

BLEACH ACTIVATION VIA ANHYDRIDES AND LIPASE

Bleaching agents have long been used in laundry detergents to enhance the overall cleaning action thereof. Various bleaches have long been used in numerous cleaning applications, including the washing and prewashing of fabrics as well as in other applications for instance in hard surface cleaning.

Using the bleaching agent various stains or soils on fabrics, textiles and hard surfaces are oxidized. Because of their oxidizing power peroxygen bleaching compounds like hydrogen peroxide, sodium perborate or sodium percarbonate have been found very useful in bleach formulations.

Addition of certain organic compounds, including activators such as tetracetyl ethylene diamine (TAED), to for instance perborate bleaches can improve the bleaching performance because of the formation of peracids.

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Detergent compositions have also been developed wherein various enzymes for removing certain stains or soils are implemented.

For instance, protease has been found useful for hydrolyzing protein-based stains particularly in the cleaning of fabrics.

Amylase has been found useful against carbohydrate-based stains originating from for instance food, whereas lipase has been found very useful for hydrolyzing fat-based stains in a prewash or resoak manner.

In EP-A- 130,064 applied for by Novo Industry A/S the use of enzymes in cleaning or detergent compositions is described in relation to improvements in enzymatic additives for achieving substantially improved cleaning efficiency. A need for improved bleaching or activated oxidant systems is acknowledged; said system should be capable of enhanced performance in aqueous solution at low temperature wash conditions while still remaining high temperature performance.

Such a system is described in EP-B-268,456 by the Clorox Comp. providing an activated oxidant system for achieving enzymatic perhydrolysis of a substrate in the presence of a source of hydrogen peroxide to produce a peracid. An enzyme catalyses the reaction of substrates resulting in formation of peracids.

As substrate for the enzyme, more specifically a lipase enzyme, esters are used in above-mentioned patent. However esters are in general very stable and poorly reactive compounds unless they have been synthesized with particular effective leaving groups. Although esters can generate peracids in the presence of lipase and peroxide such a reaction is not at all efficient. Therefore esters and lipase have never been actually used in detergents according to Applicant's knowledge. The present invention has solved above-identified problem and concerns an efficient system for detergency. The invention relates to a

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detergent composition or additive containing a lipase and/or enzyme having esterase activity, an anhydride and a source of hydrogen peroxide, said composition having a bleach activation effect. It has been found that anhydrides are in fact very reactive and efficient molecules that can provide peracids already without lipase in environments including hydrogen peroxide. Addition of lipase surprisingly further improves the reaction and boosts the anhydrides perhydrolysis; therefore being much more efficient as bleaching system.

Compositions comprising an anhydride, a lipase and/or enzyme having esterase activity and a source of hydrogen peroxide according to the invention are therefore of much higher interest for the detergency as very efficient.

The invention thus provides a new activation method of hydrogen peroxide by using anhydrides and lipase enzyme and/or enzyme having esterase activity. It has been found that by adding lipase and anhydrides to hydrogen peroxide solutions a substantial phenomenon of bleach activation occurs. This phenomenon has been shown as much stronger than when anhydrides or lipase are added alone to a hydrogen peroxide solution and is therefore related to the synergic presence of anhydrides and lipase in a bleaching environment.

So the addition of lipase to solutions containing anhydrides and hydrogen peroxide can significantly accelerate the formation of the peracid corresponding to the anhydride used. This effect is novel, as lipase is traditionally expected to help the hydrolysis of esters (and particularly of triglycerides). Any lipase interaction or hydrolytic action on anhydrides is, according to the invention, new and unexpected.

Such an activation system will complement the actions of known bleach activators such as TAED, NOBS, BOBS, iso NOBS, PAG, TAGU, SULFONIMINES, Metalloporphyrines, organo complexes of Manganese, quarternary ammonium or phosphonium bleach

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precursors such as (trimethyl ammonium toluoyloxybenzene sulphonate) or Acetylated Glycerol fatty esters. They will also complement the actions of preformed peracids such as DPDA, NAPAA, PAP (N,N Phtaloylimidopercaproic acid), Mono and Diperbrassylic acids. One can in fact use anhydrides with the most various structures, having cyclic or linear skeletons. Mixed anhydrides are also relevant to this invention as generating peracids of different hydrophobicity and surface activity at the same time and thus with an optimum specificity for soils having different affinities.

Dry compositions including a hydrogen peroxide source (perborate, percarbonate, etc.) or liquid compositions including hydrogen peroxide in itself can have significantly enhanced bleaching activation if they also include anhydrides and lipase. The invention applies to a wide range of products from granular detergents to granular bleaches and also to liquid compositions where pH, composition and dilution conditions allow an acceptable stability.

