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DETERGENT CONTAINING HYDROXY ALKYL AMINE OXIDE

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U.S. Cl. 252—137 5 Claims

ABSTRACT OF THE DISCLOSURE

Hydroxy alkylamine oxide having improved hygroscopicity and thermal stability properties are employed in detergent composition containing alkaline builders or other synthetic detergents.

This is a division of Ser. No. 156,993 filed Dec. 4, 1961. This is a continuation of Ser. No. 324,181 filed Nov. 18, 1963, now abandoned.

This invention relates to novel tertiary amine oxide detergents and detergent compositions containing them.

In the constant improvement of organic detergent compounds, certain features have been found to be highly desirable. These features include resistance toward the ingredients imparting hardness to water, a high degree of detergency, and capacity for solubilization of hard water soaps, such as calcium soap. Although there are a number of organic detergents which have these characteristics, detergent compounds having additional desirable characteristics, find a wider scope of application.

Thermal stability is a highly desirable property which is lacking in many detergents. Such stability is particularly desirable when detergents are subjected to heat during use or processing, as for example, in spray drying granular detergent compositions.

Another advantageous property for an organic detergent is a low degree of hygroscopicity which results in improved crystallinity. When detergent surfactants which are hygroscopic are used in bar or granular forms, desirable physical properties are impaired. Bars become soft and slimy and granules tend to cake and lose their free flowing and quick dissolving characteristics. For example, trialkylamine oxides have been found to be excellent detergent compounds but are so hygroscopic that they can be effectively used only in liquid detergent compositions.

It is the object of this invention to provide organic detergents and detergent compositions which have excellent detergency characteristics as well as improved mildness to the skin, improved thermal stability and a low degree of hygroscopicity.

It was found that these and other objects are achieved in a novel class of tertiary amine oxides having the structure set forth below and detergent compositions containing such compounds, preferably in solid form, as hereinafter more fully described.

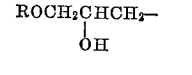
The amine oxides of this invention are:

In the above formulas R_1 is a 2-hydroxyalkyl, 3-hydroxyalkyl or 3-alkoxy-2-hydroxypropyl radical in which the alkyl and alkoxy, respectively, range from 10 to 18 carbon atoms in chain length, R_2 and R_3 are each methyl, ethyl, propyl or isopropyl. The class of compounds described above will hereinafter be referred to more simply as $R_1R_2R_3N\rightarrow O$.

Examples of the compounds of this invention are dimethyl-2-hydroxydodecylamine oxide, diethyl-3-hydroxydodecylamine oxide, dimethyl - 2-hydroxytetradecylamine oxide, dipropyl-3-hydroxyhexadecylamine oxide, propylmethyl - 2 - hydroxyoctadecylamine oxide, diethyl-2-hydroxyhexadecylamine oxide, diethyl-2-hydroxytetradecylamine oxide, diisopropyl-2-hydroxydodecylamine oxide, N,N-dimethyl-3-dodecoxy-2-hydroxypropylamine oxide, N,N-diethyl - 3-tetradecoxy-2-hydroxypropylamine oxide and methylethyl-3-hydroxydodecylamine oxide.

Tertiary amine oxides as a broad class of compounds are known. It was surprising to find, however, that the particular trialkylamine oxides containing particularly-placed hydroxy groups as described above (i.e., a hydroxy group in the 2 or 3 position in R_1) have such highly desirable properties for use as organic detergents, i.e., improved mildness, hygroscopicity and thermal stability characteristics.

It appears that only certain tertiary amine oxides have the aforementioned desirable characteristics; in these certain amine oxides, R_1, R_2 and R_3 must be as described above. If the alkyl or alkoxy in R_1 is longer in chain length than 18 carbon atoms or shorter in chain length than 10 carbon atoms, desired detergency is not obtained. Likewise, if R_2 and R_3 contain more than 3 carbon atoms, desired detergency characteristics are not obtained. The long chain R_1 radical must contain a hydroxy group in the 2 or 3 position (i.e., the second or third carbon atom from the nitrogen) in order to achieve improved mildness, hygroscopicity and thermostability characteristics in accordance with this invention. When the hydroxy group in the R_1 radical is in the 1 or alpha position, the resultant amine oxide compound has undesirable instability. The 3-alkoxy-2-hydroxypropyl R_1 radical has the following general formula:



wherein R ranges from 10 to 18 carbon atoms in chain length.

