United States Statutory Invention Registration

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Reg. Number: H1635
Published: Mar. 4, 1997

[54] DETERGENT COMPOSITIONS WITH OLEOYL SARCOSINATE AND AMINE OXIDE

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[21] Appl. No.: 251,981
[22] Filed: Jun. 1, 1994

[51] Int. Cl. 6 C11D 1/38
[52] U.S. Cl. 510/220; 510/299; 510/350; 510/475; 510/503; 510/499


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[57] ABSTRACT
The present invention provides a detergent composition comprising:

(a) at least 0.1% of an oleyl sarcosinate of the formula:

\[
\text{CH}_3
\]

wherein M is hydrogen or a cationic moiety; and

(b) from about 0.1% to about 20% of an amine oxide.

17 Claims, No Drawings

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DETERGENT COMPOSITIONS WITH OLEOYL SARCOSINATE AND AMINE OXIDE

TECHNICAL BACKGROUND

This invention relates to detergent compositions containing detergentsurfactant and amine oxide. In particular, this invention relates to detergent compositions including oleoyl sarcosinate.

BACKGROUND ART


It has been found that certain oleoyl sarcosinates can provide excellent cleaning performance and are particularly soluble in the wash solution when incorporated into a granular detergent composition. Furthermore, detergent compositions containing these oleoyl sarcosinates in combination with one or more amine oxide additionally provide excellent greasy soil removal. The compositions also provide excellent color care for dyed fabrics and excellent skin mildness for handwash operations. These and other advantages of the present invention will be seen from the disclosures hereinafter.

SUMMARY OF THE INVENTION

The present invention provides a detergent composition comprising:

(a) at least about 0.1% of oleoyl sarcosinate of the formula:

\[
\text{CH}_3\text{O}-\text{N}=\text{O}^{\text{OM}}
\]

wherein M is hydrogen or a cationic moiety; and

(b) from about 0.1% to about 20% of an amine oxide.

Preferred compositions also comprise at least about 1% of a detergentsurfactant, other than said oleoyl sarcosinate surfactant, selected from anionic and nonionic detergentsurfactants.

This invention further provides a method for improving the performance of detergents containing amine oxides and detergentsurfactant by additionally incorporating into such composition at least about 0.1% by weight, of the oleoyl sarcosinate surfactant described above.

DETAILED DESCRIPTION OF THE INVENTION

1. Oleoyl Sarcosinate:

The present invention compositions comprise oleoyl sarcosinate, in its acid and/or salt form selected as desired for the compositions and uses herein, having the following formula:

\[
\text{CH}_3\text{O}-\text{N}=\text{O}^{\text{OM}}
\]

wherein M is hydrogen or a cationic moiety. Preferred M are hydrogen and alkali metal salts, especially sodium and potassium. Oleoyl sarcosinate is commercially available, for example as Hamptonol O supplied by W. R. Grace & Co.

Compositions according to the present invention typically comprise at least 0.1%, preferably from about 0.5% to about 80%, preferably from about 1% to about 40%, and most preferably from about 2% to about 30%, of oleoyl sarcosinate by weight of the composition.

In addition to the commercially-available oleoyl sarcosinate, oleoyl sarcosinate useful herein can also preferably be prepared from the ester (preferably the methyl ester) of oleic acid and a sarcosine salt (preferably the sodium salt) under anhydrous reaction conditions in the presence of a base catalyst and a basicity equal to or greater than alkoxide catalyst (preferably sodium methoxide). For example, the reaction may be illustrated by the scheme:

\[
\text{CH}_3\text{OCH}_3\text{Na} + \text{ONa}\rightarrow \text{CH}_3\text{ONa} + \text{OCH}_3\text{Na}
\]
rapeseed oil may comprise a majority of oleic acid, and a mixture of fatty acid impurities such as palmitic, stearic, linoleic, linolenic and/or eicosenoic acid, some or all of which are converted to the sarcosinate by this reaction method. If desired for formulation purposes, some or all of such impurity materials may be excluded from the starting oil before preparing the oleoyl sarcosinate to be used in the present compositions.

Finally, sarcosine remaining in the reaction mixture can be converted to an amide by addition of maleic or acetic anhydride to the mixture, thereby minimizing the sarcosine content and any potential for formation of undesired nitrogen-containing impurities.

The synthesis of oleoyl sarcosinate may be carried out as follows to prepare the sodium oleoyl sarcosinate.

Synthesis of Oleoyl Amide of Sarcosine Sodium Salt—A 2 L, 3-neck, round bottom flask is fitted with thermometer, Dean-Stark trap with condenser, mechanical stirring, and a gas inlet adapter through which nitrogen is passed over the reaction mixture. The reaction vessel is charged with sarcosine (43.3 g, 0.476 mol), sodium methoxide 25% in methanol (97.7 g, 0.452 mol), and methanol (400 mL). The reaction is refluxed 15 min to neutralize the sarcosine and then methyl ester derived from Cargill regular high-oleyl sunflower oil (148.25 g, 0.5 mol) is added. After the methanol is removed with the Dean-Stark trap, reaction mixture is heated to 170°C for 1 h to drive off any water. The reaction is initiated by the addition of sodium methoxide 25% in methanol (15.4 g, 0.0714 mol). Reaction is kept at 170°C for 2.5 h during which methanol is collected in the Dean-Stark trap. The reaction is allowed to cool slightly and then methanol (200 g) is added. Maleic anhydride (9.43 g, 0.095 mol) is added to the methanol solution and the reaction is stirred at 60°C for 0.5 h. Then most of the methanol is removed by rotary evaporation and acetone (2 L) is added to precipitate the product. The product is collected by suction filtration and allowed to air dry to give an off-white solid. Analysis of the reaction mixture by GC indicates the majority of the product is oleoyl sarcosinate, with minor amounts of the following impurities: sarcosine, oleic acid, and the sarcosinates derived from palmitic acid, stearic acid, and linoleic acid.

Amine Oxide

The compositions of the present invention comprise amine oxide in accordance with the general formula I:

\[ R^1\text{(EO)}_n\text{(PO)}_m\text{(BO)}_{n+m}\text{N}O\text{(CH}_2\text{R}^2\text{)}_x\text{H}_y\text{O} \]

In general, it can be seen that the structure (I) provides one long-chain moiety \( R^1\text{(EO)}_n\text{(PO)}_m\text{(BO)} \), and two shorter chain moieties, \( \text{CH}_2\text{R}^2\text{R}^3\text{R}^4\text{R}^5\text{R}^6\text{R}^7\text{O} \). \( R^1 \) is preferably selected from methyl or ethyl hydrocarbon moieties which can be saturated or unsaturated, preferably, \( R^1 \) is a primary or branched hydrocarbon moiety having chainlength of from about 10 to about 18. When \( x+y+z \) is different from 0, \( R^1 \) may be somewhat shorter or longer, having a chainlength in the range C12-C16. The general formula also encompasses amine oxides wherein \( x+y+z \) is equal to 0, \( R^1=\text{C}_2\text{H}_5\text{C}_2\text{H}_4\text{H} \), and \( q=0-2 \), preferably 2. These amine oxides are illustrated by hexadecyl dimethylamine oxide, octadecylamine oxide, and their hydrates, especially the dihydrates as disclosed in U.S. Pat. Nos. 5,075,501 and 5,071,594, incorporated herein by reference.

The invention also encompasses amine oxides wherein \( x+y+z \) is different from zero, specifically \( x+y+z \) is from about 1 to about 10, \( R^1 \) is a primary alkyl group containing 8 to about 24 carbons, preferably from about 12 to about 16 carbon atoms; in these embodiments \( y+z \) is preferably 0 and \( x \) is preferably from about 1 to about 6, more preferably from about 2 to about 4; \( EO \) represents ethylenoxide; \( PO \) represents propyleneoxide; and \( BO \) represents butyleneoxide. Such amine oxides can be prepared by conventional synthetic methods, e.g., by the reaction of alklylethoxylates with dimethylamine followed by oxidation of the ethoxylated amine with hydrogen peroxide.

Highly preferred m-nine oxides herein are solids at ambient temperature, more preferably they have melting-points in the range 30°C to 90°C. Amine oxides suitable for use herein are made commercially by a number of suppliers, including Akzo Chemie, Ethyl Corp., and Procter & Gamble. See McCutcheon's compilation and Kirk-Othmer review article for alternate amine oxide manufacturers. Preferred commercially available amine oxides are the solid, dihydride ADMOX 16 and ADMOX 18, ADMOX 12 and especially ADMOX 14 from Ethyl Corp.

Preferred embodiments include hexadecylidimethylamine oxide dihydrate, octadecylidimethylamine oxide dihydrate, hexadecylis(ethylenoxide)dimethylamine oxide, and tetradecylidimethylamine oxide dihydrate.

Whereas in certain of the preferred embodiments \( R^1=\text{CH}_3 \), there is some latitude with respect to having \( R^1 \) slightly larger than H. Specifically, the invention further encompasses embodiments wherein \( R^1=\text{CH}_3\text{OH} \), such as hexadecylbis(2-hydroxyethyl)amine oxide, tallowbis(2-hydroxyethyl)amine oxide, stearyl(2-hydroxyethyl)amine oxide and oleoyl(2-hydroxyethyl)amine oxide.