Using the detergent composition or additive according to the invention during the wash cycle, a pH should be chosen in order to minimize the alkaline conversion of the anhydride (polymer) into carboxylate(s). Therefore, for instance, a 1% solution of pH between 7 and 11 is suitable.

Anhydrides, commercially available like succinic and maleic are indicative for the inclusion in a dry bleach composition in conjunction with lipase. However, other anhydrides not having a cyclic or even a symmetric structure can also be included.

Polymeric anhydrides are also very suitable as well as co-polymers including anhydride monomers. Acrylic acid and maleic anhydrides co-polymers are preferred in this respect.

To incorporate anhydrides in a dry matrix a dry material (like succinic or maleic anhydrides) and a liquid material as well

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are absorbed on a solid phase, e.g. cyclodextrines. The stability of the anhydride in the finished product can be improved by agglomerating or coating it with the appropriate protecting materials (CMC, fillers, etc.). Using this bleach activation system it allows a highly effective alternative or an integration of TAED, NOBS or other well-known activators on top of the typical soil removal advantages provided by lipase. By using this system according to the invention, the anhydrides deliver organic acids which may according to the specific molecules used, have a good building capacity in the wash.

Using the above anhydride (polymer) as a agglomerating agent or as a coating agent to bleach precursors, the bleach precursor will have a better stability in alkaline detergents. Subsequently a better compatibility with fabrics and surprisingly a synergistic bleach activation occurs.

A typical formulation based on the invention comprises :

Sodium percarbonate	3-80%
Anhydrides or anhydrides sources	0.1-10%
Lipase	0.1-10%
TAED	0-20%
Buffers/Fillers	0-90%
Builders	0-90%
Surfactants	0-20%
Other enzymes	0-5%
Others	0-10%

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Specific examples to illustrate the present invention are typical laundry bleach formulation (A) and a typical laundry detergent formulation (B) :

	<u>A</u>	<u>B</u>
	<u>%</u>	<u>%</u>
Sodium percarbonate	40	20
TAED	12	5
Granular polymer of maleic anhydride/acrylic acid	5	5
Buffers	38	20
Lipase (Lipolase Novo 100T)	0.5	0.5
Builders	--	30
Surfactants	--	15
Other enzymes	0.5	1.5
Others	--	4

Further specific examples to illustrate the present invention are typical granular automatic dishwashing formulations (C) and (D) :

In the granular automatic dishwashing detergent compositions (C) and (D), the abbreviated identifications have the following meanings:

Perborat�:	Anhydrous sodium perborate monohydrate
Percarbonate:	Anhydrous sodium percarbonate
TAED	Tetraacetyl ethylene diamine
Citrate:	Tri-Sodium citrate dihydrate
MA/AA:	Copolymers of 1:4 maleic/acrylic acid, average molecular weight about 80,000
Silicate:	Amorphous Sodium Silicate (SiO ₂ :Na ₂ O ratio normally follows).
Protease:	Proteolytic enzyme sold under the trade name

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Savinase by Novo Industries A/S

Amylase: Amylolytic enzyme sold under the trade name
Termamyl by Novo Industries A/S

Lipase Lipolytic enzyme sold under the trade name
Lipolase by Novo Industries A/S

Nonionic: C₁₃-C₁₅ mixed ethoxylated/propoxylated fatty
alcohol with an average degree of
ethoxylation of 3.8 and an average degree of
propoxylation of 4.5 sold under the trade
name Plurafac LF404 by BASF GmbH.

PVP Polyvinylpyrrolidone with an average Molecular
weight of 12,000

Sulphate: Anhydrous Sodium Sulphate

The following machine dishwashing detergents according to the
invention are prepared (parts by weight):

Ingredients	Parts by weight	
	C	D
Citrate	38.0	35.0
Perborate	3.5	-
Percarbonate	-	3.5
TAED	2.0	2.0
MA/AA	4.0	6.0
Silicate (2.0 ratio)	26.0	30.0
Paraffin oil (1)	0.5	0.5
Protease	2.0	2.5
Amylase	1.5	0.5
Lipase	2.0	2.0
Nonionic (2)	1.5	1.5
Limesoap dispersant (3)	2.0	-
PVP	-	0.5
Sulphate	balance to 100	
pH	10.7	10.7

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- (1) WINOG 70 ex Wintershall
- (2) Pre-mixed with the paraffin oil before incorporation
- (3) Lutensol AO12 ex BASF

Lipase

The lipase used in the present invention is included in the detergent and bleaching composition in such an amount that the final composition has a lipolytic enzyme activity of from 10 to 0.005 LU/mg, preferably 5 to 0.05 LU/mg of the composition.