The 2-hydroxyalkyl, 3-hydroxyalkyl and the 3-alkoxy-2-hydroxypropyl compounds have about the same reduced hygroscopicity characteristics as compared to the corresponding compound containing unsubstituted R_1 alkyl group. The 3-hydroxyalkyl compound has about the same water solubility as the corresponding compound containing an unsubstituted R_1 alkyl group whereas the water solubility of the 2-hydroxyalkyl compound is somewhat less than the solubility of the corresponding compound containing an unsubstituted R_1 group.

In tertiary amine oxides of this invention, R_1 can be derived from naturally occurring fats and oils or from synthetic sources such as olefins. Mixtures of amine oxides are very suitable wherein the alkyl or alkoxy in R_1 varies in chain length in the C_{10} to C_{18} range, as for example, the alkyl or alkoxy groups derived from coconut fatty alcohol (or distilled coconut fatty alcohol). Those amine oxides in which the alkyl or alkoxy in R_1 ranges from 12 to 14 carbon atoms are preferred.

The tertiary amine oxides of this invention can be prepared, in general, by oxidizing the corresponding tertiary amine. See, for example, British Patent 437,566. The corresponding tertiary amine, in general, can be prepared by alkylating, with an appropriate long chain alkyl compound, the appropriate secondary amine. If necessary, the long chain alkyl compound can be such (e.g., ketoalkane) that treatment (e.g., reduction) of the tertiary amine, prior to oxidation, will result in hydroxy substitution at the desired location in the R_1 group. The examples explain in detail such reactions. The preparation of alkyl glycidyl ethers (a source of the 3-alkoxy-2-hydroxypro-

pyl R_1) is described in Canadian Patent 582,404, issued Sept. 1, 1959 and U.S. Patent 2,989,547, issued June 20, 1961.

Compounds of this invention are useful per se as detergents and surface active agents. Desirably they are used with other materials to form detergent compositions, particularly solid form compositions as for example, bar, flake, granular or tableted granular compositions. (The tertiary amine oxides of this invention can also be used to make liquid detergent compositions.) Such detergent compositions can contain from about 5% to about 80% of the tertiary amine oxides of this invention and from about 95% to about 20% of anionic organic detergents, nonionic organic detergents, water-soluble inorganic alkaline builder salts, water-soluble organic alkaline sequestrant builder salts or mixtures thereof.

Granular or flake detergents preferably contain about 5% to about 50% of the amine oxides of this invention and from about 95% to about 50% normally solid, water-soluble inorganic alkaline builder salts, or water-soluble organic alkaline sequestrant builder salts. Bar formulations contain about 5% to about 50% of the amine oxides of this invention when uhed with anionic detergents, such as a soap base, and, if desired, alkaline inorganic or organic builders or inert fillers. Bar formulations can contain about 40% to about 80% of the amine oxides of this invention as the only detergent component, if desired, and the balance inert fillers or builders.

Anionic organic detergenets used alone or in admixture include both the soap and non-soap detergents. Examples of suitable soaps are the sodium, potassium, ammonium and alkylolammonium salts of higher fatty acids (C_{10}-C_{20}). Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap. Examples of anionic organic non-soap detergents are: alkyl glyceryl ether sulfonates; alkyl sulfates; alkyl monoglyceride sulfates or sulfonates; alkyl polyethyenoxy ether sulfates; acyl sarcosinates; acyl esters of isethionates; acyl N-methyl taurides; alkylbenzenesulfonates; alkyl phenol polyethenoxy sulfonates. In these compounds the alkyl and the acyl groups, respectively, contain 10 to 20 carbon atoms. They are used in the form of water-soluble salts, the sodium, potassium, ammonium and alkylolammonium salts, for example. Specific examples are: sodium lauryl sulfate; potassium N-methyl lauroyl tauride; triethanolammonium dodecylbenzenesulfonate.

ammonium or substituted ammonium amino polycarboxylates, e.g., sodium and potassium ethylenediaminetetraacetate, sodium and potassium N-(2-hydroxyethyl)-ethylenediaminetriacetates, sodium and potassium nitrilotriacetates and sodium, potassium, and triethanolammonium N-(2-hydroxyethyl)nitrilodiacetates. Mixed salts of those polycarboxylates are also suitable. Other organic alkaline sequestrant builder salts which can be used are: Hydroxyethylethylenediaminetriacetates; 2-hydroxyethyliminodiacetates; diethylenetriaminepentaacetates; 1,2-diaminocyclohexanetetraacetates. The alkali metal salts of phytic acid, e.g., sodium phytate are also suitable as alkaline organic sequestrant builder salts (see U.S. Patent 2,739,942).