As noted, certain preferred embodiments of the instant ADD compositions comprise amine oxide dihydrates. Conventional processes can be used to control the water content and crystallize the amine oxide in solid dihydrate form. A new process comprises (a) conventionally making amine oxide as an aqueous solution or aqueous/organic solvent solution by reacting appropriate parent amine and aqueous hydrogen peroxide (for example, 50% \( \text{H}_2\text{O}_2 \)); (b) drying the product to secure substantially anhydrous amine oxide (with or without an organic solvent being present to keep the viscosity low); (c) adding two mole equivalents of water per mole of amine oxide; and (d) recrystallizing the wet amine oxide from a suitable solvent, such as ethyl acetate.

In formulating the instant detergent compositions, the amine oxide may be added to a composition as a powder. This is especially appropriate in the case of the amine oxide dihydrates, since these are nonhygroscopic solids. When it is desired to use the anhydrous form of the amine oxides, it is preferable to protect the amine oxide from moisture. It is contemplated to achieve this by conventional means, such as by applying a relatively nonhygroscopic coating, e.g., an anhydrous coating polymer, to amine oxide particles. Alternately, and more preferably, the anhydrous amine oxide should be melt-blended with a conventional low-melting, low-foaming waxy nonionic surfactant which is other than an amine oxide material. Such surfactants are commonly used as “sheeting agents” in granular automatic dishwashing compositions and are illustrated more fully hereinafter (see description herein below of low foaming nonionic surfactant).

Preferred amine oxides herein are substantially free of amine and/or nitrosamine (“impurity”). Preferably, the amine oxide comprises less than about 2% free amine, more preferably about 1% or less; and less than about 500 parts per billion, more preferably less than about 50 parts per billion by weight nitrosamine.

In liquid detergent compositions, the shorter-chain length amine oxides such as octylidimethylamine oxide, decylidim-
ethylamine oxide, dodecylamine oxide and tetradecylamine oxide may be preferred, most preferred is C12 cocoamine oxide, and C14 amine oxide.

The short chain amine oxide are also useful as solubilizing agents for the long-chain amine oxide component discussed above. For example, short-chain amine oxides, such as octyl(dimethyl)amine oxide, decyl(dimethyl)amine oxide, dodecylamine oxide and tetradecylamine oxide may be added as solubilizing aids to the long-chain amine oxide. This is especially preferred if the composition is for use in cold-fill automatic dishwashing machines. When present in such compositions, a short-chain amine oxide solubilizer is preferably at not more than 1/6 of the total mass of the cleaning amine oxide component. Thus, levels of short-chain amine oxide are typically in the range from about 0 to about 2.0%, preferably about 0.1% to about 1% of the ADD composition. Moreover, it has been disclosed that a short-chain amine oxide, if used, is preferably uniformly dispersed within the long-chain amine oxide rather than being added to the ADD in a separate particle.

Washing granular dishwashing compositions are desired for use in hot-fill machines, e.g., those commonly available in the United States, the essential long-chain amine oxide preferably comprises R1= C18 and is preferred over R1= C16 on grounds of mass efficiency; in this circumstance the use of short-chain amine oxide solubilizers is typically avoided.

The present invention can contain from 0.1% to about 20%, preferably from about 1% to about 10%, more preferably from about 1.5% to about 7%, by weight of the composition.

Detritive Surfactants—Surfactants useful herein typically at levels at least from 1%, preferably from about 1% to about 55%, by weight, include the conventional C14-C18 alkyl benzene sulfonates ("LAS") and primary, branched-chain and random C10-C14 alkyl sulfates ("AS"), the C10-C18 secoundary (2,3) alkyl sulfates of the formula CH2(CH3)(CHO2SO3-M)+ CH3 and CH2(CH2)(CHO2SO3-M)+CH3 where x and y+1 are integers of at least 7, preferably at least 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C10-C18 alkyl alkoxy sulfates ("AE-Ss", especially x up to about 7 EO ethoxy sulfates), C10-C18 alkyl alkoxy carboxylates (especially the EO 1–5 ethoxy-carboxylates), the C10-C18 glycerol ethers, the C10-C14 alkyl polysaccharides and their corresponding sulfated polyglycosides, and C12-C18 alpha-sulfonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the C12-C18 alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C6-C12 alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/proxoxy), C12-C14 betaines and sulfobetaines ("sultaines") and the like, can also be included in the overall compositions. The C10-C18 N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C12-C18 N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C10-C18 N-(3-methoxypropyl) glucamides. The N-propyl through N-hexyl C10-C18 glucamides can be used for low sudsing. C12-C20 conventional soaps may also be used. If high sudsing is desired, the branched-chain C10-C15 soaps may be used. Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful surfactants are listed in standard texts.

Builders—Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used.

Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils.

The level of builder can vary widely depending upon the end use of the composition and its desired physical form. When present, the compositions will typically comprise at least about 1% builder. Liquid formulations typically comprise from about 5% to about 50%, more typically about 5% to about 30%, by weight, of detergent builder. Granular formulations typically comprise from about 10% to about 80%, more typically from about 15% to about 50% by weight, of the detergent builder. Lower or higher levels of builder, however, are not meant to be excluded.

Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric metaphosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

Examples of silicate builders are the alkali metal silicates, particularly those having a SiO2:Na2O ratio in the range 1:1 to 3:2:1 and layered silicates, such as the layered sodium silicates described in U.S. Pat. No. 4,664,839, issued May 12, 1987 to H. P. Rick. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta-Na4SiO4 morphology form of layered silicate. It can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula NaMgSi2O5·xH2O wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta-Na4SiO4 (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a creasing agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of sands control systems.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on Nov. 15, 1973. Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:

$$M_{z}[(AlO_{2})_{x}(SiO_{2})_{y}]·nH_{2}O$$

wherein z and y are integers usually of at least 6, the molar ratio of z to y is in the range from 1.0 to 0, and x is an integer from 0 to about 264, and M is a Group IA or IIA element, e.g., Na, K, Mg, Ca with valence n.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occur-
ring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Pat. No. 3,985,699, Krummel et al., issued Oct. 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (β), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:

$$\text{Na}_{x+2}[\text{AlO}_2\text{SiO}_2]_x\text{H}_2\text{O}$$

wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites (x=0–10) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1–1.0 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, “polycarboxylate” refers to compounds having a plurality of carboxylic acid groups, preferably at least 3 carboxylic acids. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkalolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the other polycarboxylates, including oxydisuccinates, as disclosed in Berg, U.S. Pat. No. 3,128,287, issued Apr. 7, 1964, and Lamberti et al., U.S. Pat. No. 3,635,830, issued Jan. 18, 1972. See also “TMS/TDS” builders of U.S. Pat. No. 4,663,071, issued to Bush et al., on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Pat. Nos. 3,923,679; 3,835,163; 4,138,635; 4,120,874 and 4,102,903.

Other useful detergent builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxybenzene-2, 4, 6-trisulphonic acid, and carboxymethylxylosuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polycarboxylic acids such as ethylenediamine tetracetic acid and nitrioltriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymeric acid, benzene 1,3,5-tricarboxylic acid, and carboxymethylxylosuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanediotes and the related compounds disclosed in U.S. Pat. No. 4,566,984, Bush, issued Jan.28, 1986. Useful succinic acid builders include the C5–C10 alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecanesuccinic acid, and its salts, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundrying operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diposphonate and other known phosphonates (see, for example, U.S. Pat. Nos. 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

Enzymes—Enzymes can be included in the formulations herein for a wide variety of fabric laundering purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, and for the prevention of refugee dye transfer, and for fabric restoration. The enzymes to be incorporated include proteases, amylases, lipases, cellulases, and peroxidases, as well as mixtures thereof. Other types of enzymes may also be included. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their choice is governed by several factors such as pH-activity and/or stability optima, thermostability, stability versus active detergents, builders and so on. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Enzymes are normally incorporated at levels sufficient to provide up to about 5 mg by weight, more typically about 0.001 mg to about 3 mg, of active enzyme per gram of the composition. Stated otherwise, the compositions herein will typically comprise from about 0.001% to about 5%, preferably 0.01–2% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of B. subtilis and B. licheniforms. Another suitable protease is obtained from a strain of Bacillus, having maximum activity throughout the pH range of 8–12, developed and sold by Novo Industries A/S (Denmark) and MAXATASE by International Bio-Synthetics, Inc. (The Netherlands). Other proteases include Protease A (see European Patent Application 130,756, published Jan.9, 1983) and Protease B (see European Patent Application Serial No. 87307610.8, filed Apr. 28, 1987, and European Patent Application 130,756, Bott et al., published Jan.9, 1985). Most preferred is what is called herein “Protease C”, which is a variant of an alkaline serine protease from Bacillus, particularly Bacillus lentus, in which
arginine replaced lysine at position 27, tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is described in EP 90915958:4; U.S. Pat. No. 5,185,250; and U.S. Pat. No. 5,204,015. Also preferred are protease which are described in copending application U.S. Ser. No. 08/136,797, entitled Protease-containing Cleaning Compositions and copending Application U.S. Ser. No. 08/136,626, entitled Bleaching Compositions Comprising Protease Enzymes, which are incorporated herein by reference. Genetically modified variants, particularly of Protease C, are also included herein.

