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54 **Prespotter laundry detergent.**

57 A heavy duty clear liquid built detergent composition. The composition comprises at least one nonionic surfactant builders, a water soluble polymeric anionic hydrotrope and water wherein the composition has a pH in the range of from 6 to 9.

**EP 0 237 075 A2**

This invention relates to clear stable single phase built liquid detergent composition.

Normal powder detergents are a mixture of surfactants and inorganic builders in a ratio of about 1:1 to 1:2. When these components are concentrated into a liquid detergent form, there is a multiphase separation.

Historically, liquid detergents have recognized and struggled with this incompatibility. The result has been that current commercial liquid laundry detergents are almost all surfactants with very little or no inorganic builders present. The inorganic builders are desirable because they are the lowest cost cleaning components in detergents.

Recent developments have partially solved this problem by using more expensive organic, polycarboxylate builders and by suspending inorganic builders in the liquid detergent system. Whereas these systems have been successful as a detergent, they have not provided good prespotter properties.

Good detergency and good prespotting properties have also historically been incompatible in a single liquid. The best cleaning detergents have been highly built, high alkaline system. However, in a liquid detergent, high alkalinity will fix certain stains such as coffee, tea and red wine. Highly alkaline liquids can also cause skin irritations.

Detergent compositions containing polymers as builders are old and well known in the art. A number of these patents can be seen by viewing the literature.

U.S. Patent No. 3,691,107 discloses a detergent composition comprising a mixture of one or more surfactants with a unique builder of compositions which comprises a cross-linked, water-insoluble copolymer of at least one  $C_4$ - $C_{10}$  olefin and at least one polycarboxyl vinyl monomer. The cross linked water insoluble copolymer is a water-swellaable gel forming material. This patent is of particular interest to the present art in examining Example I, Table I as contained in column II, lines 7-35. Specifically, alpha olefin maleic anhydride copolymers are disclosed as old and well known in the art. However, a reading of the Example indicates that they are being used in the patent example as a powder detergent composition. No hydrotrope properties are inherent in the alpha olefins of the composition and they are cross linked with diamines and triamines and with diols and triols. They are then hydrolyzed to make water insoluble swellaable gels. All the examples are for powdered detergents and although they do mention an aqueous dispersion of the detergent composition, they are cloudy, two-phased liquids. Moreover, the levels at which the alpha olefin maleic anhydride copolymers are used at are a level of 40% by weight of the composition from which it would appear that the use of the copolymer is as a builder substitute.

U.S. Patent No. 3,208,949 discloses ethylene maleic anhydrides and polyvinyl methacrylate maleic anhydride interpolymers for use in a heavy duty or built liquid detergent system. This patent discloses the use of a caprylic acid salt to function as a binary system to stabilize a built detergent into a substantially homogeneous pourable liquid detergent.

U.S. Patent No. 3,830,745 depicts a detergent composition which includes anionic or nonionic surface active agents and as a builder a novel water soluble salt of a copolymer of cyclopentene or its derivatives with maleic anhydrides. These cyclopentene maleic anhydride copolymers are hydrolyzed to an alkali metal salt to function as novel builders. The molecular weight of the copolymer is stated as 350 to 2000. This is a powder system.

U.S. Patent No. 3,852,213 discloses chelating compositions comprising 90 to 70% of polyvinyl methacrylate maleic anhydride copolymer and a 3 to 30% borax, detergent dyeing, scouring and similar compositions containing the ingredients and a process for chelating varies Group II and Group III metal ions.

U.S. Patent No. 3,328,309 depicts a liquid detergent composition having a surface active detergent ingredient in a liquid medium. The detergent may be any commonly used surfactants of the nonionic and anionic types and mixtures thereof. The patent discloses the use of polymeric anhydrides having ethoxylated esters and anhydrides.

The copolymers are all partial esters made by heating the anhydrides with ethoxylated or hydroxy containing surfactants to make partial esters.

U.S. Patent No. 3,509,059 depicts a stable, heavy duty liquid detergent composition which contains high electrolyte content as a builder which is produced in a stabilized form by polymerizing to a polymer a monomer in the presence of the detergent material. The polymer acts as a stabilizer for the compositions. The composition is essentially a polymerization of an alpha, beta unsaturated carboxylic acid to a surfactant. In other words, this is a polymer which is grafted onto a surfactants. The acid has to be converted to salt first in order to have a functioning system.

Accordingly, the object of this invention is to provide a clear homogeneous built liquid system which is neutral to slightly alkaline and which has good prespotter properties.

The present invention provides a clear, stable, single phase built liquid detergent composition, characterized by a) at least one nonionic surfactant in an amount of from about 5 to 25% by weight of the composition; b) a builder in an amount of from about 2 to 25% by weight of the composition; c) a water soluble polymeric anionic hydrotrope anti-redeposition agent in an amount of about 1 to 10% by weight of the composition, said hydrotrope being selected from the group of hydrolyzed alpha olefin maleic anhydride polymers, copolymers and terpolymers having a carbon content of about C<sub>4</sub> to C<sub>30</sub>+, and; d) the balance water wherein said composition has a pH in the range of about 6 to 9.

The hydrolyzed alpha olefin maleic anhydride copolymer preferably has a carbon range from C<sub>4</sub> to C<sub>18</sub>, and most preferably C<sub>6</sub> to C<sub>10</sub>. The liquid laundry detergent is a heavy duty or built liquid detergent which is basically nonionic in nature and yet, is able to utilize borates, phosphates and carbonates as the main builders by the use of the hydrolyzed alpha olefin maleic anhydride copolymers. The hydrolyzed alpha olefin maleic anhydride copolymers function as a hydrotrope to bring two different phases of a normally two phase system into a single clear phase liquid detergent which has remarkable cleaning and prespotting properties when compared to the prior art liquid detergents and powdered detergents. Liquid detergents as a rule contain no builders or much lower concentrations of builders than powdered detergents. These builders, which are common in the art, are normally ionic, and by raising the concentration of ionics in solution, the nonionic surfactants of a liquid detergents tend to separate or phase out. In order to make up for the loss of detergency for lack of builders, liquid detergents must use higher surfactant levels. It has been discovered in the present invention that by using a water soluble polymeric anionic alpha olefin maleic anhydride copolymer having a carbon content of C<sub>4</sub> to C<sub>30</sub>+ and more preferably from C<sub>4</sub> to C<sub>18</sub> and most preferably from C<sub>6</sub> to C<sub>10</sub>, the polymer acts as a hydrotrope to bring the builders in phase with the nonionic surfactants in an aqueous system which forms a stable single phase liquid detergent which is resistant to phase separation.

Moreover, the hydrolyzed alpha olefin maleic anhydride copolymers useful in the present invention have surprisingly been found to act as an excellent anti-redeposition agent as well as an additional builder which aids in the cleaning of the detergent. Accordingly, detergents formed according to the present invention have excellent prespotting and cleaning properties when compared with other liquid detergents as known in the art.