A Lipase Unit (LU) is that amount of lipase which produces 1/micromol of titratable fatty acid per minute in a pH stat. under the following conditions : temperature 30 °C; pH = 9.0; substrate is an emulsion of 3.3 wt% of olive oil and 3.3% gum arabic, in the presence of 13 mmol/l Ca ++; and 20 mmol/l NaCl in 5 mmol/l Tris-Buffer. An alternative definition of the lipase unit is given in EP 0 258 068 (Novo), which mentions (inter alia) lipases suitable for use in the practice of this invention and is hereby incorporated by reference.

Naturally, mixtures of the above lipase with other known lipases can be used. The lipase(s) can be used in its (their) non-purified form or in a purified form, e.g., purified with the aid of well-known adsorption methods, such as phenyl sepharose adsorption techniques.

The detergent composition or additive of the invention may be formulated in any convenient form, preferably as a powder. This composition may have different applications and can be used in dry bleach formulations and detergent formulations including laundry and automatic dishwashing detergent formulations.

The compositions of the invention are of use in machine dishwashing processes of the conventional type performed using



a dishwasher machine, which may be selected from any of those commonly available on the market. In more detail, such machine dishwashing processes comprise treating soiled articles, such as crockery, glassware, hollowware and cutlery, with an aqueous liquid having dissolved or dispersed therein an effective amount of the detergent composition as described herein above. By an effective amount of the detergent composition it is generally meant from 8g to 60g of detergent composition per wash, dissolved or dispersed in a wash solution volume of from 3 to 10 litres, as are typical product dosages employed in conventional machine dishwashing processes. The wash temperature may be in the range 40°C to 65°C as commonly is employed in such processes. A rinse aid composition may also be used, if desired.

Detergent compositions or additives of the invention may contain as above-mentioned other detergent ingredients known in the art as e.g. builders, anti soil redeposition agents, perfumes, surfactants, anti-dye transfer ingredients, optical brighteners, other enzymes (e.g. proteases and amylases) etc.

Additionally detergent compositions comprise surfactants which may be of the anionic, non-ionic, amphoteric, cationic or zwitterionic type as well as mixtures of these types.

A typical listing of these surfactants is given in US Patent 3,664,961 issued to Norris on May 23, 1972.

Mixtures of anionic surfactants are particularly suitable herein, especially mixtures of sulphonate and sulphate surfactants in a weight ratio of from 5:1 to 1:2, preferably from 3:1 to 2:3, more preferably from 3:1 to 1:1. Preferred sulphonates include alkyl benzene sulphonates having from 9 to 15, especially 11 to 13 carbon atoms in the alkyl radical, and alpha-sulphonated methyl fatty acid esters in which the fatty acid is derived from a C₁₂-C₁₈ fatty source preferably from a C₁₆-C₁₈ fatty source. In each instance the cation is an alkali

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metal, preferably sodium. Preferred sulphate surfactants are alkyl sulphates having from 12 to 18 carbon atoms in the alkyl radical, optionally in admixture with ethoxy sulphates having from 10 to 20, preferably 10 to 16 carbon atoms in the alkyl radical and an average degree of ethoxylation of 1 to 6.

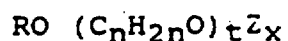
Examples of preferred alkyl sulphates herein are tallow alkyl sulphate, coconut alkyl sulphate, and C₁₄₋₁₅ alkyl sulphates.

An example of a preferred ethoxy sulphate is the so-called AE3S (C₁₂₋₁₅ alkyl 3 times ethoxylated sulphate). The cation in each instance is again an alkali metal cation, preferably sodium.

One class of nonionic surfactants useful in the present invention are condensates of ethylene oxide with a hydrophobic moiety to provide a surfactant having an average hydrophilic-lipophilic balance (HLB) in the range from 8 to 17, preferably from 9.5 to 13.5, more preferably from 10 to 12.5. The hydrophobic (lipophilic) moiety may be aliphatic or aromatic in nature and the length of the polyoxyethylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements. In order to maximize the lipase activity preferably a so-called nil-LAS containing detergent composition or additive is used according to the invention.

Especially preferred nonionic surfactants of this type are the C₉-C₁₅ primary alcohol ethoxylates containing 3-8 moles of ethylene oxide per mole of alcohol, particularly the C₁₄-C₁₅ primary alcohols containing 6-8 moles of ethylene oxide per mole of alcohol and the C₁₂-C₁₄ primary alcohols containing 3-5 moles of ethylene oxide per mole of alcohol.

Another class of nonionic surfactants comprises alkyl polyglucoside compounds of general formula



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wherein Z is a moiety derived from glucose; R is a saturated hydrophobic alkyl group that contains from 12 to 18 carbon atoms; t is from 0 to 10 and n is 2 or 3; x is from 1.3 to 4, the compounds including less than 10% unreacted fatty alcohol and less than 50% short chain alkyl polyglucosides. Compounds of this type and their use in detergent are disclosed in EP-B 0 070 077, 0 075 996 and 0 094 118.