Amylases include, for example, α-amylases described in British Patent Specification No. 1,296,839 (Novo), RAPIDASE, International Bio-Synthetics, Inc. and TERYMYL, Novo Industries. The cellulase usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Pat. No. 4,435,307, Barbesgourd et al., issued June 6, 1984, which disclosed fungal cellulase produced from Humicola insolens and Humicola strain DSM1800 or a cellulase 212-producing fungus belonging to the genus Amonomas, and cellulase extracted from the hepatopancreas of a marine mollusk (Dolabella Auricular Solander). suitable cellulases are also disclosed in GB-A-2.075.028, GB-A-2.095.275 and DE-OS-2.247.832. CAREZYME (Novo) is especially useful.

Suitable lipase enzymes for detergent usage which include those produced by microorganisms of the Pseudomonas group, such as Pseudomonas stutzeri ATCC 19.154, as disclosed in British Patent 1.372,034. See also lipases in Japanese Patent Application 53.20487, laid open to public inspection on Feb. 24, 1978. This lipase is available from Amano Pharmaceutic Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P." Other commercial lipases include Amano-CES, lipases ex Chromobacter viscosus, ex Chromobacter viscosus var. lipolyticum NRRLB 3673, commercially available from Toyo Jozo Co., Tagata, Japan; and further Chromobacter viscosus lipases from U.S. Biochemical Corp., U.S.A. and Diosynth Co., The Netherlands, and lipases ex Pseudomonas gladioli. The LIPOLASE enzyme derived from Humicola lanuginosa and commercially available from Novo (see also EPO 341,947) is a preferred lipase for use herein.

 Peroxidase enzymes are used in combination with oxygen sources, e.g., percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching," i.e., to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/00984 13, published Oct. 19, 1989, by O. Kirk, assigned to Novo Industries A/S. It may be desired to use, in combination with these peroxidases, materials viewed as being peroxidase accelerators such as phenolsulfonate and/or phenothiazine.


Enzyme Stabilizers—The enzymes employed herein are stabilized by the presence of water-soluble sources of calcium and/or magnesium ions in the finished compositions which provide such ions to the enzymes. (Calcium ions are generally somewhat more effective than magnesium ions and are preferred herein if only one type of cation is being used.) Additional stability can be provided by the presence of various other art-disclosed stabilizers, especially borate species: see Severson, U.S. 4,537,706. Typical detergents, especially liquids, will comprise from at least 1 to at least 30, preferably from at least 2 to at least 20, more preferably from about 5 to about 15, and most preferably from about 5 to about 12, millimoles of calcium ion per liter of finished composition. This can vary somewhat, depending on the amount of enzyme present and its response to the calcium or magnesium ions. The level of calcium or magnesium ions should be selected so that there is always some minimum level available for the enzyme, after allowing for complexation with builders, fatty acids, etc., in the composition. Any water-soluble calcium or magnesium salt can be used as the source of calcium or magnesium ions, including, but not limited to, calcium chloride, calcium sulfate, calcium malate, calcium maleate, calcium hydroxide, calcium formate, and calcium acetate, and the corresponding magnesium salts. A small amount of calcium ion, generally from about 0.05 to about 0.4 millimoles per liter, is often also present in the composition due to calcium in the enzyme slurry and formula water. In solid detergent compositions the formulation may include a sufficient quantity of a water-soluble calcium ion source to provide such amounts in the laundry liquor. In the alternative, natural water hardness may suffice.

It is to be understood that the foregoing levels of calcium and/or magnesium ions are sufficient to provide enzyme stability. More calcium and/or magnesium ions can be added to the compositions to provide an additional measure of enzyme removal performance. Accordingly, as a general proposition the compositions herein will typically comprise from about 0.05% to about 2% by weight of a water-soluble source of calcium or magnesium ions, or both. The amount can vary, of course, with the amount and type of enzyme employed in the composition.

The compositions herein may also optionally, but preferably, contain various additional stabilizers, especially borate-type stabilizers. Typically, such stabilizers will be used at levels in the compositions from about 0.25% to about 10%, preferably from about 0.5% to about 5%, more preferably from about 0.75% to about 3%, by weight of boric acid or other boron compound capable of forming boric acid in the composition (calculated on the basis of boric acid). Boric acid is preferred, although other compounds such as boron oxide, borax and other alkali metal borates (e.g., sodium ortho-, meta- and pyroborate, and sodium pentaborate) are suitable. Substituted boric acids (e.g., phenylboronic acid, butane boronic acid, and p-bromo phenylboronic acid) can also be used in place of boric acid. It is to be recognized that such materials may also be used in formulations as the sole stabilizer as well as being used in combination with added calcium and/or magnesium ions.
Finally, it may be desired to add chlorine scavengers, especially to protease-containing compositions, to protect the enzymes from chlorine typically present in municipal water supplies. Such materials are described, for example, in U.S. Pat. No. 4,810,413 to Pancheri et al.

Bleaching Compounds—Bleaching Agents and Bleach Activators—The detergent compositions herein may optionally contain bleaching agents or bleaching compositions containing a bleaching agent and one or more bleach activators. When present, bleaching agents will typically be at levels of from about 1% to about 30%, more typically from about 5% to about 20%, of the detergent composition, especially for fabric laundering. If present, the amount of bleach activators will typically be from about 0.1% to about 60%, more typically from about 0.5% to about 40% of the bleaching composition comprising the bleaching agent-plus-bleach activator.

The bleaching agents used herein can be any of the bleaching agents useful for detergent compositions in textile cleaning or other cleaning purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents. Peroxide bleaches, e.g., sodium peroxide (e.g., mono- or tetra-hydrate) can be used herein.

Another category of bleaching agent that can be used without restriction encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxysulfate hexahydrate; the magnesium salt of meta chloro perbenzoic acid; 4-nonylaminoo-4-oxoperoxybutyric acid and diperoxylodecanedioic acid. Such bleaching agents are disclosed in U.S. Pat. No. 4,483,781, Hartman, issued Nov. 20, 1984, U.S. patent application Ser. No. 740,446, Burns et al., filed Jun. 3, 1985, European Patent Application 0,133,354, Banks et al., published Feb. 20, 1985, and U.S. Pat. No. 4,412,934, Chung et al., issued Nov. 1, 1983. Highly preferred bleaching agents also include 6-nonylaminoo-6-oxoperoxyacaproic acid as described in U.S. Pat. No. 4,634,551, issued Jan. 6, 1987 to Burns et al.

Peroxogen bleaching agents can also be used. Suitable peroxygen bleaching compounds include sodium carbonate peroxypolyhydrate and equivalent “percarbonate” bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used.

A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

Mixtures of bleaching agents can also be used.

Peroxogen bleaching agents, the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the in situ production in aqueous solution (i.e., during the washing process) of the peroxo acid corresponding to the bleach activator. Various nonlimiting examples of activators are disclosed in U.S. Pat. No. 4,915,854, issued Apr. 10, 1990 to Mao et al., and U.S. Pat. No. 4,412,934. The nonoxynolbenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical, and mixtures thereof can also be used. See also U.S. Pat. No. 4,634,551 for other typical bleaches and activators useful herein.

Highly preferred amido-derived bleach activators are those of the formulae:

$$R'NR^3CONR^2COO^-$ or $R^3CONR^3R^2COO^-$

wherein $R'$ is an alkyl group containing from about 6 to about 12 carbon atoms, $R^2$ is an alkylenec containing from 1 to about 6 carbon atoms, $R^3$ is an alkyl, aryl, or alkaryl group containing from 1 to about 20 carbon atoms, and $L$ is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenyl sulfonate.

Preferred examples of bleach activators of the above formulae include (6-oxanamido-caproyl)oxybenzenesulfonate, (6-oxanamidecaproyl)oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S. Pat. No. 4,634,551, incorporated herein by reference.

Another class of bleach activators comprises the benoxazin-type activators disclosed by Hodge et al. in U.S. Pat. No. 4,966,723, issued Oct. 30, 1990, incorporated herein by reference. A highly preferred activator of the benoxazin-type is:

![Benoxazin-type activator structure]

Still another class of preferred bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:

$$R^6-C=O$$

wherein $R^5$ is an alkyl, alkoxylaryyl, or alkaryl group containing from 1 to about 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethyloxanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethyloxanyol valerolactam and mixtures thereof. See also U.S. Pat. No. 4,545,784, issued to Sanderson, Oct. 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photo activated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. See U.S. Pat. No. 4,033,718, issued Jul. 5, 1977 to Holcombe et al. If used, detergent compositions will typically contain from about 0.025% to about 1.25%, by weight, of such bleaches, especially sulfonated zinc phthalocyanine.

