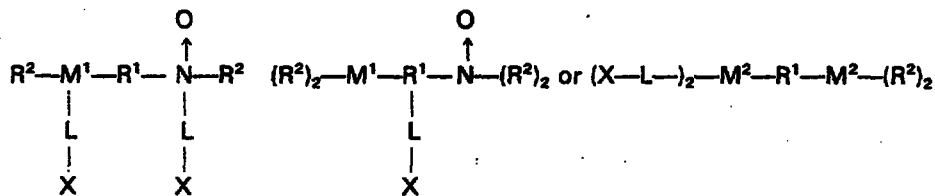
1. A water-soluble amine oxide having clay soil removal/anti-redeposition properties characterised in that it is selected from the group consisting of:

(1) ethoxylated monoamine oxides having formula I:



I

35 (2) ethoxylated amine oxides having formulas IIA, IIB or IIC;

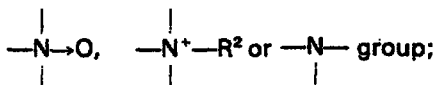


IIA

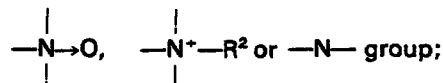
IIB

IIC

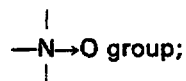
wherein M¹ is an



each M² is an

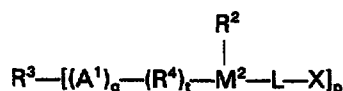


and at least one M² is an



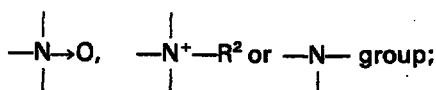
(3) ethoxylated amine oxides having formula III:



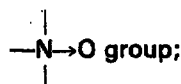


III

5 wherein M^2 is an

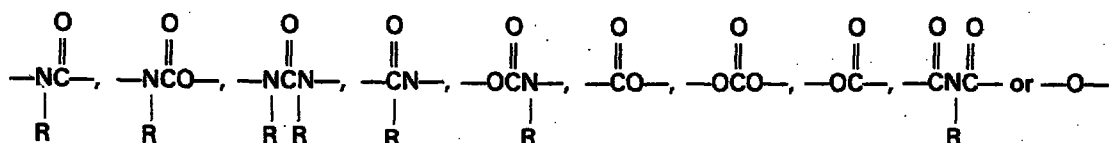


10 and at least one M^2 is an



15 (4) ethoxylated amine oxide polymers which comprise a polymer backbone, at least 2 M^3 groups and at least one $L-X$ group, wherein M^3 is an amine oxide group attached to or integral with the backbone; and L connects groups M^3 and X , or connects group X to the polymer backbone; and

(5) mixtures thereof; wherein A^1 is



25 R is H or C_1-C_4 alkyl or hydroxyalkyl; R^1 is C_2-C_{12} alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene, or a C_2-C_3 oxyalkylene moiety having from 2 to 20 oxyalkylene units provided that no $O-N$ bonds are formed; each R^2 is C_1-C_4 alkyl or hydroxyalkyl, the moiety $-L-X$, or two R^2 together form the moiety $-(CH_2)_r-A^2-(CH_2)_s-$, wherein A^2 is $-O-$ or $-CH_2-$, r is 1 or 2, s is 1 or 2 and $r+s$ is 3 or 4; R^3 is a substituted C_3-C_{12} alkyl, hydroxyalkyl, alkenyl, aryl or alkaryl group having p substitution sites; R^4 is C_1-C_{12} alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene, or a C_2-C_3 oxyalkylene moiety having from 2 to 20 oxyalkylene units provided that no $O-N$ bonds are formed; X is a nonionic group, or a mixture of nonionic and anionic groups; L is a hydrophilic chain which contains the polyoxyalkylene moiety $-[(R^5O)_m(CH_2CH_2O)_n]-$, wherein R^5 is C_3-C_4 alkylene or hydroxyalkylene, and m and n are numbers such that the moiety $-(CH_2CH_2O)_n-$ comprises at least 50% by weight of said polyoxyalkylene moiety; n is at least 12 for said monoamine oxides of formula I, is at least 6 for said amine oxides of formulas IIA, IIB or IIC, and is at least 3 for said amine oxides of formula III and said amine oxide polymers; p is from 3 to 8; q is 1 or 0; t is 1 or 0, provided that t is 1 when q is 1.