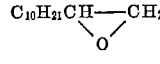
Preferred detergent compositions contain about 10% to about 30% of the tertiary amine oxides of the invention and at least an equal amount of sodium tripolyphosphate. Desirably the amine oxides wherein the alkyl or alkoxy in R_1 contains 12 to 14 carbon atoms are used in such preferred compositions. Particularly desirable is dimethyl-2-hydroxydodecylamine oxide which has good sudsing characteristics, being superior in this respect to dimethyldodecylamine oxide. It also is an effective suds enhancing (building) agent for anionic non-soap detergent compounds.

The detergent compositions of this invention can contain any of the usual adjuvants, diluents or additives, for example, ampholytic or zwitterionic detergents, cationic detergents, perfumes, anti-tarnishing agents, anti-redeposition agents, bacteriostatic agents, dyes, fluorescers, oxygen or chlorine bleaches, suds builders, suds depressors and the like.

The following are examples which illustrate the tertiary amine oxide compounds and compositions of this invention.

EXAMPLE I

5 moles of dimethyl amine were liquified under anhydrous conditions using a Dry Ice-acetone condenser. 0.05 mole of anhydrous aluminum chloride was added to the dimethyl amine and a mixture was placed in a cold, glass autoclave liner (3 liter). One mole of C_{12} olefin oxide



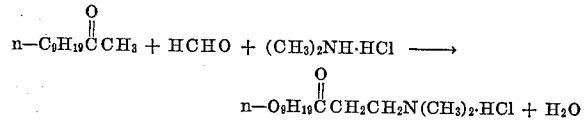
was added to the dimethylamine with mixing and cooling. The liner was placed in a cooled autoclave. After

The corresponding diethyl and dipropyl compounds can be obtained by using molar equivalent amounts of diethylamine or dipropylamine in the process of Example I.

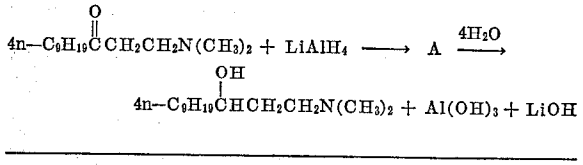
20 parts of dimethyl-2-hydroxydodecyl amine oxide are combined with 50 parts of sodium tripolyphosphate and 30 parts of sodium sulfate to form a solid form detergent composition which cleans well in a laundering operation and suds well in a dishwashing operation. The dishpan sudsing of dimethyl-2-hydroxydodecyl amine oxide in such a composition is superior to that of sodium dodecylbenzene sulfonate in a like composition.

EXAMPLE II

170 grams of 2-undecanone, 22.5 grams of paraformaldehyde, 40.8 grams of dimethyl amine hydrochloride were mixed with 500 ml. of ethanol and stirred for 24 hours at 78° C. The reaction mixture was acidified and extracted with ethyl ether to remove the unreacted 2-undecanone. The mixture was then made alkaline and extracted again with ethyl ether to obtain 81 grams of 3-ketododecyl dimethyl amine. The reaction is represented by the following equation:



38 grams of $LiAlH_4$ was dissolved in 600 ml. of anhydrous diethylether. 57 grams of the 3-keto dodecyl dimethyl amine obtained above was dissolved in 400 ml. of diethylether and added drop-wise to the $LiAlH_4$ solution. This mixture was then stirred for an additional 1½ hours. The unreacted $LiAlH_4$ was decomposed by the addition of ethyl acetate followed by water. The solution was filtered to remove solids. The filtrate split into aqueous and ether layers. The ether layer was evaporated on a steam bath to yield the hydroxy amine. This reaction is represented by the following equation:

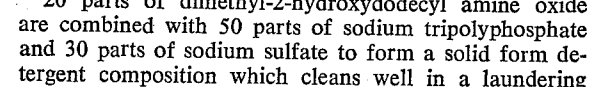
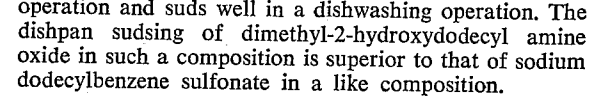


	Found	Calculated
Amine number	240	244
Hydroxyl number	227	244

45 grams of the dimethyl-3-hydroxydodecyl amine obtained above, was mixed with 8.5 grams of hydrogen peroxide (28.5 grams of a 30% aqueous solution) and 250 ml. of ethanol and 125 ml. of water. This mixture was stirred for 6 hours at 50° C. After cooling to room temperature the solution was diluted with 400 ml. of water and the remaining peroxide decomposed catalytically. The unreacted amine was removed with a triple ether extraction. The ethanol was largely removed from solution on a steam bath and the product was isolated by freeze drying. The amine oxide was recrystallized from acetone and had the following element analysis.