Further, it is another unexpected result of the use of the hydrolyzed alpha olefin maleic anhydride copolymers that this built single phased clear liquid detergent is compatible with cationic quaternary ammonium fabric softeners which would normally separate out of solution in the presence of anionic detergents. Accordingly, the use of the hydrolyzed alpha olefin maleic anhydride copolymers function as hydrotropes to bring the nonionic surfactants and builder together in a clean stable single phase liquid detergent and also allow the use of quaternary ammonium fabric softeners which are cationic in nature and would ordinarily separate out of a normal liquid detergent.

A preferred embodiment of the invention will now be described in greater detail.

The present invention is concerned with a clear, stable, single phase built liquid detergent composition which is able to use surprisingly large amounts of ionic builders. This is achieved by the use of a water soluble polymeric anionic hydrotrope which is an alpha olefin maleic anhydride copolymer having a carbon content of about C<sub>4</sub> to C<sub>30</sub>+, more preferably from C<sub>4</sub> to C<sub>18</sub> and most preferably from C<sub>6</sub> to C<sub>10</sub>. The alpha olefin copolymers and terpolymers useful as a hydrotrope in this invention are made by the bulk process disclosed by U.S. Patent 4,358,573 and the solution process of U.S. Patent 4,522,992 incorporated herein by reference.

The alpha olefin maleic anhydride polymers useful in the present invention are polymers of maleic anhydride and at least one 1-alkene having about 4-30 carbon atoms and terpolymers with at least two different alpha olefins. Preferably, the polymers are comprised of from about 49 to 80 mole percent of maleic anhydride and from about 20 to 51 mole percent of alpha olefin. These polymers are partially disclosed in U.S. Patent No. 4,358,573 which patent is expressly incorporated by reference for its disclosure of suitable alpha olefin maleic anhydride polymers.

The anhydride included in the alpha olefin maleic anhydride polymers is most preferably maleic anhydride. However, other maleic anhydrides can be utilized in this formation of the polymers such as methylmaleic anhydride, dimethylmaleic anhydride, fluoromaleic anhydride, methylethyl maleic anhydride and the like. Accordingly, as employed herein the term "maleic anhydride" includes such anhydrides in whole or in part. It is preferred that the anhydride be substantially free of acid and the like before polymerization.

The alpha olefins suitable in the formation of the polymers have from 4 to 30+ carbon atoms and include the following: l-butene; l-pentene; l-hexene, l-heptene; l-octene; l-nonene; l-decene; l-dodecene; l-tetradecene; l-hexadecene; l-heptadecene; l-octadecene; 2-methyl-l-butene; 3,3-dimethyl-l-pentene; 2-methyl-l-heptene; 4,4-dimethyl-l-heptene; 3,3-dimethyl-l-hexene; 4-methyl-l-pentene; l-eicosene; l-docosene; l-tetracosene; l-hexacosene; l-octacosene; l-triacontene.

Mixtures of the above materials can be utilized. It is preferred to utilize straight chain l-alkenes having from 4 to 18 carbon atoms, and accordingly, l-butene, l-pentene, l-hexene, l-heptene, l-octene, l-nonene, l-decene, l-dodecene, l-tetradecene, l-hexadecene, l-heptadecene, l-octadecene, and mixtures thereof are preferred. These materials should be substantially free of diolefin as an impurity which causes gel formation and crosslinking. However, small amounts, i.e., less than 2 percent, can be present without causing undue gel formation and crosslinking in the resulting polymers. Also as noted above, either single materials, i.e., l-butene, l-decene, etc., can be used, or mixtures of these materials may be utilized.

As is well known in the art, polymers containing equimolar ratios of alpha olefin maleic anhydride are essentially alternating polymers with maleic anhydride alternating between random comonomers. Accordingly, the alpha olefin maleic anhydride polymers may contain from about 49 to 80 mole percent of maleic anhydride. Under some conditions such as high temperature and very high initiator levels, it is possible to include an excess of maleic anhydride relative to the comonomer in these polymers. The amount of alpha olefin will vary from about 50 to 20 mole percent. The optimum alpha olefin maleic anhydride polymers include about 50 mole % maleic anhydride and about 50 mole % alpha olefin.

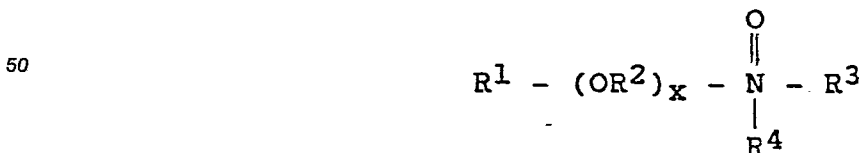
The alpha olefin maleic anhydride polymers may be prepared by any of a number of conventional polymerization processes including polymerization processes as set forth in U.S. Reissue Patent No. 28,475, U.S. Patent Numbers 3,553,177, 3,560,455, 3,560,456, 3,560,457, 3,488,311, 4,522,992 and 4,358,573.

The polymers useful in the present invention are generally low molecular weight materials having a number average molecular weight within the range of from about 500 to 50,000. Moreover, alpha olefin maleic anhydride terpolymers such as  $C_2-C_x$ , where x is an integer from 4 to 30+, may also be used.

Nonionic surfactants are usually made by the condensation of an alkylene oxide (normally ethylene or propylene oxide) with an organic hydrophobic compound which is usually aliphatic or alkyl aromatic in nature. The degree of hydrophilic/hydrophobic balance of these nonionic surfactants is adjusted by shorter or longer chain lengths of the polyoxyalkylene constituent. The following are examples of suitable nonionic surfactants: polyethylene condensates of alkyl phenols having an alkyl group containing from about  $C_6$  to  $C_{12}$  are useful. The ethylene oxide is present in an amount of about 5 to 25 moles of ethylene oxide per mole of alkyl phenol. Commercial examples of these surfactants are Igepal CO-610 marketed by GAF Corporation, Surfonic N95 marketed by Texaco and Triton X-100 sold by Rohm and Haas Company. Other surfactants useful are the condensation products of long chain fatty aliphatic alcohols having a carbon content of about  $C_8$  to  $C_{22}$  when ethoxylated with about 1 to 25 moles of ethylene oxide. Commercial examples of these surfactants are Tergitol 15-S-9 from Union Carbide Corporation and Neodol 25-3 marketed by Shell Chemical Company.

Condensation products of ethylene oxide with hydrophobic bases formed by the condensation of polypropylene oxide with polypropylene glycols are also useful as nonionic surfactants. The hydrophobic base which is reacted with polypropylene oxide and polypropylene glycol should have a molecular weight of about 1500 to 1800. Examples of these polypropylene condensates are the Pluronic surfactants from BASF Wyandotte Corporation. Condensation products of ethylene oxide with a product reaction of propylene oxide and ethylene diamine are also useful. The hydrophobic base of propylene and ethylene oxide usually has a molecular weight from 2500 to about 3000. The final surfactant has a molecular weight of from about 5,000 to 11,000. Commercial examples of these condensates are the Tetronic compounds sold by BASF Wyandotte Corporation.