If desired, the bleaching compounds can be catalyzed by means of a manganese compound. Such compounds are well known in the art and include, for example, the manganese-
based catalysts disclosed in U.S. Pat. Nos. 5,246,621, 5,244, 594; 5,194,416; and European Pat. App. Pub. Nos. 549,271A1, 549,272A1, 544,440A2, and 544,490A1; Preferred examples of these catalysts include M$n^{2-}$(u-O)$_{2}$(1,4,7-trimethyl-1,4,7-triazacyclononane)(PF$_{6}$)$_{2}$, M$n^{2-}$(u-O)(u-OAc)$_{2}$(1,4,7-trimethyl-1,4,7-triazacyclononane)$_{2}$, (ClO$_{4}$)$_{2}$, M$n^{2-}$(u-O)$_{2}$(1,4,7-triazacyclononane)(ClO$_{4}$)$_{2}$, M$n^{2-}$(o-O$_{2}$)(u-OAc)$_{2}$(1,4,7-trimethyl-1,4,7-triazacyclononane)(ClO$_{4}$)$_{2}$, M$n^{2-}$(u-O)(1,4,7-trimethyl-1,4,7-triazacyclononane)-(OCH$_{2}$)$_{2}$(PF$_{6}$)$_{2}$, and mixtures thereof. Other metal-based bleaching catalysts include those disclosed in U.S. Pat. Nos. 4,430,243 and 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following U.S. Pat. Nos: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084.

As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleaching catalyst species in the aqueous washing liquor, and will preferably provide from about 0.1 ppm to about 700 ppm, more preferably from about 1 ppm to about 500 ppm, of the catalyst species in the laundry liquor.

Adjunct Ingredients The compositions herein can optionally include one or more other detergent adjunct materials or other materials for assisting or enhancing cleaning performance, treatment of the substrate to be cleaned, or to modify the aesthetics of the detergent composition (e.g., perfumes, colorants, dyes, etc.). The following are illustrative examples of such adjunct materials.

Polymeric Dispersing Agents—Polymeric dispersing agents can advantageously be utilized at levels from about 0.1% to about 7%, by weight, in the compositions herein. Suitable polymeric dispersing agents include polymeric polycarboxylates and polyethylene glycols, although others known in the art can also be used.

Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, acetic acid, mesaconic acid, citraconic acid and methylenecarboxylic acid. The presence in the polymeric polycarboxylates herein or monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are usable herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Suitable polymers of this type are known materials. Use of polycarboxylates of this type in detergent compositions has been disclosed, for example, in Diehi, U.S. Pat. No. 3,308,067, issued Mar. 7, 1967.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000. A preferred copolymer has an average molecular weight of about 2,000 to 15,000, more preferably about 6,000 to about 13,000, and most preferably about 7,000 to about 12,000. Other preferred copolymers have an average molecular weight from about 5,000 to 75,000, most preferably from about 7,000 to 65,000. The ratio of acrylic to maleate segments in such copolymers will generally range from about 30:1 to about 1:2, more preferably from about 10:1 to 1:1, and most preferably about 2:1 to 1:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published Dec. 15, 1982, as well as in EP 193,360, published Sep. 3, 1986, which also describes such polymers comprising hydroxypropylacrylate. Still other useful dispersing agents include the maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Particularly preferred dispersant polymers are low molecular weight modified polycarboxylate copolymers. Such copolymers contain as monomer units a from about 90% to about 10%, preferably from about 80% to about 20% weight acrylic acid or its salts and b) from about 10% to about 90%, preferably from about 20% to about 80% weight of a substituted acrylic monomer or its salt and have the general formula: -[(CR$_{2}$)$_{2}$CR$_{n}$]COOR$_{3}$]- wherein the incomplete valencies inside the square braces are hydrogen and at least one of the substituents R$^{1}$, R$^{2}$ or R$^{3}$, preferably R$^{1}$ or R$^{2}$, is a 1 to 4 carbon alkyl or hydroxyalkyl group, R$^{3}$ or R$^{2}$ can be a hydrogen and R$^{3}$ can be a hydrogen or alkali metal salt. Most preferred is a substituted acrylic monomer wherein R$^{1}$ is methyl, R$^{2}$ is hydrogen and R$^{3}$ is sodium.

The low molecular weight polycarboxylate dispersant polymer preferably has a molecular weight of less than about 15,000, preferably from about 500 to about 10,000, most preferably from about 1,000 to about 5,000. The most preferred polycarboxylate copolymer for use herein has a molecular weight of 3500 and is the fully neutralized form of the polymer comprising about 70% by weight acrylic acid and about 30% by weight methacrylic acid.

Other suitable modified polycarboxylate copolymers include the low molecular weight copolymers of unsaturated aliphatic carboxylic acids disclosed in U.S. Pat. Nos. 4,530, 766, and 5,084,553, both incoporated herein by reference.

Aglomerated forms of the present invention may employ aqueous solutions of polymer dispersants as liquid binders for making the agglomerate (particularly when the composition consists of a mixture of sodium citrate and sodium carbonate). Especially preferred are polycarboxylates with an average molecular weight of from about 1,000 to about 10,000, and acrylate/maleate or acrylate/fumarate copolymers with an average molecular weight of from about 2,000 to about 80,000 and a ratio of acrylate to maleate or fumarate segments of from about 30:1 to about 1:2. Examples of such copolymers based on a mixture of unsaturated mono- and dicarboxylic monomers are disclosed in European Patent Application No. 66,915, published Dec. 15, 1982, incorporated herein by reference.

Other dispersant polymers useful herein include the polyethylene glycols and polypropylene glycols having a molecular weight of from about 950 to about 30,000 which can be obtained from the Dow Chemical Company of Midland, Mich. Such compounds for example, having a melting point within the range of from about 30°C to about 100°C can be obtained at molecular weights of 1450, 3400,
4500, 6000, 7400, 9500, and 20,000. Such compounds are formed by the polymerization of ethylene glycol or propylene glycol with the requisite number of moles of ethylene or propylene oxide to provide the desired molecular weight and melting point of the respective polyethylene glycol and polypropylene glycol. The polyethylene, polypropylene and mixed glycols are referred to using the formula HO(CH₂CH₂O)m(CH₂CH₃O)ₙ(CH₂CH₂O)ₚH wherein m, n, and p are integers satisfying the molecular weight and temperature requirements given above.

Yet other dispersant polymers useful herein include the cellulose sulfate esters such as cellulose acetate sulfate, cellulose sulfate, hydroxethyl cellulose sulfate, methylcellulose sulfate, and hydroxypropylcellulose sulfate. Sodium cellulose sulfate is the most preferred polymer of this group.

Other suitable dispersant polymers are the carbosiloxanes, particularly starches, celluloses and alginates, described in U.S. Pat. No. 3,723,322, Dietl, issued Mar. 27, 1973; the dextrin esters of polyacrylic acids disclosed in U.S. Pat. No. 3,929,107, Thompson, issued Nov. 11, 1975; the hydroxyalkyl starch ethers, starch ethers, oxidized starches, dextrins and starch hydrolysates described in U.S. Pat. No. 3,803,285, Jensen, issued Apr. 9, 1974; the carboxylated starches described in U.S. Pat. No. 3,629,121, Eldib, issued Dec. 21, 1971; and the dextrin starches described in U.S. Pat. No. 4,141,841, McDonald, issued Feb. 27, 1979; all incorporated herein by reference. Preferred cellulose-derived dispersant polymers are the carboxymethylcelluloses.

Yet another group of acceptable dispersants are the organic dispersant polymers, such as polysapartate.

Another polymeric material which can be included is polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal-agent deposition agent. Typical molecular weight ranges for these purposes range from about 500 to about 100,000, preferably from about 1,000 to about 50,000, more preferably from about 1,500 to about 10,000.

Polysapartate and polyglutamate dispersing agents may also be used, especially in conjunction with zeolite builders. In compositions containing detergent builders, it is believed, though it is not intended to be limited by theory, that polymeric dispersing agents enhance overall detergent builder performance, especially zeolite and/or silicate builders, when used in combination with other builders (including lower molecular weight polyacrylates) by crystal growth inhibition, particulate soil release peptization, and anti-redeposition. Dispersing agents such as polysapartate preferably have a molecular weight (avg.) of about 10,000.

Polymeric Soil Release Agent—An additional soil release agent known to those skilled in the art can optionally be employed in the compositions and processes of this invention. Polymeric soil release agents are characterized by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

The polymeric soil release agents useful herein especially include those soil release agents having: (a) one or more nonionic hydrophilic components consisting essentially of (i) polyoxyethylene segments with a degree of polymerization of at least 2, or (ii) oxypropylene or polyoxypropylene segments with a degree of polymerization of from 2 to 10, wherein said hydrophilic segment does not encompass any oxypropylene unit unless it is bonded to adjacent moieties at each end by ether linkages, or (iii) a mixture of oxyalkylene units comprising oxyethylene and from 1 to about 30 oxypropylene units wherein said mixture contains a sufficient amount of oxyethylene units such that the hydrophilic component has hydrophilicity great enough to increase the hydrophilicity of conventional polyester synthetic fiber surfaces upon deposit of the soil release agent on such surface, said hydrophilic segments preferably comprising at least about 25% oxyethylene units and more preferably, especially for such components having about 20 to 30 oxypropylene units, at least about 50% oxyethylene units; or (b) one or more hydrophobe components comprising (i) C₃ oxyalkylene terephthalate segments, wherein, if said hydrophobe components also comprise oxyethylene terephthalate, the ratio of oxyethylene terephthalate C₆ oxyalkylene terephthalate units is about 2:1 or lower, (ii) C₃-C₆ alkylene or oxy C₃-C₆ alkylene segments, or mixtures thereof, (iii) poly (vinyl ester) segments, preferably polyvinyl acetate, having a degree of polymerization of at least 2, or (iv) C₅-C₁₀ alkyl ether or C₆ hydroxyalkyl ether substituents, or mixtures wherein, wherein said substituents are present in the form of C₅-C₁₀ alkyl ether or C₆ hydroxyalkyl ether cellulose derivatives, or mixtures wherein, and such cellulose derivatives are amphiphilic, whereby they have a sufficient level of C₅-C₁₀ alkyl ether and/or C₆ hydroxyalkyl ether units to deposit on conventional polyester synthetic fiber surfaces and retain a sufficient level of hydrolys, once adhered to such conventional synthetic fiber surface, to increase fiber surface hydrophilicity, or a combination of (a) and (b).