Also suitable as nonionic surfactants are poly hydroxy fatty acid amide surfactants of the formula $R^2 - C - N - Z$,



wherein R^1 is H, C_{1-4} hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R_2 is C_{5-31} hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative thereof. Preferably, R_1 is methyl, R_2 is a straight C_{11-17} alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

According to the invention the detergent composition or additive preferably comprises anionic surfactant to non-ionic surfactant in a ratio between 1 : 1 to 10 : 1.

A further class of surfactants are the semi-polar surfactants such as amine oxides. Suitable amine oxides are selected from mono C_8-C_{20} , preferably $C_{10}-C_{14}$ N-alkyl or alkenyl amine oxides and propylene-1,3-diamine dioxides wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

Another class of surfactants are amphoteric surfactants, such as polyamine-based species.

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Cationic surfactants can also be used in the detergent compositions herein and suitable quaternary ammonium surfactants are selected from mono C₈-C₁₆, preferably C₁₀-C₁₄ N-alkyl or alkenyl ammonium surfactants wherein remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

Mixtures of surfactant types are preferred, more especially anionic-nonionic and also anionic-nonionic-cationic mixtures. Particularly preferred mixtures are described in British Patent No. 2040987 and European Published Application No. 0 087 914. The detergent compositions can comprise from 1%-70% by weight of surfactant, but usually the surfactant is present in the compositions herein an amount of from 1% to 30%, more preferably from 10-25% by weight. More surfactant would be detrimental to lipase activity.

BUILDER

Builder materials will typically be present at from 0% to 90% preferably up to 30% of the detergent compositions herein.

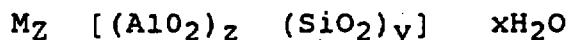
The compositions herein should preferably be free or substantially free of phosphate-containing builders (substantially free being herein defined to constitute less than 1% of the total detergent builder system). The builder system herein may consist of water-soluble builders, water-insoluble builders, or mixtures thereof. However, where the detergent compositions are for use in an automatic dishwashing process the builder material is most preferably water-soluble.

Water insoluble builders can be an inorganic ion exchange material, commonly an inorganic hydrated aluminosilicate material, more particularly a hydrated synthetic zeolite such as hydrated Zeolite A, X, B, P, MAP or HS.

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Preferred aluminosilicate ion-exchange materials have the unit cell formula



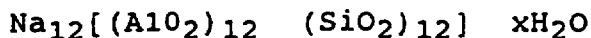
wherein M is a calcium-exchange cation, z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate materials are in hydrated form and are preferably crystalline containing from 10% to 28%, more preferably from 18% to 22% water.

The above aluminosilicate ion exchange materials are further characterized by a particle size diameter of from 0.1 to 10 micrometers, preferably from 0.2 to 4 micrometers. The term "particle size diameter" herein represents the average particle size diameter of a given ion exchange material as determined by conventional analytical techniques such as, for example, microscopic determination utilizing a scanning electron microscope. The aluminosilicate ion exchange materials are further characterized by their calcium ion exchange capacity, which is at least 200 mg equivalent of $CaCO_3$ water hardness/g of aluminosilicate, calculated on an anhydrous basis, and which generally is in the range of from 300 mg eq./g to 352 mg eq./g. The aluminosilicate ion exchange materials herein are still further characterized by their calcium ion exchange rate which is described in detail in GB-1,429,143.

Aluminosilicate ion exchange materials useful in the practice of this invention are commercially available and can be naturally occurring materials, but are preferably synthetically derived. A method for producing aluminosilicate ion exchange materials is discussed in US Patent No. 3,985,669. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designation Zeolite A, Zeolite B, Zeolite X, Zeolite HS and mixtures thereof. In an especially preferred embodiment, the crystalline



aluminosilicate ion exchange material is Zeolite A and has the formula



wherein x is from 20 to 30, especially 27. Zeolite X of formula $\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 10$

$\cdot 276\text{H}_2\text{O}$ is also suitable, as well as Zeolite HS of formula $\text{Na}_6[(\text{AlO}_2)_6(\text{SiO}_2)_6] \cdot 7.5 \text{H}_2\text{O}$.

Another suitable water-insoluble, inorganic builder material is layered silicate, e.g. SKS-6 (Hoechst). SKS-6 is a crystalline layered silicate consisting of sodium silicate ($\text{Na}_2\text{Si}_2\text{O}_5$). The high $\text{Ca}^{++}/\text{Mg}^{++}$ binding capacity is mainly a cation exchange mechanism. In hot water, the material becomes more soluble.