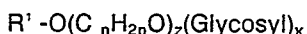
Other examples are the semi polar nonionic water soluble amine oxide surfactants having the formula:



wherein  $R^1$  is an alkyl, hydroxyl, or alkyl phenol having a carbon content of about  $C_8$  to  $C_{22}$ ,  $R^2$  is an alkylene or hydroxy alkylene having a carbon content of about  $C_{23}$  to  $C_{31}$ ,  $x$  is a number of from 0 to 3 preferably 2, and  $R^3$  and  $R^4$  can be an alkyl or hydroxy alkyl having a carbon content of about  $C_1$  to  $C_3$  or a polyethylene oxide group containing from about 1 to 3 ethylene oxide groups. APG 23-3 from A. E. Staley Manufacturing Company is an example of an ethoxylated polysaccharide.

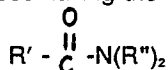
Examples of commercial amine oxide surfactants are Ammonyx CDO or Ammonyx LO from Anyx Chemical Company. Other examples are tallow dimethyl amine oxide and coco alkoxyethyl dihydroxyethyl amine oxide.

Other useful condensation products include alkyl polysaccharides having the formula:



wherein R' is an alkyl, alkylphenol, hydroxyalkyl or hydroxyalkyl phenol, said alkyl containing groups having a carbon content of from about C<sub>10</sub> to C<sub>18</sub>, n is a number from about 2 to 3, z is a number from about 0 to 10, and x is a number of from about 1 to 3.

Fatty acid amines are also useful as nonionic surfactants in this invention. The fatty acid amines are those having the formula:



wherein R' is an alkyl group having a carbon content of about C<sub>7</sub> to C<sub>21</sub>, R'' is hydrogen, a C<sub>1</sub> to C<sub>4</sub> alkyl, a C<sub>1</sub> to C<sub>4</sub> hydroxyalkyl, and (C<sub>2</sub>H<sub>4</sub>O)<sub>x</sub>, where x varies from about 1 to 3, and mixtures of these surfactants. Mazamide C-2, POE (2) cocomonethanol amide from Mazer Chemicals, Inc. is an example of a fatty acid amide nonionic surfactant.

More specifically, the surfactants which are especially useful in the present invention are the NEODOL'S available from Shell Chemical Company and identified as C<sub>8</sub> to C<sub>15</sub> linear primary alcohol ethoxylates. Other suitable surfactants include the Tergitols available from Union Carbide Corporation and identified as polyethylene glycol ethers of secondary alcohols, polyethylene glycol ethers of primary alcohols, mixed polypropylene glycols of linear alcohols, nonylphenyl polyethylene glycol ethers, trimethyl nonyl polyalkylene glycol ethers, and polyalkylene glycol ethers.

Other nonionic surfactants which are especially useful in the present invention are ethoxylated nonylphenols and the ethoxylated octylphenols. Commercial examples of these chemicals are Surfonic N95 from Texaco, Triton X100 from Rohm and Haas Company and Igepal CA620 from GAF Corporation. The ethoxylated secondary linear alcohols such as Tergitol 15-S-9 from Union Carbide Corporation are also especially useful.

A builder such as borax is present in an amount of from about 2 to 25% by weight of the composition. Presumably, all effective ionic builders known in the art will prove effective in this system. However, those of special interest are the borates, citrates, the non-phosphorous inorganic builders, the phosphates, the non-phosphorous organic builders, and mixtures thereof.

The borates are the builders of first choice and may be selected from the group consisting of sodium tetraborate, disodium octaborate tetrahydrate, sodium metaborate, the analogous potassium salts and mixtures thereof. The phosphates, although currently in disfavor with ecologists, may also be useful in this invention. The phosphates may be selected from the group consisting of sodium tripolyphosphate, tetrapolyphosphate, tetrasodium pyrophosphate, disodium pyrophosphate, sodium metaphosphate, sodium hexamethaphosphate the analogous potassium salts of these compounds, and mixtures thereof.

The non-phosphorous inorganic builders are carbonates and particularly those selected from the group consisting of sodium carbonate, potassium carbonate, bicarbonate, sesquicarbonate, and mixtures thereof.

The non-phosphorous organic builders useful in the present invention are those which are selected from the group consisting of alkali metals and alkyl ammonium salts of polyacetates, the carboxylates, polycarboxylates, and polyhydroxy sulfonates as well as mixtures thereof.

This system also optionally further includes at least one additional builder and preferably two or more additional builders as an additional builder system which is present in an amount from about 2 to 10% by weight of the composition. The additional builder system may be selected from the group consisting of the salts of ethylene diamine tetracetic acid, the salts of nitrilotriacetic acid, the salts of hexamethylene diamine tetracetic acid, the salts of diethylene triamine pentacetic acids, silicates, and mixtures thereof.

Additionally, but not preferably, anionic surfactants are also useful in the present invention but not in a preferred embodiment. The anionic surfactants are useful in a range of from about 2 to 25% by weight of the composition and preferably at about 5% by weight of the composition. The anionic surfactants include at least one anionic surfactant selected from the group consisting of alkaline metal salts, ammonium and alkyl ammonium salts of fatty acids having a carbon content of from about C<sub>10</sub> to C<sub>20</sub> range, water soluble salts such as ammonium and alkyl ammonium salts of organic sulfuric reaction products having an alkyl group containing from about C<sub>10</sub> to C<sub>20</sub> carbon atoms, and a sulfonic or sulfuric acid ester group.

Other useful anionics include the water soluble salts of the esters of alpha sulfonated fatty acids having a carbon content of about C<sub>6</sub> to C<sub>20</sub> in the fatty acid groups and from about C<sub>1</sub> to C<sub>10</sub> in the ester groups.

Other water soluble salts useful in the present invention include the water soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from about C<sub>2</sub> to C<sub>9</sub> carbon atoms in the acyl group and about C<sub>9</sub> to C<sub>23</sub> in the alkane moiety, alkyl ether sulfates containing from about C<sub>10</sub> to C<sub>20</sub> carbon atoms in the alkyl groups and from about 1 to 30 moles of ethylene oxide, water soluble salts of olefin sulfonates containing from about C<sub>12</sub> to C<sub>24</sub> beta alkyloxyalkane sulfonates which contain from about C<sub>1</sub> to C<sub>3</sub> carbon atoms in the alkyl group and from about C<sub>18</sub> to C<sub>20</sub> carbon atoms in the alkane moiety, anionic phosphate surfactants, n-alkyl substituted succinamates, and mixtures thereof.

The composition may also optionally further include a pH adjuster to keep the liquid detergent near neutral or slightly alkaline in pH value. The preferred pH ranges are from about 6 to 9, more preferably from about 7 to 8.5, and most preferably at about 8. The pH adjusters may be selected from any acid group and citric acid is especially preferred because of its builder properties. The pH adjusters are present in a range of from about 0.1 to 5% by weight of the composition.

