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3,706,676 ETHOXYLATED AMINO ALKANES AS SURFACTANTS

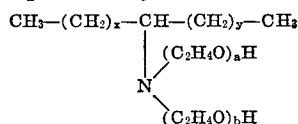
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4 Claims

ABSTRACT OF THE DISCLOSURE

Surface active agents are formed of substantially uniform mixtures of the various amine isomers of ethoxylated aminoalkanes represented by the formula:



wherein the total number of carbons in the linear paraffin chain is from about 8 to 22; wherein x is a whole number from about 0-19 and y is a whole number from about 0-19; and wherein a and b are each greater than zero, the sum of which is greater than about 4.

This invention relates to novel surfactants. More particularly, this invention relates to various ethoxylated aminoalkanes which may be effectively used as surfactants in soaps and detergents.

Surfactants find wide use throughout industry. One of the most important industries in which surfactants are used is the detergent industry. Detergents, according to the well known meaning of this term, are formulated in various ways to suit differing needs. For example, a detergent used to clean hardware such as dishes, glass, silverware, and the like is usually formulated differently than a detergent used to clean software such as textile etc. Generally, however, detergents are built of four basic ingredients: (a) surfactants, including various synthetic surfactants and soaps; (b) inorganic salts, acids, and bases, usually referred to as builders, examples of which include carbonates, silicates, phosphates, and the like; (c) organic builders which enhance detergency, foaming power, emulsifying power, or soil-suspension; and (d) special purpose additives such as brighteners, disinfectants, bleaches, and the like.

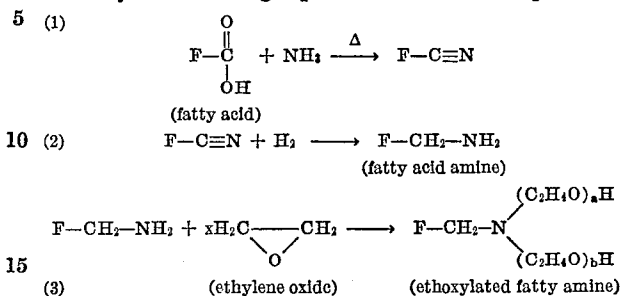
In any given detergent, one or more of the above-described four basic ingredients may be present or eliminated. For example, when cleaning software, all ingredients but the surfactant may be eliminated. For cleaning hardware, on the other hand, the alkalinity of the inorganics is the critical feature and thus all other ingredients may be eliminated. Surfactants, however, aid detergency of hardware and thus are usually not eliminated altogether.

Examples of surfactants useful as wetting agents generally and in detergent compositions more specifically, are numerous indeed. The various organic surfactants constitute one type of surfactant so used. Basically, organic surfactants are constituted so that one segment of their molecule is hydrophobic while another segment is hydrophilic. In addition to this characteristic, an organic surfactant to be industrially acceptable must exhibit the necessary levels of surface activity, wetting, foaming, foam stability, detergency and dispersion.

One typical type of organic surfactant prevalently used in the industry is the ethoxylated fatty acid amines. These

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compounds are generally formed by aminating a fatty acid and then ethoxylating the amine. The product so formed has a terminal ethoxylated amine group as indicated by the following representative reaction equations:



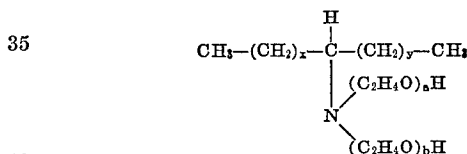
where $a+b=x$

The type of ethoxylated fatty amine formed, be it a secondary or tertiary amine, and the degree of polymerization of the ethoxy groups therein, depends upon the reaction parameters and number of moles of ethylene oxide used. In essentially all situations, however, the ethoxylated amine group is a terminal group on the fatty acid radical.

Although this and other surfactants have proven useful and acceptable in industries requiring their presence, there is a need for further surfactants which are equally as good or superior to surfactants heretofore used.

It is a purpose of this invention to fulfill this need by providing novel surfactants and compositions made therefrom.

The surfactants as contemplated by this invention are mixtures of amine isomers represented by the formula:



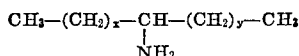
wherein the total number of carbons in the linear paraffin chain is from about 8 to 22 and preferably from 14 to 20; wherein x is a whole number from about 0-19 and y is a whole number from about 0-19; and wherein a and b are each greater than zero, the sum of a and b being greater than about 4.