The water-soluble builder can be a monomeric or oligomeric carboxylate chelating agent.

Suitable carboxylates containing one carboxy group include lactic acid, glycolic acid and ether derivatives thereof as disclosed in Belgian Patent Nos. 831,368, 821,369 and 821,370. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates described in German Offenlegenschrift 2,446,686, and 2,446,687 and U.S. Patent No. 3,935,257 and the sulfinyl carboxylates described in Belgian Patent No. 840,623. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

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Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,082,179, while polycarboxylates containing phosphone substituents are disclosed in British Patent No. 1,439,000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydrofuran - cis, cis, cis-tetracarboxylates, 2,5-tetrahydrofuran -cis - dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane-hexacarboxylates and and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic polycarboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent No. 1,425,343.

Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates. Preferred builder systems for use in the present compositions include a mixture of a water-insoluble aluminosilicate builder such as zeolite A or of a layered silicate (sks/6), and a water-soluble carboxylate chelating agent such as citric acid.

Other builder materials that can form part of the builder system for the purposes of the invention include inorganic materials such as alkali metal carbonates, bicarbonates and silicates.

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Other suitable water-soluble organic salts are the homo- or co-polymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms.

Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 70,000, especially about 40,000.

The compositions of the invention may fully contain from 0.05% to 5% by weight of the composition, preferably from 0.05% to 1% by weight, most preferably from 0.1% to 0.5% by weight of a chelant (heavy metal sequestrant).

A suitable chelant for inclusion in the detergent compositions in accordance with the invention is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof. Preferred EDDS compounds are the free acid form and the sodium or magnesium salt thereof. Examples of such preferred sodium salts of EDDS include Na_2EDDS and Na_4EDDS . Examples of such preferred magnesium salts of EDDS include MgEDDS and Mg_2EDDS . The magnesium salts are the most preferred for inclusion in compositions in accordance with the invention.

Other chelants include the organic phosphonates, including amino alkylene poly (alkylene phosphonate), alkali metal ethane 1-hydroxy diphosphonates, nitrilo trimethylene phosphonates, ethylene diamine tetra methylene phosphonates and diethylene triamine penta methylene phosphonates. The phosphonate compounds may be present either in their acid form or as a complex of either an alkali or alkaline metal ion, the molar ratio of said metal ion to said phosphonate compound being at least 1:1. Such complexes are described in US-A-4,259,200.

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Preferably, the organic phosphonate compounds where present are in the form of their magnesium salt. The level of phosphorus containing chelants in the compositions of the invention is preferably minimised, with their complete exclusion from the compositions being most preferred. Other chelants suitable for inclusion herein include amino polycarboxylate chelants such as EDTA and HEDTA.

OPTIONAL INGREDIENTS

The present compositions will typically include optional ingredients that normally form part of detergent compositions. Antiredeposition and soil suspension agents, optical brighteners, bleaches, bleach activators, suds suppressors, anticaking agents, dyes and pigments are examples of such optional ingredients and can be added in varying amounts as desired.

Antiredeposition and soil suspension agents suitable herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts. Polymers of this type include the polyacrylates and maleic anhydride-acrylic acid copolymers previously mentioned as builders, as well as copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the copolymer. These materials are normally used at levels of from 0.5% to 10% by weight, more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

Preferred optical brighteners are anionic in character, examples of which are disodium 4,4¹-bis-(2-diethanolamino-4-anilino -s- triazin-6-ylamino)stilbene-2:2¹ disulphonate, disodium 4, - 4¹-bis-(2-morpholino-4-anilino-s-triazin-6-ylaminostilbene-2:2¹ - disulphonate, disodium 4,4¹

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- bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2:2¹ - disulphonate, monosodium 4¹,4¹¹ -bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2-sulphonate, disodium 4,4¹ -bis-(2-anilino-4-(N-methyl-N-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2¹ - disulphonate, disodium 4,4¹ -bis-(4-phenyl-2,1,3-triazol-2-yl)-stilbene-2,2¹ disulphonate, disodium 4,4¹ bis(2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2¹ disulphonate and sodium 2(stilbyl-4¹¹-(naphtho-1¹,2¹:4,5)-1,2,3 - triazole-2¹¹-sulphonate.

Any particulate inorganic perhydrate bleach can be used. If used for a bleach additive, the amount of inorganic perhydrate can be used in an amount from 3% to 80% by weight, more preferably from 8% to 60% by weight, most preferably from 12% to 50%. If to be used in a fully formulated detergent in European washing machines, the amount of inorganic perhydrate can be used in an amount from 3% to 80% by weight, more preferably from 12% to 40% by weight, most preferably from 8% to 30%. If to be used in a fully formulated detergent for US and Japanese washing machine, the amount of inorganic perhydrate can be used in an amount from 3% to 80% by weight, more preferably from 3% to 15% by weight, most preferably from 3% to 10%. Preferred examples of such bleaches are sodium perborate monohydrate and tetrahydrate, percarbonate, and mixtures thereof.