30 2. The amine oxide of Claim 1, characterized in that it is a monoamine oxide of formula I.

3. The amine oxide of Claim 1 characterized in that it is an amine oxide of formulas IIA, IIB, IIC or III and wherein each R^2 is the moiety $-L-X$.

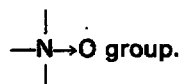
4. The amine oxide of Claim 3 characterized in that numbers m and n are such that the moiety $-(CH_2CH_2O)_n-$ comprises at least 85% by weight of said polyoxyalkylene moiety.

5. The amine oxide of Claims 3 or 4 characterized in that it is an amine oxide of formulas IIA, IIB or IIC.

6. The amine oxide of Claim 5 characterized in that R^1 is C_2-C_6 alkylene.

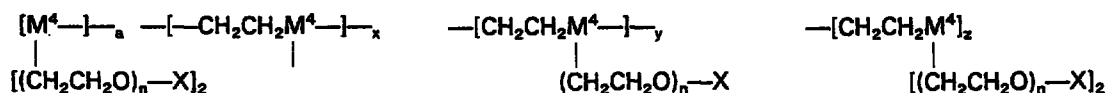
7. The amine oxide of Claim 6 characterized in that R^1 is C_2-C_3 alkylene.

8. The amine oxide of Claims 3 to 7 characterized in that M^1 and each M^2 are an

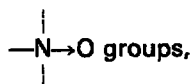


9. The amine oxide of Claim 1 characterized in that it is an amine oxide polymer.

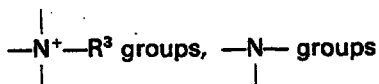
10. The amine oxide polymer of Claim 9 characterized in that it has the general formula:



wherein M^4 comprises from 70 to 100%



and from 0 to 30%



5

or mixtures thereof;

X is H; a is 0 or 1; x + y + z is at least 2.

11. The amine oxide polymer of Claims 9 or 10 characterized in that x + y + z is from 2 to 9.
12. The amine oxide polymer of Claims 9 or 10 characterized in that x + y + z is at least 10.
13. The amine oxide of Claims 1 to 12 characterized in that X is nonionic group.
14. The amine oxide of Claims 1 to 13 characterized in that X is H.
15. The amine oxide of Claims 1 to 14 characterized in that n is at least 12.
16. A detergent composition containing from 1 to 75% by weight of a nonionic, anionic, ampholytic, zwitterionic, or cationic detergent surfactant or mixture thereof; characterized in that it contains from 0.05 to 95% by weight of the amine oxide of Claims 1 to 15.
17. The composition of Claim 16 characterized in that it comprises from 0.1 to 10% by weight of said amine oxide.
18. The composition of Claims 16 to 17 characterized in that it comprises from 1 to 3% by weight of said amine oxide.
19. The composition of Claims 16 to 18 characterized in that said detergent surfactant is a nonionic surfactant, an anionic surfactant or a mixture thereof.
20. The composition of Claims 16 to 19 characterized in that it further comprises from 0 to 80% by weight of a detergent builder.

25

Patentansprüche:

1. Ein wasserlösliches Aminoxid mit Tonschmutzentfernungs-/Antiwiederablagerungseigenschaften, dadurch gekennzeichnet, daß es aus der Gruppe ausgewählt ist, die besteht aus:

30

(1) ethoxylierten Monoaminoxiden mit der Formel I:

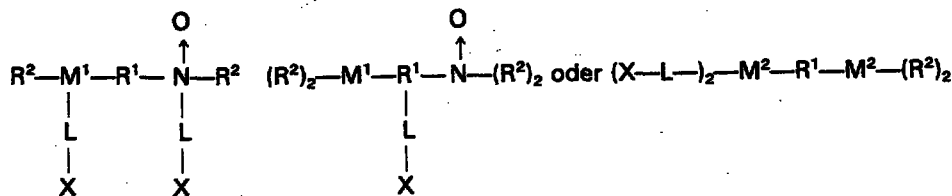


I;

35

(2) ethoxylierten Aminoxiden mit den Formeln IIA, IIB oder IIC:

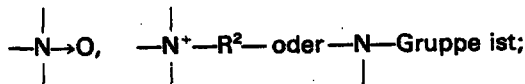
40



45

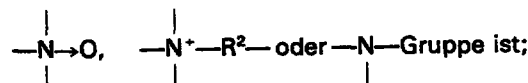
worin M¹ eine

50

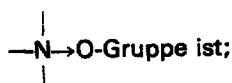


55

jeder Rest M² eine



60 und wenigstens ein Rest M² eine



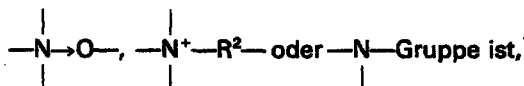
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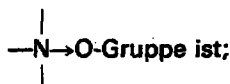
(3) ethoxylierten Aminoxiden mit der Formel III:



worin M^2 eine

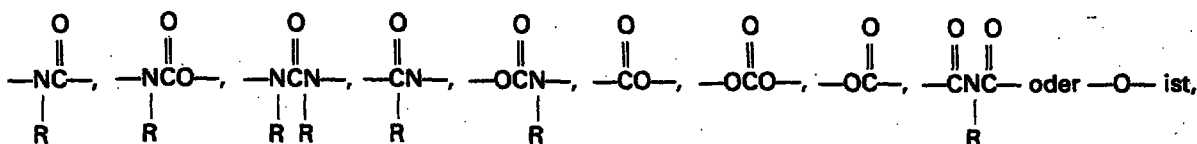


und wenigstens ein Rest M^2 eine



(4) ethoxylierten Aminoxidpolymeren, welche ein Polymergerüst, wenigstens 2 M^3 -Gruppen und wenigstens eine $L-X$ -Gruppe enthalten; worin M^3 eine an das Gerüst gebundene oder in das Gerüst eingebaute Aminoxidgruppe ist; und L die Gruppen M^3 und X verbindet, oder die Gruppe X mit dem Polymergerüst verbindet; und

(5) Mischungen davon; worin A^1



R H oder C_1-C_4 -Alkyl oder Hydroxyalkyl ist; R^1 C_2-C_{12} -Alkylen, Hydroxyalkylen, Alkenylen, Arylen oder Alkarylen oder ein C_2-C_3 -Oxyalkylenrest mit 2 bis 20 Oxyalkyleneinheiten mit der Maßgabe ist, daß keine $O-N$ -Bindungen gebildet werden; jeder Rest R^2 C_1-C_4 -Alkyl oder Hydroxyalkyl, oder den Rest $-L-X$ bedeutet, oder zwei Reste R^2 gemeinsam den Rest $-(CH_2)_r-A^2-(CH_2)_s-$ bilden, wobei A^2 $-O-$ oder $-CH_2-$ ist, r 1 oder 2 ist, s 1 oder 2 ist, und $r+s$ 3 oder 4 ist; R^3 eine substituierte C_3-C_{12} -Alkyl-, Hydroxyalkyl-, Alkenyl-, Aryl- oder Alkarylgruppe ist, die p -Substitutionsstellen aufweist; R^4 C_1-C_{12} -Alkylen, Hydroxyalkylen, Alkenylen, Arylen oder Alkarylen, oder ein C_2-C_3 -Oxyalkylenrest mit 2 bis 20 Oxyalkyleneinheiten mit der Maßgabe, daß keine $O-N$ -Bindungen gebildet werden, ist; X eine nichtionische Gruppe, oder ein Gemisch nichtionischer und anionischer Gruppen ist; L eine hydrophile Kette ist, die den Polyoxyalkylenrest $-[(R^5O)_m(CH_2CH_2O)_n]-$ enthält, wobei R^5 C_3-C_4 -Alkylen oder Hydroxyalkylen ist, und m und n solche Zahlen sind, daß der Res $-(CH_2CH_2O)_n-$ wenigstens 50 Gew.-% des genannten Polyoxyalkylenrestes ausmacht; n für die genannten Monoaminoxide der Formel I wenigstens 12 ist, für die genannten Aminoxide der Formeln IIA, IIB oder IIC wenigstens 6 ist, und für die genannten Aminoxide der Formel III und die genannten Aminoxidpolymere wenigstens 3 ist; p 3 bis 8 ist; q 1 oder 0 ist; und t 1 oder 0 ist, mit der Maßgabe, daß t 1 ist, wenn q 1 ist.