By "linear paraffin chain" is meant the straight chain of carbon atoms extending from one CH_3 terminal group to the other CH_3 terminal group in the above formula and does not include the ethoxylated group (or chain) depending internally therefrom. In this respect it is understood that the number of carbon atoms may, in certain instances, be less than 8 or greater than 22, the criterion being that the compound continue to act as a surfactant.

As can be seen from the above formula, the compounds of this invention are in contrast with the ethoxylated fatty amines in that the compounds of this invention, although they be monoamines, are mixtures of the various amine to paraffin chain internal carbon atoms isomers, having no terminal amine groups. In actuality, the compounds of this invention are substantially uniform mixtures of the various isomers of ethoxylated amines which isomers on an average are uniformly distributed among all of the internal carbon atoms. For example, when the paraffin chain is a normal C_{12} paraffin, the product formed will be an isomeric mixture of the ethoxylated tertiary monoamine wherein about 10 percent of the monoamine is the 2-carbon amine isomer, about 10 percent is the 3-carbon amine isomer and so on up to the 11-carbon amine isomer. It is believed that this unique characteristic of the compounds of this invention helps to provide their unique surfactant properties.

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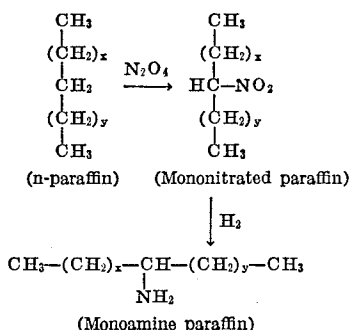
The novel compounds of this invention are formulated by ethoxylated an isomeric mixture of primary N-alkyl-monoamines represented by the formula:



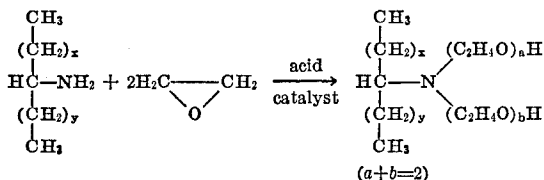
wherein x , y and the number of carbon atoms in the paraffin chain are the same as hereinbefore described. These isomeric mixtures of N-alkyl amines may be formed by reacting a normal paraffin such as from about n-octane to docosane, and preferably from tetradecane to eicosane, with N_2O_4 . The product of this reaction is found to be a mononitrated paraffin which is actually a substantially uniform mixture of each of the various mononitrated internal carbon atom isomers. In addition, the product is found to be substantially free of mononitrated terminal carbon atoms.

This nitrated paraffin product having substantially no terminal NO_2 groups is then reduced to its amine derivative by reacting the NO_2 groups with hydrogen. The moonamine groups so formed, like the NO_2 groups, are substantially uniformly distributed among the various isomeric internal carbon atoms, there being substantially no terminal amine groups.

The formation of these monoamines may be represented by the following reaction equations:

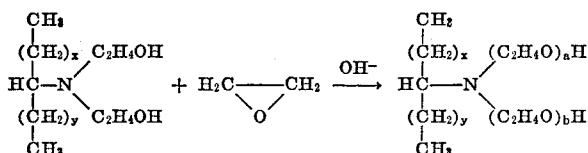


The monoamine paraffin product so formed is water insoluble and thus not a surfactant. To render it water soluble and a surfactant it is ethoxylated in a two-step process to insure the formation of a product which is a tertiary ethoxylated amine having sufficient ethylene oxide polymerization (i.e., the sum of a and b in the formula representative of the compounds of this invention) to act as a surfactant. In the first stage or step of the process, about 2 moles of ethylene oxide are charged for each mole of monoamine until all of the amino groups have been reacted, as follows:



As indicated, this reaction results in a product wherein very little, if any, ethylene oxide polymerization occurs, the product consisting almost entirely of a 2:1 molar ratio of ethylene oxide to amine.