Another preferred separately mixed ingredient is a peroxy carboxylic acid bleaching agent and salts thereof, which is preferably added in a prilled or agglomerated form.

Peroxygen bleaching agents are preferably combined with bleach activators, which lead to the in situ production in aqueous solution (i.e. during the washing process of the peroxy acid corresponding to the bleach activator). Examples of suitable compounds of this type are disclosed in British Patent Nos. 1586769 and 2143231 and a method for their formation into a prilled form is described in European Published Patent

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Application No. 0 062 523. Preferred examples of such compounds are tetracetyl ethylene diamine, sodium 3, 5, 5 trimethyl hexanoyloxybenzene sulphonate, diperoxy dodecanoic acid as described for instance in US 4 818 425 and nonylamide of peroxyadipic acid as described for instance in US 4 259 201 and n-nonanoyloxybenzenesulphonate (NOBS), and acetyl triethyl citrate (ATC) such as described in European Patent application 91870207.7.

Bleach activators are for instance normally employed at levels of from 1% to 24% by weight, more frequently from 1% to 18% and preferably from 2% to 14% by weight of the composition.

Another optional ingredient is a suds suppressor, exemplified by silicones, and silica-silicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent impermeable carrier. Alternatively the suds suppressor can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components.

As mentioned above, useful silicone suds controlling agents can comprise a mixture of an alkylated siloxane, of the type referred to hereinbefore, and solid silica. Such mixtures are prepared by affixing the silicone to the surface of the solid silica. A preferred silicone suds controlling agent is represented by a hydrophobic silanated (most preferably trimethyl-silanated) silica having a particle size in the range from 10 millimicrons to 20 millimicrons and a specific surface area above 50 m²/g intimately admixed with dimethyl silicone fluid having a molecular weight in the range from about 500 to

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about 200,000 at a weight ratio of silicone to silanated silica of from about 1:1 to about 1:2.

A preferred silicone suds controlling agent is disclosed in Bartollota et al. U.S. Patent 3,933,672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DTOS 2,646,126 published April 28, 1977. An example of such a compound is DC-544, commercially available from Dow Corning, which is a siloxane/glycol copolymer.

The suds suppressors described above are normally employed at levels of from 0.001% to 2% by weight of the composition, preferably from 0.01% to 1% by weight. The incorporation of the suds modifiers is preferably made as separate particulates, and this permits the inclusion therein of other suds controlling materials such as C20-C24 fatty acids, microcrystalline waxes and high MW copolymers of ethylene oxide and propylene oxide which would otherwise adversely affect the dispersibility of the matrix. Techniques for forming such suds modifying particulates are disclosed in the previously mentioned Bartolotta et al U.S. Patent No. 3,933,672.

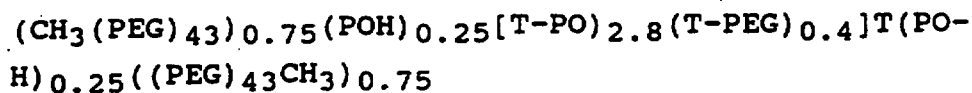
Other useful polymeric materials are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000. These are used at levels of from 0.20% to 5% more preferably from 0.25% to 2.5% by weight. These polymers and the previously mentioned homo- or co-polymeric polycarboxylate salts are valuable for improving whiteness maintenance, fabric ash deposition, and cleaning performance on clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

Soil release agents useful in compositions of the present invention are conventionally copolymers or terpolymers of terephthalic acid with ethylene glycol and/or propylene glycol

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units in various arrangements. Examples of such polymers are disclosed in the commonly assigned US Patent Nos. 4116885 and 4711730 and European Published Patent Application No. 0 272 033. A particular preferred polymer in accordance with EP-A-0 272 033 has the formula



where PEG is $-(\text{OC}_2\text{H}_4)_n-$, PO is $(\text{OC}_3\text{H}_6\text{O})$ and T is $(\text{pOC}_6\text{H}_4\text{CO})$.

Also very useful are modified polyesters as random copolymers of dimethyl terephthalate, dimethyl sulfoisophthalate, ethylene glycol and 1-2 propane diol, the end groups consisting primarily of sulphobenzoate and secondarily of mono esters of ethylene glycol and/or propane-diol. The target is to obtain a polymer capped at both end by sulphobenzoate groups, "primarily", in the present context most of said copolymers herein will be end-capped by sulphobenzoate groups. However, some copolymers will be less than fully capped, and therefore their end groups may consist of monoester of ethylene glycol and/or propane 1-2 diol, thereof consist "secondarily" of such species.