Calculated (percent): C, 68.50; H, 12.73; N, 5.71.
Found (percent): C, 67.89; H, 12.40; N, 5.67.

The resulting dimethyl-3-hydroxydodecyl amine oxide was tested for hygroscopicity, being compared with the 2-hydroxydodecyldimethyl amine oxide of Example I and with an unsubstituted dimethyldodecyl amine oxide. The hygroscopicity was determined by exposing dry recrystallized material in a constant 50% relative humidity chamber at 70° F.

Sample	Weight increase, 1 day, percent	Weight increase, 7 days, percent
	8.4	11.7
	9.9	10.7
	32	30

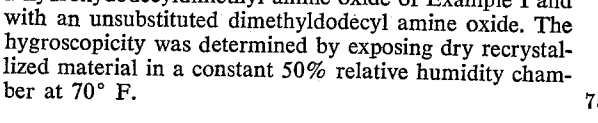
It is apparent that the 3-hydroxydodecyl and the 2-hydroxydodecyl compounds are markedly less hygroscopic than the unsubstituted dodecyl compound. The thermal stability of the compounds of this invention are indicated by decomposition temperatures of the 3-hydroxydodecyl and the 2-hydroxydodecyl compounds of 145° C. and 130° C. respectively as compared to 110° C. decomposition temperature of unsubstituted dimethyldodecyl amine oxide.

The dimethyl-3-hydroxydodecyl amine oxide and the dimethyl-2-hydroxydodecyl amine oxide were tested for detergency properties. These amine oxides were substantially equivalent in detergency to sodium dodecylbenzenesulfonate. The determination was made by washing naturally soiled cloth (desized print cloth) swatches in an 0.1% aqueous solution of a mixture of 20% of an organic detergent compound (amine oxide being tested or alkylbenzenesulfonate standard) 50% sodium tripolyphosphate and 30% sodium sulfate. The composition had a pH of 10 and the washing was done at 130° F. for 10 minutes using wash water of 7 grains per gallon hardness. The detergency effectiveness was determined by measuring the percentage of lipid soil remaining on a standard size swatch (on a dry basis) after the washing operation. The percentage of lipid soil remaining after washing with the amine oxide test composition was compared with the percentage after washing with the alkylbenzenesulfonate standard composition. On the basis of the percent residual lipid soil, the lower the percent, the better the detergency performance. A Tergotometer was used for the washing operation. (Tergotometer testing is described in "Detergency Evaluation and Testing" by J. C. Harris, Interscience Publishers, Inc. (1954) page 60.)

Diethyl-2-hydroxytetradecylamine oxide, diisopropyl-3-hydroxyhexadecylamine oxide and dimethyl-2-hydroxyalkylamino oxide wherein the alkyl is derived from coconut fatty alcohol can be made by processes similar to those described in Examples I and II. These compounds will have substantially equivalent thermal stability and hygroscopicity characteristics and the detergency efficacy will be slightly less than that of the hydroxydodecyl compounds.

EXAMPLE III

1,818 grams of dodecyl glycidyl ether was charged into a two liter autoclave. Air was purged from the head space with dimethyl amine. The autoclave was then heated to 390° F. A pressure of 450 p.s.i. was obtained in the autoclave by charging dimethyl amine into the autoclave using nitrogen pressure. A dimethyl amine bleed valve was adjusted during the reaction of the ether with the dimethyl amine to keep a constant pressure and temperature. After one hour, the autoclave was cooled. The resultant N,N-dimethyl - 3 - dodecoxy - 2 - hydroxypropylamine contained about 25% dissolved dimethylamine which was stripped off at 175° F. at 5 mm. Hg pressure. The amination reaction is represented by the following equation:



1000 grams of this tertiary amine was mixed with 2789.3 grams of water, heated to 180° F. and mixed with 462 grams of 25% aqueous solution of hydrogen peroxide. The mixture was vigorously agitated. The resultant mixture was aged overnight at about 170° F. to decompose excess peroxide.

The resultant N,N-dimethyl-3-dodecoxy-2-hydroxypropylamine oxide absorbed only 0.3% water after one week of storage in an open vessel at room temperature and conditions. Only 22% water was absorbed upon extreme storage conditions of 90° F. and 80% relative humidity for 7 days. This amine oxide exhibited excellent detergency and sudsing characteristics and has excellent thermal stability.

N,N-diethyl-3-tetradecoxy-2-hydroxypropylamine oxide and N,N-dimethyl-3-hexadecoxy-2-hydroxypropylamine oxide can be prepared by processes similar to that described in Example II. These compounds have improved characteristics similar to those of the dodecyl compound.