After all of the ethylene oxide has been reacted, the second stage or step of the process is effected by reacting the ethoxylated product of stage-one with a further amount of ethylene oxide as follows:



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The product so formed, which constitutes a compound as contemplated by this invention, is a substantially uniform mixture of isomers having ethoxylated amine groups distributed substantially uniformly among the various internally aminated carbon isomers. In addition, the product is a tertiary amine, i.e., a and b are each greater than 0, wherein sufficient ethylene oxide polymerization has occurred to render the amine segment of the molecule substantially hydrophilic. Generally speaking the amine segment is rendered substantially hydrophilic when the sum of a and b (i.e., the ethylene oxide to amine molar ratio) is above about four. The upper range of the sum of a and b is usually a practical consideration and for most purposes need not exceed about 35. Preferably the ethylene oxide to amine molar ratio is from about 6 to about 10 and most preferably is about 7. It is understood, of course, that the most appropriate ethylene oxide to amine molar ratio (i.e., the sum of a plus b) may be different for compounds having different numbers of carbon atoms in the paraffin chain. The above preferred ranges are generally applicable, however, for all paraffin chains having between about 8 and 22 carbon atoms.

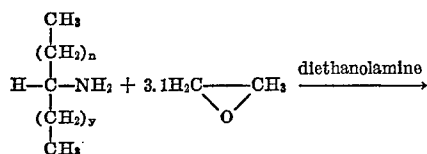
In practice, the two stage process for ethoxylating primary N-alkyl monoamines to form compounds as contemplated by this invention, may be accomplished by using either of two separate techniques. In the first technique, a solution comprising an N-alkyl monoamine as above described, and an inorganic acid catalyst, is initially sparged with nitrogen at about 90° C. to remove water. Into this solution there is added about 2 moles of ethylene oxide per mole of amine. The solution is then held at slightly elevated pressures and at temperatures from 90-100° C. for a sufficient period of time to allow all of the ethylene oxide to condense with the aminoalkane. The product mixture is then neutralized with an inorganic base and the resulting salt removed by organic solvent extraction. The solvent is then removed by vacuum distillation. The product so formed is an ethoxylated aminoalkane as described above having an ethylene oxide to amine molar ratio of about 2:1. Very little, if any, ethylene oxide polymerization occurs and the ethoxylated product at this point is substantially water insoluble and thus, as yet, not a surfactant.

The product formed at the first stage is next redissolved with an inorganic basic catalyst such as NaOH. The mixture is then heated to above about 160° C. and ethylene oxide is passed into the solution at slightly elevated pressures whereupon the ethylene oxide polymerizes with the ethoxylate group in the amine to form a surfactant. Ethylene oxide addition is continued until the desired degree of polymerization (i.e., until the desired sum of a and b) is achieved. Usually in order to form an effective surfactant, the sum of a and b must be greater than 4, preferably greater than 6 and most preferably about 7. The solution is then cooled and neutralized with an inorganic acid and the resulting salt removed by filtration. The final product so formed is found to have an ethoxylated amine segment which is highly water soluble (i.e., hydrophilic). Since the paraffin chain segment of the molecule having from about 8 to 22 carbon atoms, is highly hydrophobic, the compound is an excellent surfactant useful alone as a detergent or with other ingredients to form various detergent compositions as described hereinabove.

The second technique for forming ethoxylate surfactants according to this invention utilizes the diethanolamine product formed by acid catalysis in the first stage of the above-described first technique, as the catalyst in the first step of this second technique. A solution of primary N-alkyl-monoamine (whole formulation has heretofore been described), and the diethanolamine is then formulated and sparged with nitrogen at 90° C. To this solution there is added about 3 moles of ethylene oxide per mole of primary N-alkyl-monoamine over a period of about 4 hours, during which time, pressure is held at

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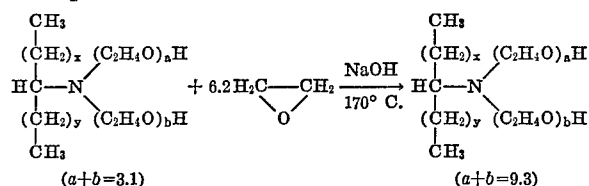
slightly above atmospheric and temperatures are from about 90–100° C. The reaction mixture is allowed to react for a sufficient period of time to insure that all of the ethylene oxide has reacted. The product of condensation is an ethoxylated amine having an ethylene oxide to amine molar ratio of about 3. This condensation reaction is adequately represented by the following equation:



In most instances a molar ratio of about 3 does not provide sufficient hydrophilic characteristics to the ethoxylated segment of the molecule to render it an acceptable surfactant. However, it has been found in accordance with this invention that this first stage product having a molar ratio of about 3 and preferably from about 3 to 5, may be used to catalyze its own formation. Therefore, after startup, the preliminary step of forming a diethanolamine catalyst may be eliminated and a portion of the ethoxylated product recycled as the catalyst.