The selected polyesters herein contain about 46% by weight of dimethyl terephthalic acid, about 16% by weight of propane -1.2 diol, about 10% by weight ethylene glycol about 13% by weight of dimethyl sulfobenzoid acid and about 15% by weight of sulfoisophthalic acid, and have a molecular weight of about 3.000. The polyesters and their method of preparation are described in detail in EPA 311 342.

Certain polymeric materials such as polyvinyl pyrrolidones typically of MW 5000-20000, preferably 10000-15000, also form useful agents in preventing the transfer of labile dyestuffs between fabrics during the washing process.

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Fabric softening agents can also be incorporated into detergent compositions in accordance with the present invention. These agents may be inorganic or organic in type. Inorganic softening agents are exemplified by the smectite clays disclosed in GB-A-1,400,898. Organic fabric softening agents include the water-insoluble tertiary amines as disclosed in GB-A-1514276 and EP-B-0 011 340 and their combination with mono C12-C14 quaternary ammonium salts are disclosed in EP-B-0 026 527 and EP-B-0 026 528 and di-long-chain amides as disclosed in EP-B-0 242 919. Other useful organic ingredients of fabric softening systems include high molecular weight polyethylene oxide materials as disclosed in EP-A-0 299 575 and 0 313 146.

Levels of smectite clay are normally in the range from 5% to 20%, more preferably from 8% to 15% by weight with the material being added as a dry mixed component to the remainder of the formulation. Organic fabric softening agents such as the water-insoluble tertiary amines or di-long-chain amide materials are incorporated at levels of from 0.5% to 5% by weight, normally from 1% to 3% by weight whilst the high molecular weight polyethylene oxide materials and the water-soluble cationic materials are added at levels of from 0.1% to 2%, normally from 0.15% to 1.5% by weight. These materials are normally added to the spray dried portion of the composition, although in some instances it may be more convenient to add them as a dry mixed particulate, or spray them as a molten liquid on to other solid components of the composition.

MAKING PROCESS

Compositions according to the present invention can be made via a variety of methods including dry mixing, spray drying, agglomeration and granulation and combinations of any of these techniques. The compositions according to the present invention can be prepared with different bulk densities, from

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conventional granular products to so-called "concentrated" products (i.e. with a bulk density above 600g/l).

Examples

Example 1 To a solution containing 5 ml of wine, 10 ml of a solution of hydrogen peroxide (35% active by weight) and 50 ml of water, in one case 1 g of succinic anhydrides and in another case 1 g of succinic anhydrides and 1 ml of lipase suspension were added. After having waited 3 hours and having filtered both solutions with a spectrophotometer the absorbance of the solution at 300 nm was measured, observing the following results :

	<u>with lipase</u>	<u>without lipase</u>
ABSORBANCY (at 300 nm)	1.781	2.944

The data indicated above are an average of four experiments each. To note that all experiments have provided extremely accurate results with small fluctuations only on the second decimal number.

The results show a much stronger decoloration of the wine solution (40% lower absorbancy) when lipase is present. They indirectly confirm the existence of a pretty strong activation phenomenon.

Example 2 To a solution containing 5 ml of wine, 10 ml of a solution of hydrogen peroxide (35% active by weight) and 50 ml of water, in one case 1 g of succinic anhydrides and in another case 1 g of succinic anhydrides and 0.3g of lipase in granulates was added. After having waited 14 hours and having filtered both solutions, with a spectrophotometer the absorbancy of the solution around 310 nm was measured (in correspondence of the absorbancy peak) observing the following results :

	<u>with lipase</u>	<u>without lipase</u>
ABSORBANCY (at 310 nm)	1.055	1.624

The data indicated above are the average of four experiments each. The accuracy among experiments has been the same of previous experiment.

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The results show a much stronger decoloration of the wine solution (35% lower absorbancy) when lipase is present. They indirectly confirm the existence of a pretty strong activation phenomenon.

Example 3

To a solution containing 10 ml of wine, 10 ml of an hydrogen peroxide solution (35% active by weight) and 50 ml of water, in one case 1 g of succinic anhydrides and in another case 1 g of succinic anhydrides and 0.3 g of lipase in granules was added. After having waited 14 hours and having filtered both solutions, with a spectrophotometer the absorbancy of the solution around 317 nm was measured (in correspondence of the absorbancy peak) observing the following results :

	<u>with lipase</u>	<u>without lipase</u>
ABSORBANCY (at 317 nm)	1.793	2.387

The data indicated above are an average of two experiments each. The accuracy among experiments has been the same of previous experiment.