Typically, the polyoxyethylene segments of (a)(i) will have a degree of polymerization of from about 200, although higher levels can be used, preferably from 3 to about 150, more preferably from 6 to about 100. Suitable oxy C₅-C₁₀ alkylene hydrophobe segments include, but are not limited to, end-caps of polymeric soil release agents such as MO₂-S(CH₂)ₙ-OCH₂CH₂O, where M is sodium and n is an integer from 4-6, as disclosed in U.S. Pat. No. 4,721,580, issued Jan. 26, 1988 to Goetschalk.

Polymeric soil release agents useful in the present invention also include cellulose derivatives such as hydroxycellulose polymers, copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, and the like. Such agents are commercially available and include hydroxyethers of cellulose such as METHOCEL (Dow). Cellulosic soil release agents for use herein also include those selected from the group consisting of C₁₀-C₁₄ alkyl and C₆ hydroxyalkyl cellulose; see U.S. Pat. No. 4,000,093, issued Dec. 28, 1976 to Nicol, et al.

Soil release agents characterized by poly(vinyl ester) hydrophobe segments include graft copolymers of poly(vinyl ester), e.g., C₃-C₆ vinyl esters, preferably poly(vinyl acetate) grafted onto polyalkylene oxide backbones, such as polyethylene oxide backbones. See European Patent Application 0 219 048, published Apr. 22, 1987 by Kud, et al. Commercially available soil release agents of this kind include the SOKALAN type of material, e.g., SOKALAN HP-22, available from BASF (West Germany).

One type of preferred soil release agent is a copolymer having random blocks of ethylene terephthalate and polyethylene oxide (PEG) terephthalate. The molecular weight of this polymeric soil release agent is in the range of from about 25,000 to about 55,000. See U.S. Pat. No. 3,959,230 to Hays, issued May 25, 1976 and U.S. Pat. No. 3,893,920 to Bagdour, issued Jul. 8, 1975.
Another preferred polymeric soil release agent is a poly-
ester with repeat units of ethylene terephthalate units con-
tains 10–15% by weight of ethylene terephthalate units
10 together with 90–80% by weight of polyoxymethylene tere-
phthalate units, derived from a polyoxymethylene glycol of
average molecular weight 300–500. Examples of this poly-
15 mer include the commercially available material ZEL-
CON 5126 (from DuPont) and MILEASE T (from ICI). See
also U.S. Pat. No. 4,702,857, issued Oct. 27, 1987 to
Gosselin.

Another preferred polymeric soil release agent is a sul-
10 fonated product of a substantially linear oligomer
comprised of an oligomeric ester backbone of terephthaloyl
and oxoalkyleneoxy repeat units and terminal moieties
covalently attached to the backbone. These soil release
agents are described fully in U.S. Pat. No. 4,968,451, issued
Nov. 6, 1990 to J. J. Scheibel and E. P. Gosselin. Other
suitable polymeric soil release agents include the terephtha-
late polyesters of U.S. Pat. No. 4,711,730, issued Dec. 8,
1987 to Gosselin et al., the anionic-terminated oligomeric
esters of U.S. Pat. No. 4,721,580, issued Jan. 26, 1988 to
Gosselin, and the block polyol oligomeric compounds of
Preferred polymeric soil release agents also include the
31, 1989 to Maldonado et al., which discloses anionic,
especially sulfonaryl, end-capped terephthalate esters.

If utilized, soil release agents will generally comprise
from about 0.01% to about 10.0%, by weight, of the deter-
genius compositions herein, typically from about 0.1% to
15 about 5%, preferably from about 0.2% to about 3.0%.

Still another preferred soil release agent is an oligomer
with repeat units of terephthaloyl units, sulfosuccinimide-
10 lyl units, oxoalkyleneoxy and oxy-1,2-propylene units.
The repeat units form the backbone of the oligomer and are
preferably terminated with modified isethionate end-caps.
A particularly preferred soil release agent of this type com-
prises about one sulfosuccinimide unit, 5 terephthaloyl
15 units, oxoalkyleneoxy and oxy-1,2-propyleneoxy units in a
ratio of from about 1.7 to about 1.8, and two end-cap units
of sodium 2-(2-hydroxyethoxy)ethanesulfonate. Said soil
release agent also comprises from about 0.5% to about 20%
20 by weight of the oligomer, of a crystalline-reducing stabil-
er, preferably selected from the group consisting of xylene
sulfonate, cumene sulfonate, tolune sulfonate, and mixtures
thereof.

Chelating Agents—The detergent compositions herein
may also optionally contain one or more iron and/or man-
geese chelating agents. Such chelating agents can be
25 selected from the group consisting of amino carboxylates,
amino phosphonates, polycyclically-substituted aromatic
chelating agents and mixtures therein, all as hereinbefore
defined. Without intending to be bound by theory, it is
believed that the benefit of these materials is due in part to
their exceptional ability to remove iron and manganese ions
from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents
include ethylenediaminetetraacetates, N-hydroxyethyl-
20 enediaminetetraacetates, nitritroacetates, ethylenediamine
dicarboxylic acid, and dipicolinic acid, bipyridyls, pyridyl-
disulfides, and ethylenediaminesulfonates, and ethanoldiglycines, alkali
metal, ammonium, and substituted ammonium salts therein
and mixtures therein.

Amino phosphonates are also suitable for use as chelating
agents in the compositions of the invention when at least
low levels of total phosphorus are permitted in detergent
20 compositions, and include ethylenediaminetetraakis (methyl-
enephosphonates) as DEQUEST. Preferred, these amino
phosphonates to not contain alkyl or alkenyl groups with
more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents
are also useful in the compositions herein. See U.S. Pat. No.
3,812,044, issued May 21, 1974, to Conn and others. Preferred
compounds of this type in acid form are dihydroxysulf-
25 ofbenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is
ethylenediamine disuccinate ("EDDS"), especially the [S, S]
iso as described in U.S. Pat. No. 4,704,233, Nov. 3,

If utilized, these chelating agents will generally comprise
from about 0.1% to about 10% by weight of the detergent
compositions herein. More preferably, if utilized, the chelat-
20 ing agents will comprise from about 0.1% to about 3.0% by
weight of such compositions.

Clay Soil Removal/Anti-redeposition Agents—The com-
positions of the present invention can also optionally contain
water-soluble ethoxylated amines having clay soil removal
25 and antiredeposition properties. Granular detergent compo-
sitions which contain these compounds typically contain
from about 0.01% to about 10.0% by weight of the water-
soluble ethoxylated amines; liquid detergent compositions
typically contain about 0.01% to about 5%.

The most preferred soil release and anti-redeposition
agent is ethoxylated tetraethylenepentamine. Exemplary
ethoxylated amines are further described in U.S. Pat. No.
of preferred clay soil removal-antiredeposition agents are
the cationic compounds disclosed in European Patent Ap-
Other clay soil removal/antiredeposition agents which can
be used include the ethoxylated amine polymers disclosed
in European Patent Application 111,984, Gosselin, published
Jun. 27, 1984; the zwitterionic polymers disclosed in Euro-
4, 1984; and the amine oxides disclosed in U.S. Pat. No.
4,548,744, Connor, issued Oct. 22, 1985. Other clay soil
removal and/or anti redeposition agents known in the art can
also be utilized in the compositions herein. Another type of
preferred antiredeposition agent includes the carboxy
30 methyl cellulose (CMC) materials. These materials are well
known in the art.

Brightener—Any optical brighteners or other brightening
or whitening agents known in the art can be incorporated
40 at levels typically from about 0.05% to about 1.2%, by weight,
to the detergent compositions herein. Commercial optical
brighteners which may be useful in the present invention can
be classified into subgroups, which include, but are not
necessarily limited to, derivatives of stilbene, pyrazoline,
coumarin, carboxylic acid, methinecyanines, diben-
zoephene-5,5-dioxide, azoles, 5- and 6-membered ring
heterocycles, and other miscellaneous agents. Examples of
such brighteners are disclosed in "The Production and
Application of Fluorescent Brightening Agents", M. Zahr-
45 adnik, Published by John Wiley & Sons, New York (1982).
Specific examples of optical brighteners which are useful
in the present compositions are those identified in U.S. Pat.
No. 4,790,856, issued to Wixon on Dec. 13, 1988. These
brighteners include the PHORBRITE series of brighteners
from Verona. Other brighteners disclosed in this reference
include: Tinpaul PLC, Tinpaul UPNA, Tinpaul CBS and
Tinpaul 5BM; available from Chia-Geigy; Artic White CC
40 and Astar White CW, available from Hilton-Davis, located
in Italy; the 2-(4-styrylphenyl)-2H-naphthol[1,2-d]triazoles;
4,4'-bis-(1,2-triazol-2-yl)-sil-
benzenes; 4,4'-bis(styyl-
bisphenyls; and the aminocoumarins. Specific examples of these brighteners include 4-methyl-7-diethyl-amino coumarin; 1,2-bis-(venzimidazol-2-yl)-ethylene; 1,3-diphenyl-phenazine; 2-ethyl-6-(4-hydroxy-1-naphthyl)-1,2-dioxazole; and 2-styryl-benzimidazol-1,2,3-naphth-[l,2,d]triazole. See also U.S. Pat. No. 3,646,015, issued Feb. 29, 1972 to Hamilton. Aromatic brighteners are preferred herein.