Further, and surprisingly, the liquid laundry detergent composition may also further include at least one cationic quaternary ammonium fabric softener selected from the group consisting of:

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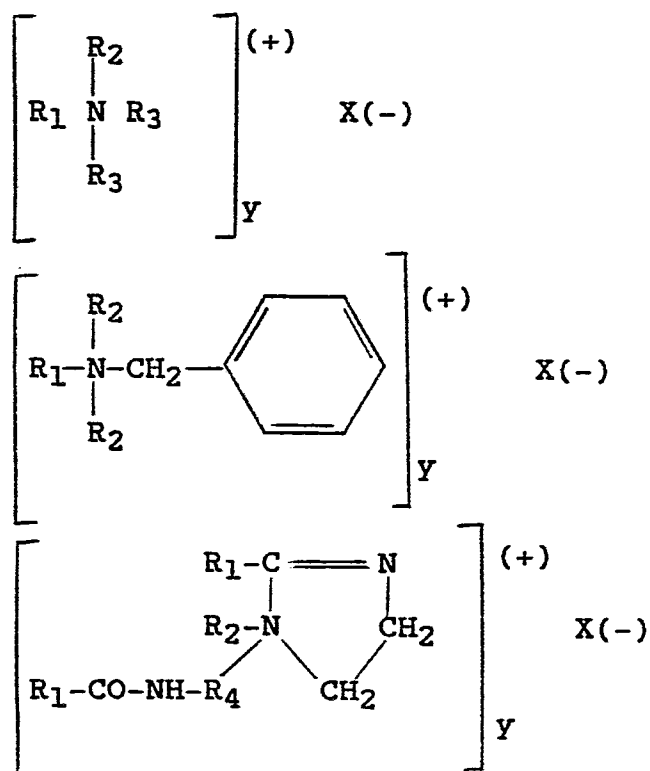
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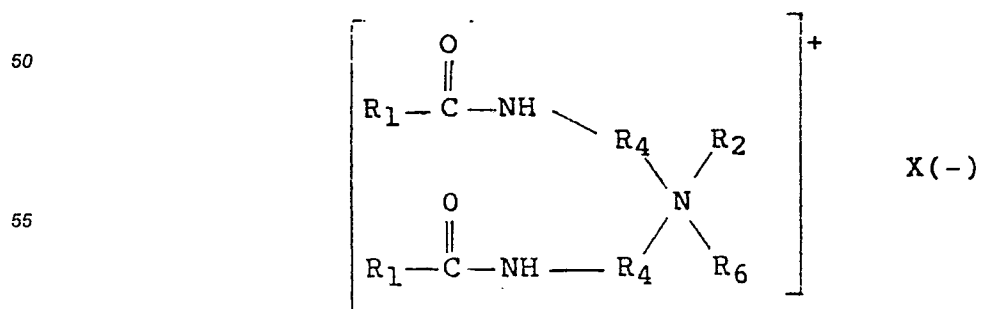
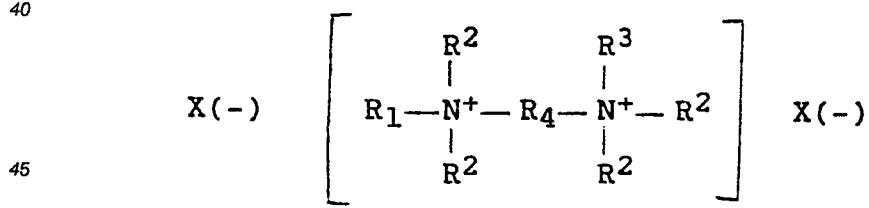
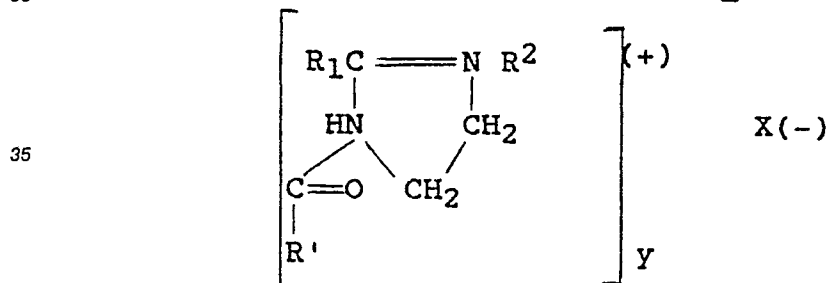
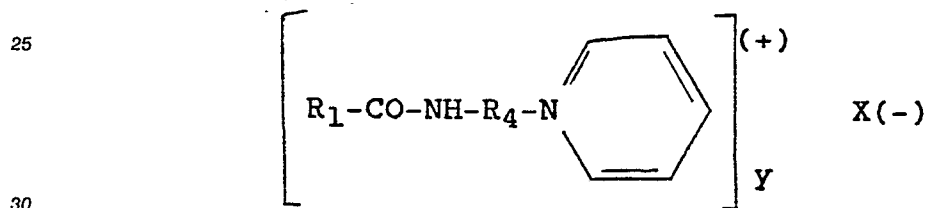
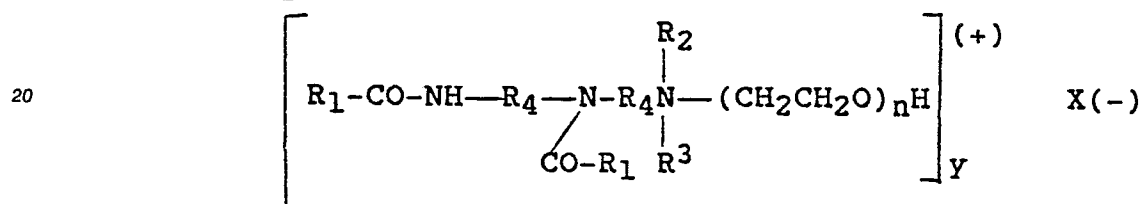
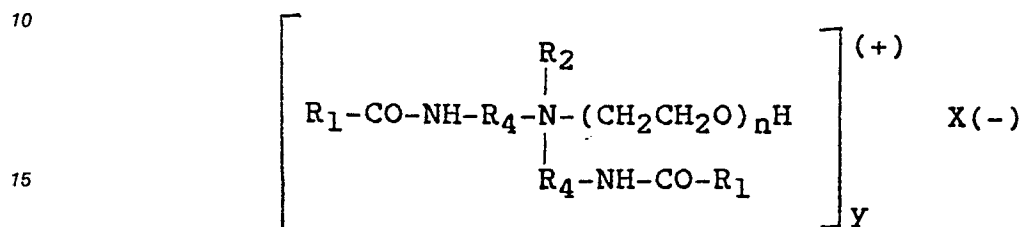
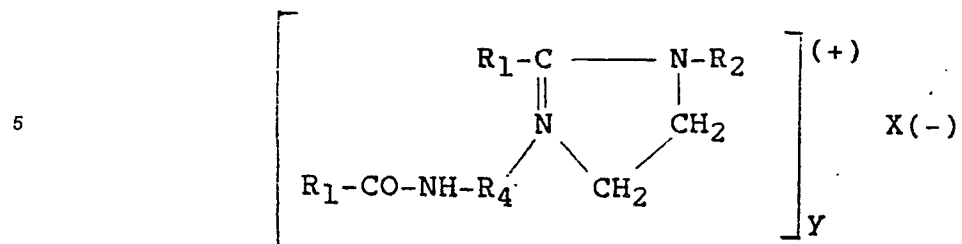
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The reaction product of about 2 moles of an acid having formula  $R_5\text{COOH}$  and about 1 mole of an alkylene diamine having formula  $\text{H}_2\text{N}-\text{C}_2\text{H}_4-\text{NHR}_6$  said reaction product being a mixture of amides, esters and imidazolines and mixtures thereof.