The tertiary amine oxides of this invention can be used in effective detergent compositions having improved hygroscopicity and thermal stability characteristics. They have the following formulas:

Granular detergent

	Percent
Dimethyl-2-hydroxydodecyl amine oxide	17.5
Sodium sulfate	23
Sodium tripolyphosphate	50
Sodium silicate	6
Water	3.5

Granular detergent

Diethyl-2-hydroxydodecyl amine oxide	10
Sodium dodecylbenzenesulfonate (the dodecyl group being derived from tetrapropylene)	10
Sodium nitrilotriacetate	35
Sodium sulfate	40
Water	5

Granular detergent

Dipropyl-3-hydroxy tetradecyl amine oxide	10
Condensation product of one mole of nonyl phenol and nine moles of ethylene oxide	10
Sodium pyrophosphate	50
Sodium carbonate	3
Trisodium phosphate	3
Sodium sulfate	24

Granular detergent

	Parts
Dimethyl-2-hydroxydodecylamine oxide	1
Potassium ethylenediaminetetraacetate	2

Granular detergent

	Parts
Dimethyl-3-hydroxydodecylamine oxide	1
Potassium pyrophosphate	5

Spray-dried granular detergent

	Percent
N,N-dimethyl-3-dodecoxy - 2 - hydroxypropylamine oxide	5
Sodium dodecylbenzenesulfonate	15
Sodium tripolyphosphate	50
Sodium sulfate	15
Sodium silicate	5
Moisture	10

Milled toilet bar

Diethyl-3-hydroxytetradecylamine oxide	10
Sodium coconut oil soap	15
Sodium tallow soap	60
Triethanolammonium ethylenediaminetetraacetate	5
Moisture	10

Framed toilet bar

	Percent
Dimethyl-2-hydroxydodecylamine oxide	5
Sodium dodecylbenzenesulfonate	57
Glyceryl tristearate	38

Scouring cleanser

Silica flour	85
Detergent consisting of 85% trisodium phosphate and 15% dimethyl-3-hydroxyhexadecylamine oxide	15

To show the improvement in mildness of the compounds of this invention over trialkylamine oxides without a hydroxy group in the long chain R_1 radical, dimethyldodecylamine oxide and dimethyl-2-hydroxydodecylamine oxide were tested in accordance with the guinea pig immersion test. This test consists of immersing guinea pigs having shaved undersides up to their thorax in a 0.2% solution of the material being tested at 37° C., for a 4½ hour period per day for three consecutive days. The animals are graded three days after the last immersion. The grades are the average of the results on not less than three animals. A 1 to 10 scale is used to rate the effects of the prolonged exposure of the test solution on the animal's skin. Grade 10 represents ideal or perfect skin (soft, smooth and flexible) and the effect of a theoretically perfectly mild detergent compound; grade 1 represents severely irritated skin. Other values represent graduations of severity between these extremes. Grade 1 in the guinea pig immersion test indicates severely thickened, dry, cracked and bleeding skin, i.e., extreme irritation. (Grade 1 in exaggerated tests on human subjects would indicate severe redness and dryness of the skin. Exaggerated exposure tests on guinea pigs are much more extreme than those conducted on human subjects.) There is a good correlation between the results of the tests on guinea pigs and the results of normal use tests on humans; the guinea pig immersion test can be relied on to grade the relative mildness of detergent compounds toward the human skin. In guinea pig immersion tests dimethyldodecylamine oxide had a grade of 2, while dimethyl-2-hydroxydodecylamine oxide has a grade of 5.

What is claimed is:

1. A detergent composition consisting essentially of from about 5% to about 80% of a tertiary amine oxide compound having the formula $R_1R_2R_3N\rightarrow O$, wherein R_1 is 2-hydroxyalkyl or 3-hydroxyalkyl in which the alkyl ranges in chain length from 10 to 18 carbon atoms and R_2 and R_3 are each methyl, ethyl, propyl or isopropyl and from about 95% to about 20% of a material selected from the group consisting of water-soluble inorganic alkaline builder salts, water-soluble organic alkaline sequestrant builder salts, water-soluble soap, water-soluble synthetic organic non-soap anionic detergents and mixtures thereof.

2. The composition of claim **1** wherein the amine oxide is dimethyl-2-hydroxydodecylamine oxide.

3. The composition of claim **2** wherein the material is sodium tripolyphosphate.

4. The composition of claim **2** wherein the material is sodium dodecyl benzene sulfonate.

5. The composition of claim **1** wherein the amine oxide is dimethyl-3-hydroxydodecylamine oxide.

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252—152; 260—584