Suds Suppressors—Compounds for reducing or suppressing the formation of suds can be incorporated into the compositions in small amounts by a conventional method. Suds suppression can be of particular importance in the so-called “high concentration cleaning process” as described in U.S. Pat. Nos. 4,489,435 and 4,489,574 and in front-loading European style washing machines.

A wide variety of materials may be used as suds suppressors, and suds suppressors are well known to those skilled in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430–447 (John Wiley & Sons, Inc., 1979). One category of suds suppressor of particular interest encompasses mono-carboxylic fatty acid and soluble salts therein. See U.S. Pat. No. 2,954,347, issued Sep. 27, 1960 to Wayne S. John. The monocarboxylic fatty acids and salts thereof as used as suds suppressor typically have hydrocarbyl chains of 10 to about 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

The detergent compositions herein may also contain non-surfactant suds suppressors. These include, for example: high molecular weight hydrocarbons such as paraffin, fatty acid esters (e.g., fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C(18–22), ketones (e.g., stearenone), etc. Other suds inhibitors include N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra-alkyl diamine chlorotriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, and monosteryl phosphates such as monosteryl alcohol phosphate ester and monosteryl di-alkali metal alcohol phosphate ester and monosteryl di-alkali metal (e.g., K, Na, and Li) phosphates and phosphate esters. The hydrocarbons such as paraffin and halo paraffin can be utilized in liquid form. The liquid hydrocarbons will be liquid at room temperature and atmospheric pressure, and will have a pour point in the range of about −40°C and about 50°C at a minimum boiling point not less than about 110°C (atmospheric pressure). It is also known to utilize waxy hydrocarbons, preferably having a melting point below about 100°C. The hydrocarbons constitute a preferred category of suds suppressor for detergent compositions. Hydrocarbon suds suppressors are described, for example, in U.S. Pat. No. 4,265,779, issued May 5, 1981 to Gandolfo et al. The hydrocarbons, thus, include aliphatic, allylic, aromatic, and heterocyclic saturated or unsaturated hydrocarbons having from about 12 to about 70 carbon atoms. The term “paraffin,” as used in this suds suppressor discussion, is intended to include mixtures of true paraffins and cyclic hydrocarbons.

Another preferred category of non-surfactant suds suppressors comprises silicone suds suppressors. This category includes the use of polyorganosiloxane oils, such as polydimethylsiloxane, dispersions or emulsions of polyorganosiloxane oils or resins, and combinations of polyorganosiloxane with silica particles wherein the polyorganosiloxane is chemisorbed or fused onto the silica. Silicone suds suppressors are well known in the art and are, for example, disclosed in U.S. Pat. No. 4,265,779, issued May 5, 1981 to Gandolfo et al. European Patent Application No. 89307851.9, published Feb. 7, 1990, by Starch N. S.

Other silicone suds suppressors are disclosed in U.S. Pat. No. 3,455,839 which relates to compositions and processes for defoaming aqueous solutions by incorporating therein small amounts of polydimethylsiloxane fluids.

Mixtures of silicone and silanlated silica are described, for instance, in German Patent Application DOS 2,124,526. Silicone defoamers and suds controlling agents in granular detergent compositions are disclosed in U.S. Pat. No. 3,933, 672, Bartolotta et al., and in U.S. Pat. No. 4,652,392, Baginski et al., issued Mar. 24, 1997.

An exemplary silicone based suds suppressor for use herein is a suds suppressing amount of a suds controlling agent consisting essentially of:

(i) polydimethylsiloxane fluid having a viscosity of from about 20 cs. to about 1,500 cs. at 25°C;

(ii) from about 5 to about 50 parts per 100 parts by weight of (i) of siloxane resin composed of (CH₃)₄SiO₁₂ units and SiO₂ units in a ratio of from (CH₃)₄SiO₁₂ and to SiO₂ units from about 0.6 to about 1.2 to 1; and

(iii) from about 1 to about 20 parts per 100 parts by weight of (i) of a solid silica gel.

In the preferred silicone suds suppressor used herein, the solvent for a continuous phase is made up of certain polyethylene glycols or polyethylene-polypropylene glycol copolymers or mixtures thereof (preferred), or polypropylene glycol. The primary suds suppressing agent is a branched/crosslinked and preferably not linear.

To illustrate this point further, typical liquid laundry detergent compositions with controlled suds will optionally comprise from about 0.001 to about 1, preferably from about 0.1 to about 0.7, most preferably from about 0.5 to about 0.5, weight % of said silicone suds suppressor, which comprises a mixture of a nonaqueous emulsion of a primary antifoam agent which is a mixture of (a) a polyorganosiloxane, (b) a resinous siloxane or a silicone resin-producing silicone compound, (c) a finely divided filler material, and (d) a catalyst to promote the reaction of mixture components (a), (b), and (c), to form silanlates; (2) at least one nonionic silicone surfactant; and (3) polyethylene glycol or a copolymer of polyethylene-polypropylene glycol having a solubility in water at room temperature of more than about 2 weight %, and without polypropylene glycol. Similar amounts can be used in granular compositions, gels, etc. See also U.S. Pat. No. 4,978,471, Starch, issued Dec. 18, 1990, and U.S. Pat. No. 4,983,316, Starch, issued Jan. 8, 1991, 5,288,431, Huber et al., issued Feb. 22, 1994, and U.S. Pat. Nos. 4,639,489 and 4,749,740, Aizawa et al at column 1, line 46 through column 4, line 55.

The silicone suds suppressor herein preferably comprises polyethylene glycol and a copolymer of polyethylene glycol/polypropylene glycol, all having an average molecular weight of less than about 1,000, preferably between about 100 and 800. The polylethylene glycol and polyethylene/polypropylene copolymers herein have a solubility in water at room temperature of more than about 2 weight %, preferably more than about 5 weight %.

The preferred solvent herein is polyethylene glycol having an average molecular weight of less than about 1,000, more preferably between about 100 and 800, most preferably between 200 and 400, and a copolymer of polyethylene glycol/polypropylene glycol, preferably PPG 200/PEG 300. Preferred is a weight ratio of between about 1:1 and 1:10, most preferably between 1:3 and 1:6, of polyethylene glycol and copolymer of polyethylene-polypropylene glycol.

The preferred silicone suds suppressors used herein do not contain polypropylene glycol, particularly of 4,000 molecular weight. They also preferably do not contain block copolymers of ethylene oxide and propylene oxide, like PLURONIC L 101.

Other suds suppressors useful herein comprise the secondary alcohols (e.g., 2-alkyl alkanols) and mixtures of such alcohols with silicone oils, such as the silicones disclosed in
The secondary alcohols include the C₁₂–C₁₆ alkyl alcohols having a C₁₂–C₁₆ chain. A preferred alcohol is 2-butyl octanol, which is available from Condea under the trademark ISO-PEL 12. Mixtures of secondary alcohols are available under the trademark ISALCHEM 123 from Enichem. Mixed sued suppressors typically comprise mixtures of alcohol + silicone at a weight ratio of 1:5 to 5:1.

For any detergent compositions to be used in automatic laundry washing machines, sueds should not form to the extent that they overrule the washing machine. Suds suppressors, when utilized, are preferably present in a “suds suppressing amount.” By “suds suppressing amount” is meant that the formulator of the composition can select an amount of this sueds controlling agent that will sufficiently control the sueds to result in a low-sudsing laundry detergent for use in automatic laundry washing machines.

The compositions herein will generally comprise from 0% to about 5% of sueds suppressor. When utilized, sueds suppressors, monocarboxylic fatty acids, and salts therein, will be present typically in amounts up to about 5%, by weight, of the detergent composition. Preferably, from about 0.5% to about 3% of fatty monocarboxylic sueds suppressor is utilized. Silicone sueds suppressors are typically utilized in amounts up to about 2.0%, by weight, of the detergent composition, although higher amounts may be used. This upper limit in nature is subject to cost. Silicone sueds suppressors are used with keeping costs minimized and efficiency of lower amounts for effectively controlling sueding. Preferably from about 0.01% to about 1% of silicone sueds suppressor is used, more preferably from about 0.25% to about 0.5%. As used herein, these weight percentage values include any silica that may be utilized in combination with polyorganosiloxane, as well as any other ingredients that may be utilized. Monostearyl phosphate sueds suppressors are generally utilized in amounts ranging from about 0.1% to about 2%, by weight, of the composition. Hydrocarbon sueds suppressors are typically utilized in amounts ranging from about 0.01% to about 3.0%, although higher levels can be used.