In the foregoing formulas,  $R_1$  is an alkyl or alkenyl straight or branched chain hydrocarbon containing from 8 to 22, preferably from 11 to 19 carbon atoms.  $R_2$  is an alkyl group containing from 1 to 3 carbon atoms.  $R_3$  represents  $R_1$  or  $R_2$ .  $R_4$  is an alkylene group containing from 1 to 2 carbon atoms.  $R_5$  is an aliphatic alkyl group containing from 15 to 19 carbon atoms.  $R_6$  is a hydroxyalkyl group containing from 1 to 3 carbon atoms. X is a suitable anion such as chloride, bromide, iodide, sulfate, alkyl sulfate having 1 to 3 carbon atoms in the alkyl group, acetate, etc. Also in the formulas, y is the valence of X and n represents an integer from 1 to 4. Mixtures of quaternary ammonium compounds may also be used to practice this invention.

Cationic fabric softeners are basically, one, two or three alkyl chains emanating from a positively charged cation such as nitrogen or phosphorous. The alkyl groups are usually  $\text{C}_{10}-\text{C}_{22}$ . These materials must be water soluble or water dispersible. The positively charged nitrogen can be a normal alkyl ammonium or in a cyclic ring such as imidazolinium or pyridinium salts. Examples of some of the more common commercial classes of cationic fabric softeners are monoalkyl trimethyl quaternary ammonium compounds, monomethyl trialkyl quaternary ammonium compounds, dimethyl dialkyl quaternary ammonium compounds, imidazolinium quaternary ammonium compounds, dimethyl alkyl benzyl quaternary ammonium compounds, complex diquaternary ammonium compounds, dimethyl dialkoxyl alkyl quaternary ammonium compounds, diamidoamine based quaternary ammonium compounds, dialkyl methyl benzyl quaternary ammonium compounds, alkyl pyridinium salts, and amido alkoxylated ammonium. Usually these commercial quaternary ammonium compounds contain alkyl groups of  $\text{C}_{10}-\text{C}_{18}$  or a mixture thereof.

It has been surprisingly found that quaternary fabric softeners may be tolerated in this detergent system.

The composition may also include proteolytic enzymes in an amount of 0.01 to 5% by weight of the composition, optical brighteners in an amounts of about 0.05 to 5% by weight of the composition as well as perfumes, dyes, disinfectants and other ingredients which are standard and well known in the art.

Preferably, the composition is comprised of from about 5 to 25% by weight of at least one nonionic surfactant, at least one builder and preferably a borate builder present in an amount of about 2 to 25% by weight of the composition and more preferably at about 5% by weight of the composition, an additional builder system in an amount of about 2 to 10% by weight of the composition, a water soluble polymeric anionic hydrotrope anti-redeposition agent which is the hydrolyzed alpha olefin maleic anhydride copolymer which is present at about 1 to 10% by weight of the composition, optionally a pH adjuster present in about 0.1 to 5% by weight of the composition as well as optionally effective amounts of proteolytic enzymes, optional cationic quaternary ammonium fabric softeners of the aforementioned type, and the balance of the composition being water. It is further contemplated that the composition have a pH in a range of about 6 to 9, more preferably from about 7 to 8.5, and most preferably at about 8.

The following examples are offered to illustrate the invention and facilitate its understanding without limiting the scope or spirit of the invention.

The Examples were each tested according to the American Society for Testing and Materials (ASTM) method for measuring soil removal from artificially soiled fabrics and for evaluating stain removal performance in home laundry. In addition, each of the formulations were also tested according to the guide lines as set forth by the American Association of Textile Chemists and Colorists (AATCC) as these test methods relate to soil redeposition and soil release. A few of the formulations tested are enclosed in the following table:



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INGREDIENT	FORMULAS						
	#1	#2	#3	#4	#5	#6	#7
1-hexene/maleic anhydride copolymer (1.0/1.0 molar ratio)	3.00	-	4.00	4.00	-	5.00	-
1-hexene/1-decene/maleic anhydride terpolymer (.5/.5/1.0 molar ratio)	-	2.50	-	-	6.00	-	-
1-decene/1-octadecene/maleic anhydride terpolymer (.5/.5/1.0 molar ratio)	-	-	-	-	-	-	4.00
Borate - sodium tetraborate	5.00	-	3.00	5.00	20.00	4.00	3.00
Tetrapotassium pyrophosphate (TKPP)	-	5.00	-	-	-	9.00	-
Nitritotriacetic acid (NTA)	4.00	-	5.00	-	2.50	-	-
Sodium citrate	-	2.50	-	-	-	-	5.00
Primary alcohol ethoxylate (9 mol)	15.00	-	-	9.00	-	12.00	15.00
Secondary alcohol ethoxylate (7 mol)	-	12.00	-	4.00	-	-	-
Ethoxylated nonyl phenol (9.5 mol)	-	-	15.00	-	10.00	-	-
Citric acid	1.75	1.20	1.50	-	2.50	2.00	1.20
Optical brightener	.20	.20	.20	.30	.15	.15	.30
Methyl bis 2-hydroxyethyl ammonium sulfate	-	-	-	3.20	-	-	-
Fragrance	.20	.20	.20	.20	.20	.20	.20
Dye	.002	.002	.002	.001	.002	.002	.002
Enzyme	.50	-	-	-	-	-	.50
Water (balance to 100%)							

Each of the formulas listed in the above table had various performance ratings. The differences in performances are noted as follows.

Formula 1 indicates the use of a C<sub>6</sub> alpha olefin maleic anhydride copolymer having a borax builder and an NTA additional builder system. The formula disclosed excellent stain removal on 100% cotton and blends of cotton and polyester when tested accordingly to the test methods enumerated above.

Formula 2 demonstrates the use of a C<sub>6</sub>-C<sub>10</sub> alpha olefin maleic anhydride terpolymer. The formulation of 2 does not contain a borax builder system however it does contain a secondary builder system. The system gives good performance overall, however, has a slightly downscale anti-redeposition properties when compared to the formulation of 1.

Formula 3 demonstrates the use of an ethoxylated nonphenol and its effect on oily stain and particulate stain or soil removal. Specifically, an ethoxylated nonphenol surfactant greatly increases oily stain and particulate soil removal. In addition, such a surfactant when coupled with a C<sub>6</sub> alpha olefin maleic anhydride copolymer was determined to have excellent soil anti-redeposition properties.

Formula 4 demonstrates the incorporation of a cationic quaternary ammonium fabric softener. The formula indicated the softener was able to function very well with a minimum of interference of detergency of the composition. Additionally, no separation of the phases occurred by the addition of the cationic quaternary ammonium fabric softener.