2. Das Aminoxid des Anspruchs 1, dadurch gekennzeichnet, daß es ein Monoaminoxid der Formel I ist.

3. Das Aminoxid des Anspruchs 1, dadurch gekennzeichnet, daß es ein Aminoxid der Formeln IIA, IIB, IIC oder III ist, und worin jeder Rest R^2 der Rest $-L-X$ ist.

4. Das Aminoxid des Anspruchs 3, dadurch gekennzeichnet, daß die Zahlen m und n derart sind, daß der Rest $-(CH_2CH_2O)_n-$ wenigstens 85 Gew.-% des genannten Polyoxyalkylenrestes ausmacht.

5. Das Aminoxid der Ansprüche 3 oder 4, dadurch gekennzeichnet, daß es ein Aminoxid der Formeln IIA, IIB oder IIC ist.

6. Das Aminoxid des Anspruchs 5, dadurch gekennzeichnet, daß R^1 C_2-C_6 -Alkylen ist.

7. Das Aminoxid des Anspruchs 6, dadurch gekennzeichnet, daß R^1 C_2-C_3 -Alkylen ist.

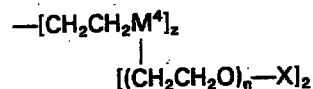
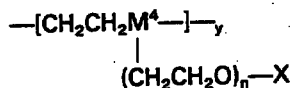
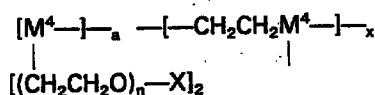
8. Das Aminoxid der Ansprüche 3 bis 7, dadurch gekennzeichnet, daß M^1 und jeder Rest M^2 eine



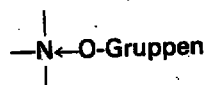
9. Das Aminoxid des Anspruchs 1, dadurch gekennzeichnet, daß es ein Aminoxidpolymer ist.

10. Das Aminoxidpolymer des Anspruchs 9, dadurch gekennzeichnet, daß es die allgemeine Formel:



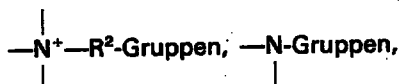


5 hat, worin M^4 70 bis 100%



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und 0 bis 30%



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oder Mischungen davon, enthält; X H ist; a 0 oder 1 ist; und $x + y + z$ wenigstens 2 ist.

11. Das Aminoxidpolymer der Ansprüche 9 oder 10, dadurch gekennzeichnet, daß $x + y + z$ 2 bis 9 ist.

20 12. Das Aminoxidpolymer der Ansprüche 9 oder 10, dadurch gekennzeichnet, daß $x + y + z$ wenigstens 10 ist.

13. Das Aminoxid der Ansprüche 1 bis 12, dadurch gekennzeichnet, daß X eine nichtionische Gruppe ist.

14. Das Aminoxid der Ansprüche 1 bis 13, dadurch gekennzeichnet, daß X H ist.

25 15. Das Aminoxid der Ansprüche 1 bis 14, dadurch gekennzeichnet, daß n wenigstens 12 ist.

16. Eine Detergenezusammensetzung, enthaltend

1 bis 75 Gew.-% eines nichtionischen, anionischen, ampholytischen, zwitterionischen oder kationischen Detergens-grenzflächenaktiven Mittels, oder von Mischungen davon; dadurch gekennzeichnet, daß sie

30 0,05 bis 95 Gew.-% des Aminoxids der Ansprüche 1 bis 15 enthält.

17. Die Zusammensetzung des Anspruchs 16, dadurch gekennzeichnet, daß sie 0,1 bis 10 Gew.-% des genannten Aminoxids enthält.

18. Die Zusammensetzung der Ansprüche 16 oder 17, dadurch gekennzeichnet, daß sie 1 bis 3 Gew.-% des genannten Aminoxids enthält.

35 19. Die Zusammensetzung der Ansprüche 16 bis 18, dadurch gekennzeichnet, daß das genannte Detergens-grenzflächenaktive Mittel ein nichtionisches grenzflächenaktives Mittel, ein anionisches grenzflächenaktives Mittel, oder ein Gemisch davon, ist.

20. Die Zusammensetzung der Ansprüche 16 bis 19, dadurch gekennzeichnet, daß sie weiterhin 0 bis 80 Gew.-% eines Detergensgerüststoffes enthält.