The alcohol sueds suppressors are typically used at 0.2%–3% by weight of the finished compositions.

Fabric Softeners—Various through-the-wash fabric softeners, especially the impalpable smectite clays of U.S. Pat. No. 4,062,647, Storm and Nirschl, issued Dec. 13, 1977, as well as other softer softener clays known in the art, can optionally be used typically at levels of from about 0.5% to about 10% by weight in the present compositions to provide fabric softener benefits concurrently with fabric cleaning. Clay softeners can be used in combination with amine and amphoteric softeners as disclosed, for example, in U.S. Pat. No. 4,375,416, Crisp et al., Mar. 1, 1983 and U.S. Pat. No. 4,291,071, Harris et al., issued Sep. 22, 1981.

Dye Transfer Inhibiting Agents—The compositions of the present invention may also include one or more materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process. Generally, such dye transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazolone, manganese phthalo cyanine, peroxides, and mixtures thereof. If used, these agents typically comprise from about 0.01% to about 10% by weight of the composition, preferably from about 0.01% to about 5%, and more preferably from about 0.05% to about 2%. More specifically, the polyamine N-oxide polymers preferred for use herein contain units having the following structural formula: Rₐ₋ₚ; wherein p is a polymerizable unit to which an N-O group can be attached or the N-O group can form part of the polymerizable unit or the N-O group can be attached to both units; A is one of the following structures: NO(O)₋, C(O)O₋, S₋, O₋, N₋,

wherein R₁, R₂, R₃ are aliphatic, aromatic or heterocyclic, polyamines or combinations thereof, x and y are 0 or 1; and the nitrogen of the N-O group can be attached or form part of any of the aforementioned groups. The amine oxide unit of the polyamine N-oxides has a pKa<10, preferably pKa<7, more preferably pKa<6.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polythioesters, polycyanides, polyacrylates and mixtures thereof. These polymers can be linear or block copolymers where one monomer type is an amine N-oxide and the other monomer type is an N-oxide. The amine N-oxide polymers typically have a ratio of amine to the amine N-oxide of 1:1 to 1:10,000,000. However, the number of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polymerization. Typically, the average molecular weight is within the range of 500 to 1,000,000; more preferred 1,000 to 500,000; most preferred 5,000 to 100,000. This preferred class of materials can be referred to as “PVNO”.

The most preferred polyamine N-oxide useful in the detergent compositions herein is poly(4-vinylpyridine-N-oxide) which has an average molecular weight of about 50,000 and an amine to amine N-oxide ratio of about 1:4.

Copolymer of N-vinylpyrrolidone and N-vinylimidazolone polymers (referred to as a class as “PVVPV”) are also preferred for use herein. Preferably the PVVPV has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000. (The average molecular weight range is determined by light scattering as described in Barth, et al., Chemical Analysis, Vol. 113. “Modern Methods of Polymer Characterization”, the disclosures of which are incorporated herein by reference.) The PVVPV copolymers typically have a molar ratio of N-vinylimidazolone to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These copolymers can be either linear or branched.

The present invention compositions also employ a polyvinylpyrrolidone (“PVP”) having an average molecular weight of from about 5,000 to about 400,000, preferably from about 5,000 to about 200,000, and more preferably from about 5,000 to about 50,000. PVP’s are known to persons skilled in the detergent field; see, for example, EP-A-262,897 and EP-A-256,696, incorporated herein by reference. Compositions containing PVP can also contain polyethylene glycol (“PEG”) having an average molecular weight of from about 500 to about 100,000, preferably from about 1,000 to about 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from about 2:1 to about 50:1, and more preferably from about 3:1 to about 10:1.
The detergent compositions herein may also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the compositions herein will preferably comprise from about 0.01% to 1% by weight of such optical brighteners.

The hydrophilic optical brighteners useful in the present invention are those having the structural formula:

wherein R₁ is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R₂ is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morpholine, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula, R₁ is anilino, R₂ is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4'-bis(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

When in the above formula, R₁ is anilino, R₂ is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis(4-anilino-6-(N-2-hydroxyethyl)-N-methylamino)-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

The specific optical brightener species selected for use in the present invention provide especially effective dye transfer inhibition performance benefits when used in combination with the selected polymeric dye transfer inhibiting agents hereinbefore described. The combination of such selected polymeric materials (e.g., PVNO and/or PVPV1) with such selected optical brighteners (e.g., Tinopal UNPA-GX, Tinopal-PLC, and/or Tinopal AMS-GX) provides significantly better dye transfer inhibition in aqueous wash solutions than does either of these two detergent composition components when used alone. Without being bound by theory, it is believed that such brighteners work this way because they have high affinity for fabrics in the wash solution and therefore deposit relatively quick on these fabrics. The extent to which brighteners deposit on fabrics in the wash solution can be defined by a parameter called the "exhaustion coefficient". The exhaustion coefficient is in general as the ratio of a) the brightener material deposited on fabric to b) the initial brightener concentration in the wash liquor. Brighteners with relatively high exhaustion coefficients are the most suitable for inhibiting dye transfer for the context of the present invention.

Of course, it will be appreciated that other, conventional optical brightener types of compounds can optionally be used in the present compositions to provide conventional fabric "brightness" benefits, rather than a true dye transfer inhibiting effect. Such usage is conventional and well-known to detergent formulations.

Other Ingredients—A wide variety of other ingredients useful in detergent compositions can be included in the compositions herein, including other active ingredients, carriers, surfactants, processing aids, dyes or pigments, solvents for liquid formulations, solid fillers for bar compositions, etc. If high sudsing is desired, suds boosters such as the C₁₀₋₁₄ alkanolamides can be incorporated into the compositions, typically at 1%–10% levels. The C₁₀₋₁₄ monononanol and diethanol amides illustrate a typical class of such suds boosters. Use of such suds boosters with high sudsing adjunct surfactants such as the amine oxides, betaines and sulfonates noted above is also advantageous. If desired, soluble magnesium salts such as MgCl₂, MgSO₄ and the like, can be added at levels of, typically, 0.1%–2%, to provide additional suds and to enhance grease removal performance.

Various detergent ingredients employed in the present compositions optionally can be further stabilized by absorbing said ingredients onto a porous hydrophobic substrate, then coating said substrate with a hydrophobic coating. Preferably, the detergent ingredient is admixed with a surfactant before being absorbed into the porous substrate. In use, the detergent ingredient is released from the substrate into the aqueous washing liquor, where it performs its intended detergent function.

To illustrate this technique in more detail, a porous hydrophobic silica (trademark SYPERNAT® D10, DeOussa) is admixed with a proteolytic enzyme solution containing 3%–5% of C₁₃₋₁₅ ethoxylated alcohol (EO 7) nonionic surfactant. Typically, the enzyme/surfactant solution is 2.5 X the weight of silica. The resulting powder is dispersed with stirring in silicone oil (various silicone oil viscosities in the range of 500–1,250 can be used). The resulting silicone oil dispersion is emulsified or otherwise added to the final detergent matrix. By this means, ingredients such as the aforementioned enzymes, bleaches, bleach activators, bleach catalysts, photo activators, dyes, fluorescenters, fabric conditioners and hydrolyzable surfactants can be "protected" for use in detergents, including liquid laundry detergent compositions.

Liquid detergent compositions can contain water and other solvents as carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monoalcohols are preferred for solubilizing surfactant, but polyols such as those containing from 2 to about 6 carbon atoms and from 2 to about 6 hydroxy groups (e.g., 1,3-propanediol, ethylene glycol, glycerine, and 1,2-propanediol) can also be used. The compositions may contain from 5% to 90%, typically 10% to 50% of such carriers.

Granular detergents can be prepared, for example, by spray-drying (final product density about 520 g/l) or agglomerating (final product density above about 600 g/l) the Base Granule. The remaining dry ingredients can then be admixed in granular or powder form with the Base Granule, for example in a rotary mixing drum, and the liquid ingredients (e.g., nonionic surfactant and perfume) can be sprayed on.
The detergent compositions herein will preferably be formulated such that, during use in aqueous cleaning operations, the wash water will have a pH of between about 6.5 and about 11, preferably between about 7.5 and 10.5. Liquid dishwashing product formulations preferably have a pH between about 6.8 and about 9.0. Laundry products are typically at pH 9–11. Techniques for controlling pH at recommended usage levels include the use of buffers, alkanolamines, acids, etc., and are well known to those skilled in the art.

As used herein, all concentrations, pans, and ratios are by weight unless otherwise stated. The following Examples illustrate the invention and facilitate its understanding, they are not meant to limit the scope of the invention.