Because no acid is added in the carrying out of the first step of this technique the second step may be effected without the need for salt extraction, neutralization, and solvent removal. This represents a distinct economic advantage over the first technique.

In effecting the second step of this second technique there is added to the product solution of the first step which contains an ethoxylated product having a molar ratio of about 3, a small amount of NaOH as a catalyst. This mixture is then heated and ethylene oxide passed into the solution at slightly above atmospheric pressure. The temperature of the solution is raised to above about 160° C. and ethylene oxide is added continuously until the desired degree of ethoxylation has occurred. The following equation is illustrative of the reaction which takes place:



This product is a substantial uniform mixture of the amine isomers as hereinabove described. The product formed, as illustrated, has an ethylene oxide to amine molar ratio of 9.3:1. This ratio provides excellent hydrophilic characteristics to the amine segment of the molecule. Other ratios are obtainable by varying the length of reaction time and amount of ethylene oxide in step two. Since the paraffin chain is hydrophobic, an effective surfactant is formed which may be used alone as a detergent, or in combination with other ingredients to form a detergent composition as above described.

Detergent compositions are well known in the art, any one of which may have added thereto the novel surfactants of this invention. As stated hereinabove detergent compositions vary widely in their make-up and ingredients which usually depend upon the end use to which the detergent is put. One example of a detergent composition useful in washing cotton fabrics, as contemplated by this invention, consists essentially of, by weight composition, about 12 percent surfactant, 40 percent sodium tripolyphosphate, 10 percent sodium metasilicate, 37 per-

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cent sodium sulfate, and 1 percent sodium carboxymethylcellulose. The detergent compositions may be formed according to conventional techniques well known in the detergent art.

While the novel compounds of this invention have been described as surfactants primarily useful in soaps and detergents, it is understood that such a description is illustrative and not limiting. That is to say, these novel compounds are useful as surfactants generally. In this respect the term "surfactant" is used in its well known sense to define a molecule which has a hydrophobic segment and a hydrophilic segment.

The following examples are illustrative of this invention and are not intended as limitations thereon.

EXAMPLE 1

Preparation of ethoxylated aminoalkanes

A paraffin consisting of a mixture of C₁₄ to C₁₈ paraffins is nitrated using N₂O₄ gas and conventional vapor phase reaction techniques. As stated above, such a reaction results in substantially no terminal NO₂ groups being formed on the paraffin chain. The nitrated paraffin is then reacted by conventional hydrogenation techniques in suitable pressure hydrogenation apparatus with hydrogen, using a suitable hydrogenation catalyst (e.g., finely divided Ni), a solvent, and superatmospheric pressures. Generally the pressures used are about 600 p.s.i. to about 2000 p.s.i. and the temperatures used are between about 15° C. and 150° C. The product formed, is a substantially uniform mixture of C_{14–18} paraffin monoamine isomers having substantially no terminal amine groups.

A solution of 180 g. (0.75 moles) of the above C_{14–18} paraffin monoamine and 8.3 ml. of 36 percent HCl is formed and sparged with nitrogen at 90° C. to remove water. Over a four-hour period at a pressure slightly greater than atmospheric 63 g. (1.43 moles) of ethylene oxide was condensed with the amine. The final ethylene oxide to amine molar ratio was 1.9:1. The product solution was neutralized with NaOH, and the sodium chloride salt formed thereby was removed by dissolving it in hexane and extracting it with a saturated solution of sodium sulfate. Isopropanol was added to the hexane solution and this mixture was filtered to remove sodium sulfate. The solvents were then removed by vacuum distillation to recover an ethoxylated amine having a molar ratio of 1.9:1 which for all practical purposes, may be considered substantially 2:1.