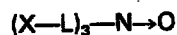
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Revendications

1. Un oxyde d'amine soluble dans l'eau ayant des propriétés d'élimination des souillures argileuses et/ou d'anti-redéposition, caractérisé en ce qu'il est choisi dans le groupe composé

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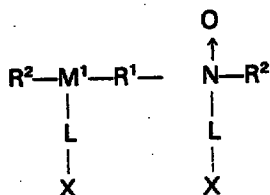
1) d'oxydes de monoamines éthoxylés répondant à la formule I:



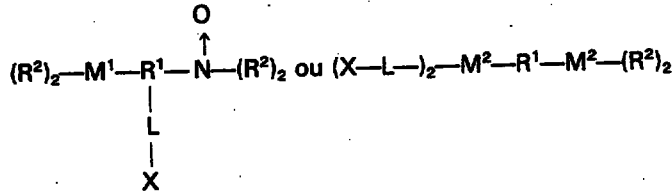
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2) d'oxydes d'amines éthoxylés répondant aux formules IIA, IIB ou IIC:

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IIA



IIB

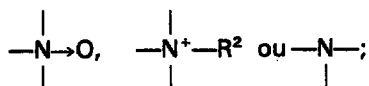
IIC

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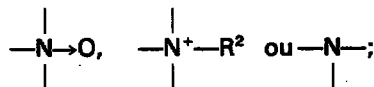
dans lesquelles M^1 est un groupe

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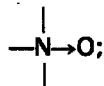


5 chaque M² est un group



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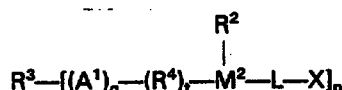
et au moins un M² est un groupe



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3) d'oxydes d'amines éthoxylés répondant à la formule III

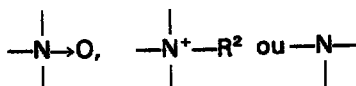
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III

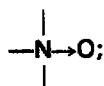
dans laquelle M² est un groupe

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et au moins un M² est un groupe

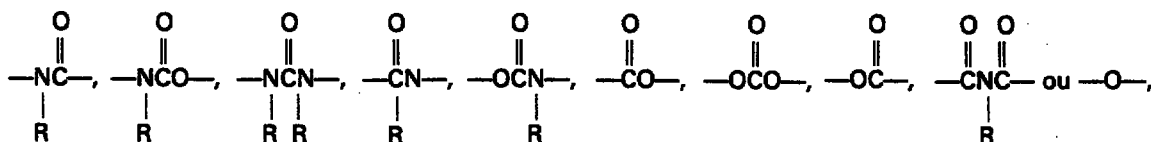


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4) de polymères d'oxydes d'amine éthoxylés comprenant une chaîne principale de polymère, au moins 2 groupes M² et au moins un groupe L—X, dans lesquels M² est un groupe oxyde d'amine fixé ou faisant partie intégrante de la chaîne principale et L relie les groupes M² et X ou relié le groupe X à la chaîne principale du polymère, et

5) de leurs mélanges, où A¹ est

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R est H, un alkyle en C₁ à C₄ ou un hydroxyalkyle; R¹ est un alkylène en C₂ à C₁₂, un hydroxyalkylène, un alcénylène, un arylène ou un alcarylène ou une portion oxyalkylène en C₂ à C₃ comportant 2 à 20 unités oxyalkylène, à condition qu'il ne se forme pas de liaisons O—N; chaque R¹ est un alkyle en C₁ à C₄ ou un hydroxyalkyle, la portion —L—X, ou deux R² forment ensemble la portion —(CH₂)_r—A²—(CH₂)_s— où A² est —O— ou —CH₂—, r est 1 ou 2, s est 1 ou 2 et r + s est 3 ou 4, R³ est un groupe alkyle substitué en C₃ à C₁₂, hydroxyalkyle, alcénylène, aryle ou alcarylène avec des sites de substitution p; R⁴ est un alkylène en C₁ à C₁₂, un hydroxyalkylène, un alcénylène, un arylène ou un alcarylène ou une portion oxyalkylène en C₂ à C₃ comportant 2 à 20 unités oxyalkylène, à condition qu'il ne se forme pas de liaisons O—N; X est un groupe non ionique ou un mélange de groupes non ioniques et anioniques; L est une chaîne hydrophile contenant le fragment polyoxyalkylène —[(R⁵O)_m(CH₂CH₂O)_n]— où R⁵ est un alkylène en C₃ à C₄ ou un hydroxyalkylène et m et n sont des nombres tels que la portion —(CH₂CH₂O)_n— représente au moins 50% en poids dudit fragment polyoxyalkylène; n est au moins 12 pour lesdits oxydes de monoamines de formule I, au moins 6 pour les oxydes d'amines de formules IIA, IIB ou IIC et au moins 3 pour les oxydes d'amines de formule III et les polymères d'oxyde d'amine; p est 3 à 8; q est 1 ou 0; t est 1 ou 0, à condition que t soit 1 lorsque q est 1.

