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(54) Enzymatic detergent compositions inhibiting dye transfer.

(57) A dye transfer inhibiting composition comprising:

A. a metallo catalyst selected from
  a) metallo porphin and water-soluble or water-dispersable derivatives thereof;
  b) metallo porphyrin and water-soluble or water-dispersable derivatives thereof;
  c) metallo phthalocyanine and water-soluble or water-dispersable derivatives thereof;
B. an efficient amount of a bleaching agent.
C. a lipolytic enzyme characterized in that the aminoacid sequence contains no methionine.

EP 0 622 447 A1

Field of the Invention

The present invention relates to detergent compositions comprising lipases. More in particular, the present invention relates to dye transfer inhibiting compositions comprising a specific class of lipase.

Background of the Invention

Detergent compositions comprising enzymes are well known in the art. It is also well recognized that enzyme deactivation occurs in detergent compositions formulated with enzymes.
The loss of detergent activity of enzymes is among others depending on the presence of adjunct detergent ingredients.
One type of adjunct detergent ingredients that is added to detergent ingredients are metallo catalysts.
Said metallo catalysts are added to detergent compositions in order to inhibit the transfer of dyes from colored fabrics onto other fabrics washed therewith. These catalysts have the ability to oxidize the fugitive dyes washed out of dyed fabrics before the dyes have the opportunity to become attached to the fabrics in the wash.
Copending European patent application No EP 92870181.2 describes metallo catalysts which are very efficient in eliminating the transfer of solubilized or suspended dyes.

It has now been found that with the use of a particular class of lipases an improved overall detergency performance can be obtained with dye transfer inhibiting compositions formulated with metallo-catalysts.

This finding allows to formulate detergent compositions which exhibit excellent dye transfer inhibiting properties while not adversely affecting the lipolytic activity.

According to another embodiment of this invention a process is also provided for laundering operations involving colored fabrics.

Summary of the Invention

The present invention relates to inhibiting dye transfer compositions comprising metallo catalysts and an efficient amount of bleaching agent in combination with a specific class of lipases.

Detailed description of the invention

Lipase :

An essential ingredient of the present invention is an active lipolytic enzyme characterized in that the aminoacid sequence contains no methionine.
Preferred lipases are the fungal lipases producible by Humicola lanuginosa.
The lipases are producible by a host organism in which the DNA encoding for the lipase has been cloned and expressed.
Preferably the lipase is producible by the host organism Aspergillus.
Highly preferred lipases are lipases producible by cloning the gene from the fungal lipases producible by Humicola languginosa and expressing the gene in in Aspergillus oryzae as described in European patent Application 0 258 068, which is commercially available under the tradename Lipolase®. This Lipolase is also described in US patent 4, 810,414.

Other suitable lipases equivalent to the lipase defined above are lipases which show a positive immunological cross-reaction with the antibody of the lipases as descibed hereinabove.

The lipases of the present invention are included in the dye transfer inhibiting composition in such an amount that the final composition has a lipolytic enzyme activity of from 10 to 10000 LU/g, preferably 20 to 5000 LU/g of the dye transfer inhibiting composition.

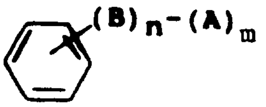
A Lipase Unit (LU) is that amount of lipase which produces 1/umol of titratable fatty acid per minute in a pH-stat under the conditions as described in Novo method (Novo publication AF 95.4/1 which is available on request)

Metallo catalyst

The preferred usage range of the catalyst in the wash is 10^{-8} molar to 10^{-3} molar, more preferred 10^{-6} - 10^{-4} molar.

The essential metallo porphin structure may be visualized as indicated in Formula I in the accompanying drawings. In Formula I the atom positions of the porphin structure are numbered conventionally and the double bonds are put in conventionally. In other formulae, the double bonds have been omitted in the drawings, but are actually present as in I.

Preferred metallo porphin structures are those substituted at one or more of the 5, 10, 15 and 20 carbon positions of Formula I (Meso positions), with a phenyl or pyridyl substituent selected from the group consisting of



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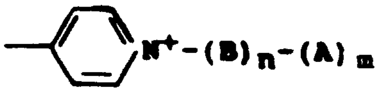
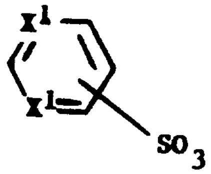


wherein n and m may be 0 or 1; A is selected from water-solubilizing group, e.g., sulfate, sulfonate, phosphate or carboxylate groups; and B is selected from the group consisting of C_1-C_{10} alkyl, C_1-C_{10} polyethoxy alkyl and C_1-C_{10} hydroxy alkyl.

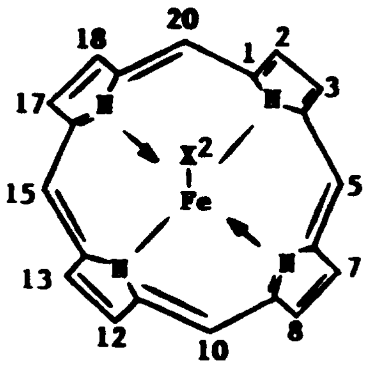
Preferred molecules are those in which the substituents on the phenyl or pyridyl groups are selected from the group consisting of $-CH_3$, $-C_2H_5$, $-CH_2CH_2CH_2SO_3$-, $-CH_2$--, and - $CH_2CH(OH)CH_2SO_3$-, $-SO_3$.

A particularly preferred metallo phorphin is one in which the molecule is substituted at the 5, 10 15, and 20 carbon positions with the substituent



This preferred compound is known as metallo tetrasulfonated tetraphenylporphin. The symbol X^1 is (=CY-) wherein each Y, independently, is hydrogen, chlorine, bromine, fluorine or meso substituted alkyl, cycloalkyl, aralkyl, aryl, alkaryl or heteroaryl.