This ethoxylated product hereinafter referred to as ethoxylated (1.9) C_{14–18} aminoalkane was further ethoxylated by redissolving 66 g. (0.2 mole) of it with 0.25 g. of NaOH. This solution was heated and ethylene oxide passed into the solution at slightly above atmospheric pressure. After 2½ hours at a temperature of about 170° C., 43 g. (0.98 mole) of ethylene oxide had been condensed. After cooling, the catalyst was neutralized with the addition of dilute sulfuric acid. The product, which has an ethylene oxide to amine molar ratio of 6.9:1, was filtered to remove sodium sulfate. The resulting ethoxylated aminoalkane was found to be an excellent surfactant.

EXAMPLE 2

Using the procedure of Example 1, ethoxylated (7.6) C₁₆ aminoalkane, ethoxylated (11.0) C₁₆ aminoalkane, ethoxylated (9.6) C_{14–18} aminoalkane are prepared. The higher ethylene oxide to amine molar ratios (as set forth in the parentheses) are obtained by increasing the amount of ethylene oxide and the reaction time in the second stage of the process. All of these compounds which are substantially uniform monoamine isomeric mixtures, are found to be highly effective surfactants.

EXAMPLE 3

The ethoxylated (7.6) C₁₆ aminoalkane and ethoxylated (9.6) C_{14–18} aminoalkane isomeric mixtures produced in Example 2 are compared for their surfactant

properties with two conventional fatty acid amine surfactants, ethoxylated (5) coco amine (trade name Ethomeen C/15) and ethoxylated (10) coco amine (trade name Ethomeen C/20). The tests conducted are for cloud point, surface activity, wetting, foaming, cotton detergency and lime soap dispersion. The cloud point test is a measurement of the hydrophobic-hydrophilic characteristics of the material. The wetting test is conducted in accordance with a standard Canvas-Square Method. In this test, a 1-inch square piece of dry canvas is dropped upon a solution of water and surfactant in the indicated concentration. The time which it takes for the canvas to become wet and drop below the surface of the solution is measured. Four runs are made for each solution and averaged to give a reported result. The 20-sec. wetting concentration is then arrived at by extrapolation of a plot of the compiled data.

Foaming is conducted according to the conventional Ross-Miles Method. In a standard apparatus the height of foam formed is initially measured and then remeasured after 5 minutes. The test indicates whether the surfactant is a high or low sudsing material and whether the suds are stable or unstable.

Cotton detergency is determined using a conventional Terg-O-tometer consisting of a set of four small agitators in 2 liter beakers. Agitation is held constant for all runs. The increase in brightness of a soiled cotton swatch is measured after washing in the device with 0.2 percent built formulation at 120° F. in soft water. The built formulation consists of 12 percent surfactant, 40 percent sodium tripolyphosphate, 10 percent sodium metasilicate, 37 percent sodium sulfate, and 1 percent sodium carboxymethylcellulose. Values are normalized against a standard linear alkylate sulfonate.

The lime soap dispersion is a conventional test which measures the percent surfactant required to disperse 100 g. of a Ca-Mg soap. The results of these tests are set forth in the following table.

TABLE A.—SURFACTANT PROPERTIES OF ETHOXYLATED AMINES

	Ethoxylated (7.6) C ₁₆ aminoalkane	Ethoxylated (9.6) C ₁₄₋₁₈ aminoalkane	Ethoxylated (5) coco amine	Ethoxylated (10) coco amine
Cloud point (° C.)	44.5	46.5	49.0	100
Surface tension (dynes/cm. at 25° C.):				
1.0%-----	30	30	30	36
0.1%-----	29	30	30	37
0.01%-----	33	35	35	36
Wetting by canvas-square method (sec.) percent concn. of surfactant in H ₂ O solution:				
1.0%-----			13	120
0.7%-----			21	
0.6%-----			29	
0.5%-----	17	19	40	
0.4%-----		28		
0.2%-----	37	69	120	
0.1%-----	120	120		
20-sec. wetting concn. (percent)	0.45	0.49	0.74	1
Foaming by the Ross-Miles method (cm., initial/after 5 min. at 120° F.):				
Distilled water:				
0.1%-----	3.0/3.1	2.0/2.0	2.5/1.5	15.5/0.5
0.05%-----	3.5/3.5	2.0/2.0	2.0/2.0	11.5/0.5
Soft water:				
0.1%-----	3.0/3.0	2.5/2.5	3.5/2.5	16.0/1.0
0.05%-----	4.0/4.0	2.0/2.0	2.0/2.0	13.0/1.5
Hard water:				
0.1%-----	3.0/3.0	2.5/2.5	3.5/3.0	16.0/1.5
0.05%-----	3.0/3.0	2.0/2.0	2.0/2.0	12.5/3.0
Cotton detergency in Terg-O-tometer (increase in fabric brightness using 0.2% of a built formulation at 120° F. in soft water)	12.8	14.5	14.0	10.7
Lime soap dispersion (percent)	5	4	5	4