Again, the results show a much stronger decoloration of the wine solution (25% lower absorbancy) when lipase is present. They indirectly confirm the existence of an activation phenomenon.

Example 4

To a solution containing 5 ml of wine, 10 ml of a solution of hydrogen peroxide (35% active by weight) and 50 ml of water in one case 1 g of maleic anhydrides and in another case 1 g of maleic anhydrides and 0.3 g of lipase in granules was added. After having waited 14 hours and having filtered both solutions, with a spectrophotometer the absorbancy of the solution around 312 nm was measured (in correspondence of the absorbancy peak) observing the following results :

	<u>with lipase</u>	<u>without lipase</u>
ABSORBANCY (at 312 nm)	1.864	2.050

The data indicated above are an average of two experiments each. All experiments have provided extremely accurate results with small fluctuations only on the third decimal number

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The results show a stronger decoloration of the wine solution (10% lower absorbancy) when lipase is present. They indirectly confirm the existence of an activation phenomenon.

Example 5

To a solution containing 10 ml of wine, 10 ml of a solution of hydrogen peroxide (35% active by weight) and 50 ml of water in one case 1 g of maleic anhydrides and in another case 1 g of maleic anhydrides and 0.3 g of lipase in granules was added. After having waited 14 hours and having filtered both solutions, with a spectrophotometer the absorbancy of the solution around 318 nm was measured (in correspondence of the absorbancy peak) observing the following results :

	<u>with lipase</u>	<u>without lipase</u>
ABSORBANCY (at 318 nm)	2.41	2.67

The data indicated above are an average of two experiments each. All experiments have provided extremely accurate results with small fluctuations only on the third decimal number.

Again, the results show a stronger decoloration of the wine solution (10% lower absorbancy) when lipase is present, indirectly confirming the existence of an activation phenomenon.

Also stain removal tests on wine, coffee and tea with different formulations have confirmed these results.

They have in fact highlighted a significantly improved stain removal result for formulations containing lipase and an anhydride source.

Example 6

SINGLE VARIABLE LAUNDRY TESTS OF THE FORMULA WITH AN ANHYDRIDE SOURCE AND LIPASE VERSUS THE ONE WITH AN ANHYDRIDE SOURCE WITHOUT LIPASE

Cleaning of collars and cuffs

A vs. A"

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Removal of bleachable stains (average of wine, coffee and tea)	+ 1.5
Removal of greasy stains	+ 0.9

A = formulations as outlined earlier in this application; A" = same formulation without lipase;

Test method: Tests were conducted in washing machine, at 40 °C, with medium water hardness (14g/US gallon). For each wash cycles 50 g of A or A" were added to 170 g of a commonly used granular detergent. Results are an average of 8 wash replicates done with each product tested. This ensures a good precision and accuracy.

According to this test method, results from 0 to 0.5 units indicate that there is no visible difference between the removal delivered by the two products tested. Results from 0.6 to 1.0 units indicate that there is a small, but visible difference between the removal delivered by the two products. Results from 1.1 to 2.0 units indicate that the two products deliver removal that are clearly different and easily detectable by eyesight. Positive results indicate better removal for the first product.

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CLAIMS:

1. Detergent composition or additive containing a lipase enzyme and/or enzyme having esterase activity, an anhydride and a source of hydrogen peroxide, said composition having a bleach activation effect.
2. Detergent composition or additive according to claim 1 wherein the anhydride is a highly active polymer containing anhydridic residues.
3. Detergent composition or additive according to claim 2 wherein the polymer is a co-polymer containing maleic anhydride and acrylic acid residues.
4. Detergent composition or additive according to any of the preceding claims wherein the enzyme is present in an amount so that the final composition has a lipolytic enzyme activity of from 10 to 0.005 LU/mg, the anhydride is present in an amount of 0.1-10% and the source of hydrogen peroxide is present in an amount of 5%-80%.
5. Detergent composition or additive according to any of the preceding claims wherein the ratio anionic surfactant to non-ionic surfactant is 1:1 to 10:1.
6. Use of detergent composition or additive according to any of the preceding claims for bleach activation.
7. Use of detergent composition or additive according to claims 1-5 for bleachable soil, in addition to triglyceride or grease removal.
8. Use of detergent composition or additive according to any of the claims 1-5 wherein the composition or additive is a 1% solution having a pH between 7.0 and 11.0 during the wash cycle.



9. Detergent composition or additive containing a lipase enzyme and/or enzyme having esterase activity, a source of hydrogen peroxide and a bleach precursor particle containing as a binder and/or as a coating agent a highly active polymer having anhydridic residues.
10. Detergent composition or additive according to claim 9 wherein the bleach precursor is TAED.

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