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2. L'oxyde d'amine selon la revendication 1, caractérisé en ce qu'il est un oxyde de monoamine de formule I.

3. L'oxyde d'amine selon la revendication 1, caractérisé en ce qu'il est un oxyde d'amine de formule IIA,

IIB, IIC ou III et dans lequel R² est la portion —L—X.

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4. L'oxyde d'amine selon la revendication 3, caractérisé en ce que les nombres m et n sont tels que la portion $-(CH_2CH_2O)_n-$ représente au moins 85% en poids de ladite portion polyoxyalkylène.

5. L'oxyde d'amine selon la revendication 3 ou 4, caractérisé en ce qu'il est un oxyde d'amine de formule IIA, IIB ou IIC.

6. L'oxyde d'amine selon la revendication 5, caractérisé en ce que R^1 est un alkylène en C_2 à C_6 .

7. L'oxyde d'amine selon la revendication 6, caractérisé en ce que R^1 est un alkylène en C_2 à C_3 .

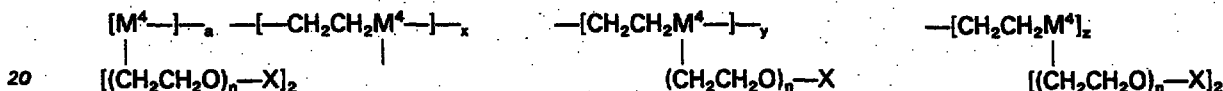
8. L'oxyde d'amine selon les revendications 3 à 7, caractérisé en ce que M^1 et chaque M^2 sont un groupe

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9. L'oxyde d'amine selon la revendication 1, caractérisé en ce qu'il est un polymère d'oxyde d'amine.

10. Le polymère d'oxyde d'amine selon la revendication 9, caractérisé en ce qu'il répond à la formule générale



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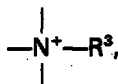
dans laquelle M^4 représente 70 à 100% de groupes

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et 0 à 30% de groupes

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35 de groupes



40 ou leurs mélanges; X est H; a est 0 ou 1; $x + y + z$ est au moins 2.

11. Le polymère d'oxyde d'amine selon la revendication 9 ou 10, caractérisé en ce que $x + y + z$ s'échelonne de 2 à 9.

12. Le polymère d'oxyde d'amine selon la revendication 9 ou 10, caractérisé en ce que $x + y + z$ est au moins 10.

13. L'oxyde d'amine selon les revendications 1 à 12, caractérisé en ce que X est un groupe non ionique.

14. L'oxyde d'amine selon les revendications 1 à 13, caractérisé en ce que X est H.

15. L'oxyde d'amine selon les revendications 1 à 14, caractérisé en ce que n est au moins 12.

16. Une composition détergente contenant environ 1 à 75% en poids d'un agent de surface détergent non ionique, anionique, amphotère, zwitterionique ou cationique ou leur mélange, caractérisé en ce qu'elle renferme 0,05 à 95% en poids de l'oxyde d'amine des revendications 1 à 15.

17. Composition selon la revendication 16, caractérisé en ce qu'elle contient 0,1 à 10% en poids dudit oxyde d'amine.

18. Composition selon la revendication 16 ou 17, caractérisé en ce qu'elle contient 1 à 3% en poids dudit oxyde d'amine.

19. Composition selon les revendications 16 à 18, caractérisé en ce que ledit agent de surface détergent est un agent de surface non ionique, un agent de surface anionique ou leur mélange.

20. Composition selon les revendications 16 à 19, caractérisé en ce qu'elle contient en outre 0 à 80% en poids d'un adjuvant de détergence.

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