The data in this table is self-explanatory to those skilled in the art. Although the cloud points of the lower ethoxylated aminoalkanes of this invention are lower

than the ethoxylated (10) coco amine, all cloud points are well within acceptable limits. Surface tension and dispersion characteristics are substantially comparable for all of the surfactants tested, all of which are within acceptable limits. The ethoxylated aminoalkanes of this invention show a slightly improved cotton detergency level over the ethoxylated coco amines. Also illustrated is the fact that the surfactants of this invention are low sudsing agents which form very stable foams. The ethoxylated (5) coco amine, while a low sudser forms a less stable foam. The ethoxylated (10) coco amine, on the other hand, is high sudsing agent which forms relatively unstable and quickly dissipating foams.

By far the most striking comparison between the compounds of this invention and conventional ethoxylated fatty acid amines is in their ability to wet fabric. This characteristic is vital in forming good software detergents and detergent compositions. As is seen from the data in Table A, the surfactants of this invention have wetting characteristics which are about twice as effective as those of the ethoxylated fatty acid amine surfactants. Such a characteristic makes the surfactants of this invention very useful indeed.

EXAMPLE 4

Five N-alkyl primary amines, C₁₄, C₁₅, C₁₆, C₁₇ and C₁₈ were prepared in accordance with Example 1 and prior to ethoxylation their isomer distribution measured and averaged. Measurement of the isomeric mixture of each individual primary amine was conducted by converting them to cyclohexylimines and applying conventional gas chromatographic techniques with the following results:

Amine isomer ^a (carbon atom No.)	Percent isomer
2 -----	11
3 -----	13
4 -----	14
5 -----	13
6, 7, 8 and 9 -----	48

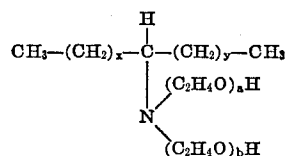
^a No distinction is made between the 2 carbon atom and the 18 carbon atom for example in C₁₄ or the 14 carbon atom, as another example in C₁₆. Both isomers are listed together and are called the 2 carbon atom. The percent value, therefore, indicates the total percent of both symmetrical carbon atoms. The same is true with respect to the other symmetrical carbon atoms.

As can be seen, the compounds of this invention are substantially uniform mixtures of the various amine isomers thereof.

Many modifications, variations, and other features of this invention will become apparent to the skilled artisan once given the above disclosure. Such modifications, variations, and other features are therefore considered a part of this invention, the scope of which is to be determined by the following appended claims.

We claim:

1. A detergent composition consisting essentially of (A) a builder selected from the group consisting of inorganic and organic compounds and (B) a surfactant consisting essentially of a mixture of ethoxylated amine isomers of an aminoalkane represented by the formula:



wherein the total number of carbons in the linear paraffin chain is from about 8 to 22; wherein x is a whole number from about 0-19 and y is a whole number from about 0-19; and a and b are each greater than zero, the sum of a and b being from about 4 to about 35, wherein said ethoxylated amine isomers on the average are uniformly distributed among all of the internal carbon atoms.

2. A detergent composition according to claim 1 wherein said paraffin chain comprises about 14 to 20 carbon atoms.

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3. A detergent composition according to claim 1 wherein the sum of *a* and *b* is about 6 to 10.

4. A detergent composition according to claim 1 wherein said builders are selected from the group consisting essentially of sodium tripolyphosphate, sodium metasilicate, sodium sulfate and sodium carboxymethyl-cellulose.

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U.S. Cl. X.R.

252—542; 260—584 B