Formula 5 indicates the effects of increasing the borax builder system. Specifically, excellent whiteness readings were obtained along with an improvement in particulate and soil removal on 100% cotton. The formula was stable, from 40 to 120°F.

Formula 6 indicate a combination of borax as the main builder system along with tetrapotassium pyrophosphate as a secondary builder and a C<sub>6</sub> alpha olefin maleic anhydride copolymer in a detergent composition. The composition offered excellent anti-redeposition and cleaning properties.

Formula 7 indicates the use of a C<sub>10</sub>-C<sub>18</sub> alpha olefin maleic anhydride terpolymer and demonstrates very good stain removal with this formula. Anti-redeposition properties were slightly downscaled but still within the acceptable range.

All of the above formulas perform equal to or better than current commercial liquid detergents.

#### Processing Examples

The polymer in this invention is hydrolyzed with sodium tetraborate, ammonium hydroxide, potassium hydroxide, or sodium hydroxide. A concentrate is prepared with water, base, and polymer at a temperature of 40°C-95°C until a clear solution is formed.

#### Processing Example I:

<u>Polymer Cut #1</u>	<u>% by Weight</u>
Water	70.0
Sodium tetraborate	10.0
1 hexene/maleic anhydride copolymer	20.0
	<u>100.0</u>

#### Processing for Formula #1:

Charge 59.848 grams of water together with 3.5 grams of sodium tetraborate and 1.75 grams of citric acid. Agitate until dissolved. Add 15 grams of the polymer cut shown above. Add the rest of materials in the following order: 15.0 grams of primary alcohol ethoxylate, 0.020 grams of optical brightener, 0.50 grams of enzyme, 4.0 grams of NTA, 0.002 grams of dye, and 0.20 grams of fragrance.

Processing Example #2:

	<u>Polymer Cut #.2</u>	<u>% by Weight</u>
5	Water	70.0
	Ammonium hydroxide	10.0
10	1-hexene/maleic anhydride copolymer	20.0
		<hr/> 100.0

15 Processing for Formula #4:

Charge 58.229 grams of water with 5.0 grams of sodium tetraborate. Add 20.0 grams of polymer cut #2 shown above. Agitate until dissolved. Meanwhile, heat 9.0 grams of primary alcohol ethoxylate and 4.0 grams of secondary alcohol ethoxylate with 3.2 grams of methyl bis 2-hydroxyethyl ammonium sulfate to 100°F. Slowly add the heated surfactants to the water, sodium tetraborate, and polymer cut mixture until

uniform. Add 0.30 grams of optical brightener, 0.001 grams of dye, and 0.20 grams of fragrance.

There is an amide formation up to 30% with a cut prepared with ammonium hydroxide. Performance is similar to cuts prepared with sodium hydroxide, potassium hydroxide, and sodium tetraborate.

25 **Claims**

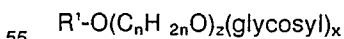
1. A clear, stable, single phase built liquid detergent composition characterized by
- a) at least one nonionic surfactant in an amount of from about 5 to 25% by weight of the composition;
  - 30 b) a builder in an amount of from about 2 to 25% by weight of the composition;
  - c) a water soluble polymeric anionic hydrotrope anti-redeposition agent in an amount of about 1 to 10% by weight of the composition, said hydrotrope being selected from the group of hydrolyzed alpha olefin maleic anhydride polymers, copolymers and terpolymers having a carbon content of about C<sub>4</sub> to C<sub>30</sub> + , and;
  - d) the balance water

35 wherein said composition has a pH in the range of about 6 to 9.

2. The composition of Claim 1, characterized in that said surfactants are selected from the group consisting of the polyethylene condensates of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms with ethylene oxide, said ethylene oxide present in an amount of about 5 to 25 moles of ethylene oxide per mole of alkyl phenol, condensation products of ethylene oxide with a hydrophobic base
- 40 formed by the condensation of propylene oxide with propylene glycol, said hydrophobic base having a molecular weight of from about 1500 to 1800, condensation products of ethylene oxide with the product reaction of propylene oxide and ethylene diamine, semi-polar nonionic water soluble amine oxide surfactants having the formula:

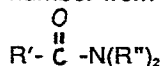


50 wherein R<sup>1</sup> is an alkyl, hydroxyl, hydroxyl or alkyl phenyl having a carbon content of about C<sub>8</sub> to C<sub>22</sub>, R<sup>2</sup> is an alkylene or hydroxyalkylene having a carbon content of about C<sub>2</sub> to C<sub>3</sub>, X is a number from 0 to about 3, and R<sup>3</sup> and R<sup>4</sup> can be an alkyl or hydroxyalkyl having a carbon content of about C<sub>1</sub> to C<sub>3</sub>, or a polyethylene oxide group containing from about 1 to 3 ethylene oxide groups, alkyl polysaccharides having the formula:



wherein R<sub>1</sub> is an alkyl, alkylphenyl, hydroxyalkyl, or hydroxyalkyl phenyl, said alkyl contains groups having a carbon content of about C<sub>10</sub> to C<sub>18</sub>, n is a number from about 2 to 3, z is a number from about 0 to 10, x is a

number from about 1 to 3; fatty acid amides having the formula:



5 wherein R' is an alkyl group having carbon content of about C<sub>7</sub> to C<sub>21</sub>, R'' is hydrogen, C<sub>1</sub> to C<sub>4</sub> alkyl, C<sub>1</sub> to C<sub>4</sub> hydroxyalkyl, and -(C<sub>2</sub>H<sub>4</sub>O)<sub>x</sub> where x varies from about 1 to 3, and mixtures thereof.

3. The composition of Claim 1 or 2, characterized in that said builder is selected from the group consisting of borates, citrates, non-phosphorus inorganic builders, phosphates, non-phosphorus organic builders and mixtures thereof.

10 4. The composition of Claim 3, wherein said borates are selected from the group consisting of sodium tetraborate, disodium octoborate, tetrahydrate, sodium metaborate and mixtures thereof.

5. The composition of Claim 3, wherein said phosphates are selected from the group consisting of sodium tripolyphosphate, tetrapyropolyphosphate, tetrasodium pyrophosphate, disodium pyrophosphate, sodium metaphosphate, sodium hexametaphosphate, the analogous potassium salts, and mixtures thereof.

15 6. The composition of Claim 3, wherein said nonphosphorus inorganic builders are selected from the group consisting of sodium carbonate, potassium carbonate, bicarbonate, sesquicarbonate and mixtures thereof.

7. The composition of Claim 3, wherein said non-phosphorous organic builders are selected from the group consisting of alkali metals, ammonium, and alkyl ammonium salts of polyacetates, carboxylates, 20 polycarboxylates, polyhydroxysulfonates, and mixtures thereof.

8. The composition of any of Claims 1 to 7, characterized by at least one additional builder in an amount of from about 2 to 10% by weight of the composition.

9. The composition of Claim 8, wherein said additional builder is selected from the group consisting of salts of ethylene diamine tetra acetic acid, salts of nitrilotriacetic acid, salts of hexamethylene diamine tetra 25 acetic acid, salts of diethylene triamine penta acetic acid, silicates, and mixtures thereof.