**EXAMPLE I**

A granular laundry detergent for washing machines is shown below.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sokalan CP5 (100% active as Na salt)*</td>
<td>3.52</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dequest 2060 (100% as acid)**</td>
<td>0.45</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oleoyl sarcosinate</td>
<td>4.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcium formate</td>
<td>0.50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zeolite A</td>
<td>17.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carboxy methyl cellulose</td>
<td>0.45</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>9.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Citric acid</td>
<td>3.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Layered silicate SKS-6</td>
<td>12.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C14-sulfate</td>
<td>2.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C14–16 sulfate</td>
<td>2.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C12–14 alkyl ethoxylate (3.0) sulfate</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C12–14 amine oxide</td>
<td>10.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Branched fatty acid</td>
<td>2.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neodol C14-9</td>
<td>2.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Starch</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stearyl alcohol</td>
<td>0.15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium percarbonate (coated)</td>
<td>15.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetracetyltrimellamid (TAED)</td>
<td>4.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc phthalocyanin</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water and other balance</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1Sokalan is sodium polymethylacrylate from Hoechst
2Amino phosphonate chelating agent

**EXAMPLE II**

Granular automatic dishwashing detergents of the present invention are as follows:

**TABLE 1**

<table>
<thead>
<tr>
<th>% by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ingredients</td>
</tr>
<tr>
<td>A</td>
</tr>
<tr>
<td>Octadecylamidinium—N-oxide dihydroxide*</td>
</tr>
<tr>
<td>Hexadecylamidinium—N-oxide dihydroxide*</td>
</tr>
<tr>
<td>DMAO Blend*</td>
</tr>
<tr>
<td>Octetradecylamidinium—N-oxide, anhydrous</td>
</tr>
<tr>
<td>Sodium citrate, dihydrate</td>
</tr>
<tr>
<td>Sodium carbonate or bicarbonate</td>
</tr>
<tr>
<td>Hydrated 2.0 ratio sodium silicate</td>
</tr>
<tr>
<td>3500 MW modified polyacrylate (active basis)</td>
</tr>
<tr>
<td>Oleoyl sarcosinate</td>
</tr>
<tr>
<td>Nonionic surfactant</td>
</tr>
<tr>
<td>Sodium percarbonate</td>
</tr>
<tr>
<td>Tetra-esteryldihydroxy amino(92% active)</td>
</tr>
<tr>
<td>SS-ethylenediamine disuccinic</td>
</tr>
</tbody>
</table>

**EXAMPLE III**

Heavy duty liquid laundry detergent compositions are prepared by mixing the listed ingredients in the stated proportions in the order shown. Product is cooled to room temperature before addition of the protease enzyme.

**TABLE 1-continued**

<table>
<thead>
<tr>
<th>% by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ingredients</td>
</tr>
<tr>
<td>A</td>
</tr>
<tr>
<td>acid, magnesium salt</td>
</tr>
<tr>
<td>Alcalase 3F</td>
</tr>
<tr>
<td>Rapidase C</td>
</tr>
<tr>
<td>Termamyl 60T</td>
</tr>
<tr>
<td>Lipase*</td>
</tr>
<tr>
<td>Suds suppressor</td>
</tr>
<tr>
<td>Perfume, dye, water and filler balance</td>
</tr>
</tbody>
</table>

1C12H10MAO2.H2O ADMOX 18, Ethyl Corp.
2C14H10MAO2.H2O ADMOX 16, Ethyl Corp.
380/20 wt.
46L 18 Oil Corp.
5From pseudomonas pseudocaligenes, 100,000 LU/g

**What is claimed is:**

1. A detergent composition comprising
   (a) at least about 0.1% of an oleoyl sarcosinate of the formula:
   \[
   \begin{array}{c}
   \text{O} \\
   \text{N} \\
   \text{OM} \\
   \text{CH}_{2}
   \end{array}
   \]
   wherein M is hydrogen or a cationic moiety; and
   (b) from about 0.1% to about 20% of an amine oxide.

2. A composition according to claim 1 comprising from about 0.1% to about 10% by weight of an amine oxide having the general formula
   \[
   \text{R}^1(\text{EO})_x(\text{PO})_y(\text{BO})_z(\text{NO})_d(\text{CH}_3)_2\text{R}_2\text{SH}_2\text{H}_2\text{O}
   \]
   wherein \( \text{R}^1 \) represents a saturated or unsaturated hydrocarbyl moiety having a chain length of from about 8 to about
24 carbon atoms, x is from 0 to about 10, y is from 0 to about 10, z is from 0 to about 10, R is H or CH₂OH, q is from 0 to about 2, EO represents ethyleneoxy, PO represents propyleneoxy, and BO represents butyleneoxy; provided that when x+y+z=0, R¹ has a chain length of from about 10 to about 18 carbon atoms; and further provided that when x+y+z is different from 0, x+y+z has a maximum value of 10; said composition having a pH from about 6 to about 11.

3. A composition according to claim 2 wherein R² is a primary alkyl moiety and said amine oxide is selected from the group consisting of

(i) amine oxides according to said general formula wherein x+y+z = 0, the R¹ chain length is from about 12 to about 18, R²=H and q is from 0 to about 2;

(ii) amine oxides according to said general formula wherein x+y+z=0, the R¹ chain length is from about 12 to about 18, R²=CH₂OH and q is 0;

(iii) amine oxides according to said general formula wherein x+y+z=1 to about 10, the R¹ chain length is from about 12 to 24, y+z=0, and x is from about 1 to about 6; and

(iv) mixtures thereof.

4. A detergent composition according to claim 3, wherein said amine oxide is selected from the group consisting of:

(i) amine oxides according to said general formula wherein x+y+z=0, the R¹ chain length is from 12 to 18, R²=H and q=2; and

(ii) amine oxides according to said general formula wherein x+y+z=0, the R¹ chain length is from 16 to 18, R²=CH₂OH and q=0 and wherein said composition is substantially phosphate free.

5. A composition according to claim 3 wherein said amine oxide comprises less than about 2% of free amine.

6. A composition according to claim 5 comprising from about 1% to about 10% of said amine oxide and wherein said amine oxide comprises less than about 500 ppm of nitrosoamine.

7. A composition according to claim 6 substantially free of boron and comprising from about 1.5% to about 10% of said amine oxide.

8. A detergent composition according to claim 1 wherein M is selected from hydrogen or alkali metal salts.

9. A detergent composition comprising from about 1% to about 10% of said amine oxide and wherein said amine oxide comprises less than about 500 ppm of nitrosoamine.

10. A detergent composition according to claim 1 further comprising at least about 1% detergent builder and at least about 1% of a detriasive surfactant, other than said oleoyl sarcosinate surfactant, selected from anionic and nonionic detriasive surfactants.

11. A detergent composition according to claim 10 comprising from about 1% to about 40% by weight of the composition of said oleoyl sarcosinate surfactant.

12. A detergent composition according to claim 11 comprising at least about 1 ppm of said amine oxide having the general formula:

\[ \text{R}'(\text{EO})₉(\text{PO})₆(\text{BO})₅(\text{N(O)}₃\text{CH}_3\text{R},\text{R})₂\text{H}_2\text{O} \]

where R¹ represents a saturated or unsaturated hydrocarbon moiety having a chain length of from about 12 to 24 carbon atoms, x is from 0 to about 10, y is from 0 to about 10, z is from 0 to about 10, R is H or CH₂OH, q is from 0 to about 2, EO represents ethyleneoxy, PO represents propyleneoxy, and BO represents butyleneoxy; provided that when x+y+z=0, R¹ has a chain length of from about 12 to about 18 carbon atoms; and further provided that when x+y+z is different from 0, x+y+z has a maximum value of 10.

13. A detergent composition according to claim 12 wherein R¹ is a primary alkyl moiety, said amine oxide is selected from the group consisting of:

(i) amine oxides according to said general formula wherein x+y+z=0, the R¹ chain length is from about 12 to 18, R²=H and q is from 0 to 2;

(ii) amine oxides according to said general formula wherein x+y+z=0, the R¹ chain length is from about 12 to 18, R²=CH₂OH and q is 0;

(iii) amine oxides according to said general formula wherein x+y+z=1 to about 10, the R¹ chain length is from about 12 to 24, y+z=0, and x is from 1 to 6; and

(iv) mixtures thereof.

14. A detergent composition according to claim 13 wherein R¹ is a primary alkyl moiety, said amine oxide is selected from the group consisting of:

(a) at least about 0.5% of oleoyl sarcosinate of the formula:

\[ \text{O} \quad \text{N} \quad \text{OM} \]

wherein M is hydrogen or a cationic moiety;

(b) at least about 0.1% by weight of an amine oxide selected from the group consisting of tetradecyldimethylamine N-oxide, hexadecyldimethylamine N-oxide, octadecyldimethylamine N-oxide, hydrates thereof, and mixtures thereof; and

(c) from about 1% to about 50% of a pH adjusting component consisting of water-soluble salt or salt/builder mixture selected from sodium carbonate, sodium sesquicarbonate, sodium silicate, sodium citrate, citric acid, sodium bicarbonate, sodium hydroxide, and mixtures thereof; wherein said composition has a pH of from about 8.5 to about 10.5.

15. A composition according to claim 14 comprising from about 10% to about 30% sodium citrate and from about 7% to about 25% sodium carbonate.

16. A method for removing greasy soil from a substrate, said method comprising an aqueous solution containing detriasive surfactant and an amine oxide, wherein the improvement comprises including in said detergent composition at least about 0.5% by weight of the composition of a oleoyl sarcosinate surfactant and from about 1% to about 10% amine oxide.