10. The composition of any of Claims 1 to 9, characterized by at least one cationic quaternary ammonium fabric softener selected from the group consisting of:

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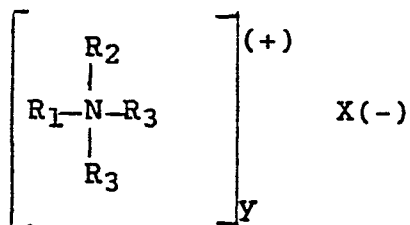
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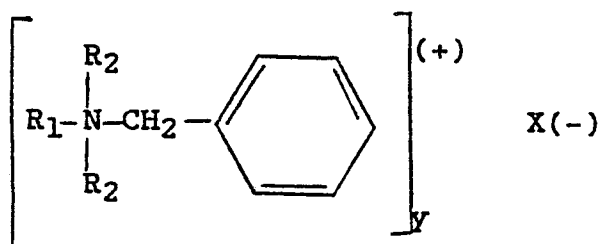
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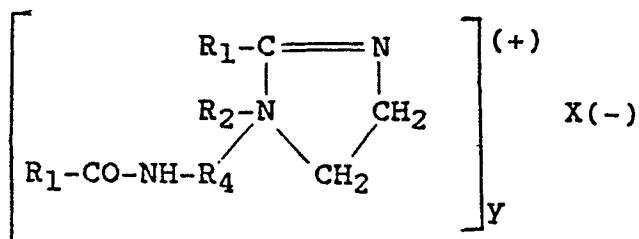


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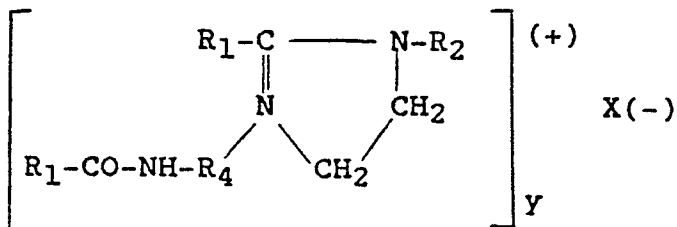


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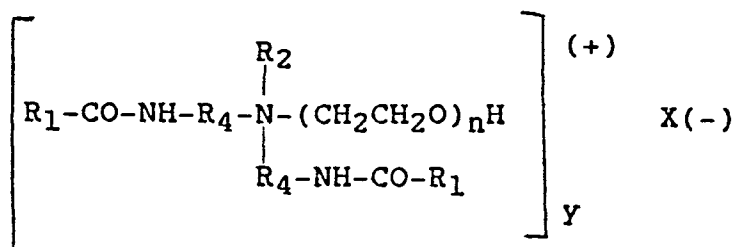


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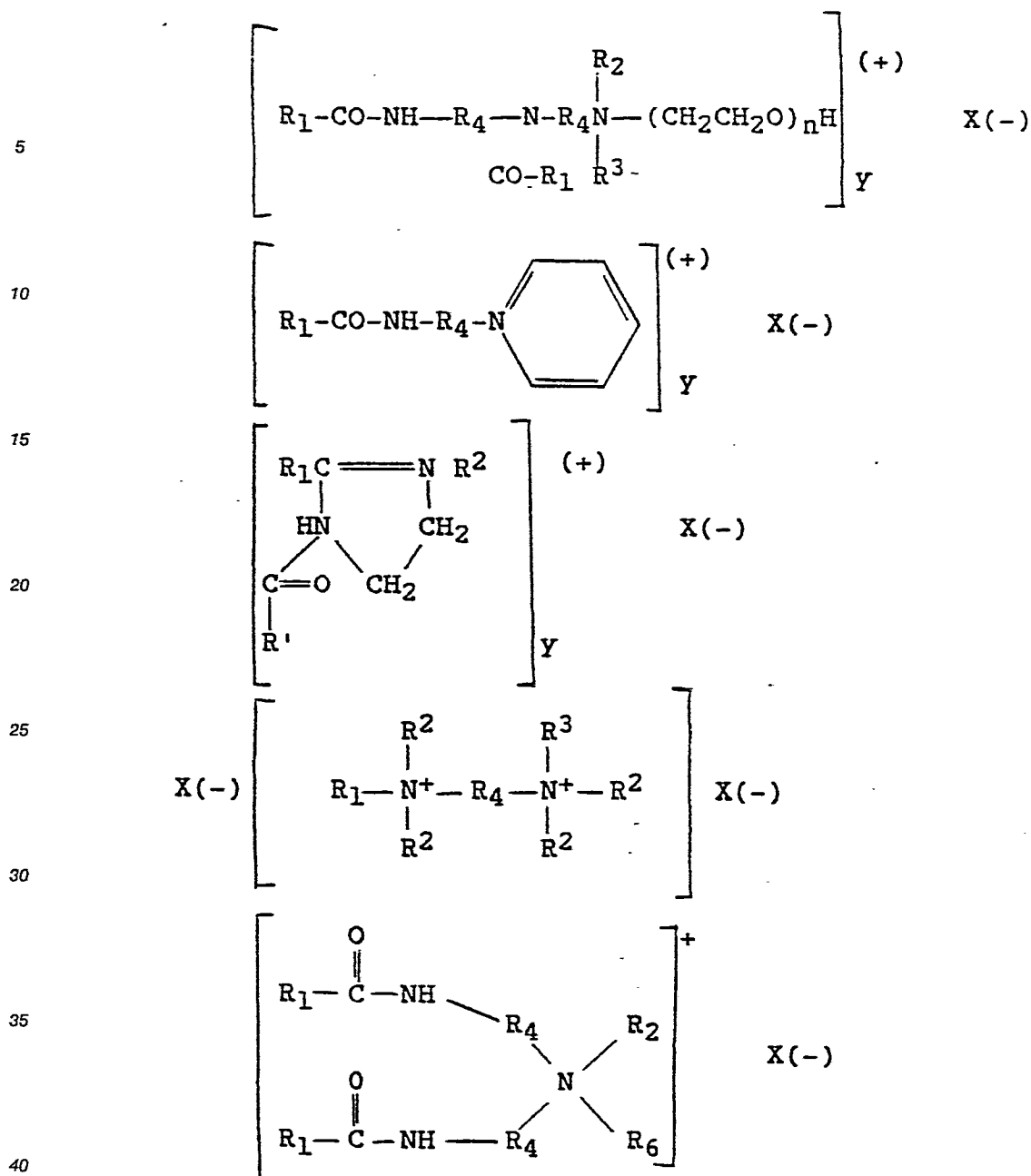


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The reaction product of about 2 moles of an acid having formula  $R_5COOH$  and about 1 mole of an alkylene diamine having formula  $H_2N-C_2H_4-NHR_6$  said reaction product being a mixture of amides, esters and imidazolines, wherein  $R_1$  is an alkyl or alkenyl straight or branched chain hydrocarbon containing from 8 to 22, preferably from 11 to 19 carbon atoms,  $R_2$  is an alkyl group containing from 1 to 3 carbon atoms,  $R_3$  can be  $R_1$  or  $R_2$ ,  $R_4$  is an alkylene group containing from 1 to 2 carbon atoms,  $R_5$  is an aliphatic alkyl group containing from 15 to 19 carbon atoms,  $R_6$  is a hydroxyalkyl group containing from 1 to 3 carbon atoms,  $X$  is a water soluble anion,  $Y$  is the valence of  $X$  and  $n$  represents an integer from 1 to 4, and mixtures thereof.

11. The composition of Claim 10, wherein said quaternary ammonium fabric softener is selected from the group consisting of ditallow dimethyl ammonium chloride, methyl-1-tallow amido ethyl-2-tallow imidazolium methylsulfate, methyl bis(tallow amido ethyl)-2-hydroxyethyl ammonium methyl sulfate, methyl-bis-2-hydroxyethyl coco ammonium methyl sulfate, and mixtures thereof.

12. The composition of any of Claims 1 to 11, characterized by from about 2 to 25% by weight of the composition of at least one anionic surfactant selected from the group consisting of alkali metal salts, ammonium and alkylammonium salts of fatty acids having a carbon content of about  $C_{10}$  to  $C_{20}$ , water soluble salts, ammonium and alkylammonium salts or organic sulfuric reaction products having an alkyl group containing about  $C_{10}$  to  $C_{20}$  and a sulfonic acid or sulfuric acid ester group, water-soluble salts of esters of alpha sulfonated fatty acids having a carbon content of about  $C_6$  to  $C_{20}$  in the fatty acid group and from about  $C_1$  to  $C_{10}$  in the ester group, water soluble salts of 2 acryloxy-alkane-1-sulfonic acids containing

from about C<sub>2</sub> to C<sub>9</sub> in the alkyl group and about C<sub>9</sub> to C<sub>23</sub> in the alkane moiety, alkyl ether sulfates containing from about C<sub>10</sub> to C<sub>20</sub> in the alkyl group and from 1 to 30 moles of ethylene oxide, water soluble salts of olefin sulfonates containing from about C<sub>12</sub> to C<sub>24</sub>, beta alkyloxy alkane sulfonates containing from about C<sub>1</sub> to C<sub>3</sub> in the alkyl group and from about C<sub>8</sub> to C<sub>20</sub> in the alkane moiety, anionic phosphate surfactants, N-alkyl substituted succinamates, and mixtures thereof.

13. The composition of any of Claims 1 to 12, characterized by from about 0.01 to 5% by weight of the composition proteolytic enzymes.

14. The composition of any of Claims 1 to 13, characterized by an optical brightener present in an amount from about 0.05 to 5% by weight of the composition.

15. The composition of Claim 1, wherein said pH is 7 to 8.5

16. The composition of Claim 1, wherein said hydrotrope is a hydrolyzed alpha olefin maleic anhydride copolymer having a carbon content of about C<sub>6</sub> to C<sub>10</sub>.

17. The composition of Claim 1, wherein said hydrotrope is a hydrolyzed alpha olefin maleic anhydride terpolymer selected from the group consisting of C<sub>2</sub>-C<sub>x</sub>, wherein x is an integer from 4 to 30+, said terpolymer contains at least two different alpha olefins.

18. The composition of Claim 1, further including an acid pH adjuster, said pH adjuster present in an amount of about 0.1 to 5% by weight of the composition.

19. The composition of Claim 18, wherein said pH adjuster is selected from the group consisting of boric acid, citric acid, succinic acid, maleic acid, and mixtures thereof.

20. A clear, stable single phase built liquid detergent composition, comprising:

a) at least one nonionic surfactant in an amount of from about 5 to 25% by weight of the composition, said nonionic surfactant selected from the group consisting of nonyl phenol ethoxylated with about 12 to 4 moles of ethylene oxide, C<sub>9</sub> to C<sub>15</sub> linear primary alcohol ethoxylate, C<sub>8</sub> to C<sub>20</sub> secondary alcohol ethoxylates, and mixtures thereof;

b) at least one borate builder in an amount of about 2 to 25% by weight of the composition selected from the group consisting of sodium tetra borate, disodium octaborate, tetrahydrate, sodium meta borate, and mixtures thereof;

c) an additional builder system in an amount of about 2 to 10% by weight of the composition, said system selected from the group consisting of salts of nitroacetic acid, salts of ethylene diamine tetra acetic acid, salts of hexamethylene diamine tetra acetic acid, salts of diethylene triamine penta acetic acid, salts of citric acid, silicates, non-phosphorous inorganic builders, non-phosphorous organic builders and mixtures thereof;

d) a water soluble polymeric anionic hydrotrope anti-redeposition agent in an amount of about 1 to 10% by weight of the composition, said hydrotrope being selected from the group of hydrolyzed alpha olefin maleic anhydride polymers, copolymers and terpolymers having a carbon content of about C<sub>4</sub> to C<sub>30</sub> +;

e) an acid pH adjuster present in an amount of from about 0.1 to 5% by weight of the composition;

f) effective amounts of proteolytic enzymes;

g) at least one cationic quaternary ammonium fabric softener selected from the group consisting of ditallow dimethyl ammonium chloride, methyl-1-tallow amido ethyl-02-tallow imadazilium methyl sulfate, methyl bis(tallow amido ethyl)2-hydroxyethyl ammonium methyl sulfate, methyl-bis-2-hydroxyethyl coco ammonium methyl sulfate and mixtures thereof;

h) further including from about 2 to 25% byweight of the composition of at least one anionic surfactant selected from the group consisting of alkali metal salts, ammonium and alkylammonium salts of fatty acids having a carbon content of about C<sub>10</sub> to C<sub>20</sub>, water soluble salts, ammonium and alkylammonium salts or organic sulfuric reaction products having an alkyl group containing about C<sub>10</sub> to C<sub>20</sub> and a sulfonic acid or sulfuric acid ester group, water-soluble salts of esters of alpha sulfonated fatty acids having a carbon content of about C<sub>6</sub> to C<sub>20</sub> in the fatty acid group and from about C<sub>1</sub> to C<sub>10</sub> in the ester group, water soluble salts of 2 acryloxy-alkane-1-sulfonic acids containing from about C<sub>2</sub> to C<sub>9</sub> in the alkyl group and about C<sub>9</sub> to C<sub>23</sub> in the alkane moiety, alkyl ether sulfates containing from about C<sub>10</sub> to C<sub>20</sub> in the alkyl group and from 1 to 30 moles of ethylene oxide, water soluble salts of olefin sulfonates containing from about C<sub>12</sub> to C<sub>24</sub>, beta alkyloxy alkane sulfonates containing from about C<sub>1</sub> to C<sub>3</sub> in the alkyl group and from about C<sub>8</sub> to C<sub>20</sub> in the alkane moiety, anionic phosphate surfactants, N-alkyl substituted succinamates, and mixtures thereof;

i) the balance water;

wherein said composition has a pH in the range of about 7 to 8.5