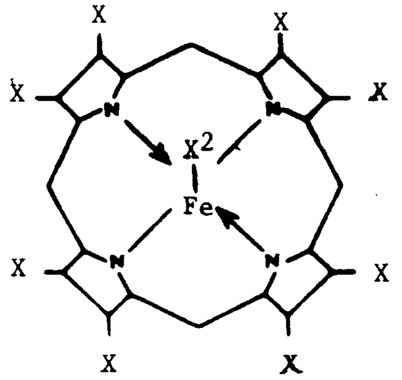
The symbol X^2 of Formula I represents an anion, preferably OH^- or Cl^-. The compound of Formula I may be substituted at one or more of the remaining carbon positions with C_1-C_{10} alkyl, hydroxyalkyl or oxyalkyl groups.



(I)

Porphin derivatives also include chlorophyls, chlorines, i.e. isobacterio chlorines and bacteriochlorines.

Metallo porphyrin and water-soluble or water-dispersable derivatives thereof have a structure given in formula II.



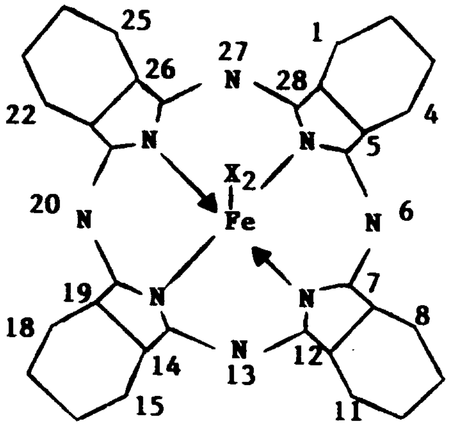
(II)

where X can be alkyl, alkyl carboxy, alkyl hydroxyl, vinyl, alkenyl, alkyl sulfate, alkylsulfonate, sulfate, sulfonate, aryl.

The symbol X^2 of Formula II represents an anion, preferably OH^- or Cl^-.

The symbol X can be alkyl, alkylcarboxy, alkylhydroxyl, vinyl, alkenyl, alkylsulfate, alkylsulfonate, sulfate, sulfonate.

Metallo phthalocyanines and derivatives have the structure indicated in Formula III, wherein the atom positions of the phthalocyanine structure are numbered conventionally. The anionic groups in the above structures contain cations selected from the group consisting of sodium and potassium cations or other non-interfering cations which leave the structures water-soluble. Preferred phthalocyanine derivatives are metallo phthalocyanine trisulfonate and metallo phthalocyanine tetrasulfonate.



(III)

Another form of substitution possible for the present invention is substitution of the central metal by Fe, Mn, Co Rh, Cr, Ru, Mo or other transition metals.

Still a number of considerations are significant in selecting variants of or substituents in the basic porphin or azaporphin structure. In the first place, one would choose compounds which are available or can be readily synthesized.

Beyond this, the choice of the substituent groups can be used to control the solubility of the catalyst in water or in detergent solutions. Yet again, especially where it is desired to avoid attacking dyes attached to solid surfaces, the substituents can control the affinity of the catalyst compound for the surface. Thus, strongly negatively charged substituted compounds, for instance the tetrasulfonated porphin, may be repelled by negatively charged stained surfaces and are therefore most likely not to cause attack on fixed dyes, whereas the cationic or zwitterionic compounds may be attracted to, or at least not repelled by such stained surfaces.

An efficient amount of bleaching agent

The dye transfer inhibiting compositions according to the present invention comprise an efficient amount of bleaching agent.

According to the present invention, an efficient amount of bleach is by definition the necessary amount of bleach which combined with a bleach catalyst leads to a level of dye oxidation which is between 40% to 100%, preferably 40% to 60%, more preferred 60% to 80%, most preferred 80%-100% of the maximum (Z) per cent of dye oxidation that can be achieved under the most optimal conditions determined by those skilled in the art.

The bleaches suitable for the present invention can be activated or non-activated bleaches.

Preferably, the bleaches suitable for the present invention include peroxygen bleaches. Examples of suitable water-soluble solid peroxygen bleaches include hydrogen peroxide releasing agents such as hydrogen peroxide, perborates, e.g. perborate monohydrate, perborate tetrahydrate, persulfates, percarbonates, peroxydisulfates, perphosphates and peroxyhydrates. Preferred bleaches are percarbonates and perborates.

The hydrogen peroxide releasing agents can be used in combination with bleach activators such as tetraacetylethylenediamine (TAED), nonanoyloxybenzenesulfonate (NOBS, described in US 4,412,934),3,5,5-trimethylhexanoloxybenzenesulfonate (ISONOBS, described in EP 120,591), or pentaacetylglucose (PAG), which are perhydrolyzed to form a peracid as the active bleaching species, leading to improved bleaching effect.

The hydrogen peroxide may also be present by adding an enzymatic system (i.e. an enzyme and a substrate therefore) which is capable of generating hydrogen peroxide at the beginning or during the washing and/or rinsing process. Such enzymatic systems are disclosed in EP Patent Application 91202655.6 filed October 9, 1991.

Other peroxygen bleaches suitable for the present invention include organic peroxyacids such as percarboxylic acids.

Test Methods:

For a given catalyst concentration, temperature and pH, the following two test methods can be used to estimate the optimum bleach level that gives the maximum level of dye oxidation, i.e. Z.

(a) In solution dye bleaching:

In a detergent solution, fix the initial concentration of dye (e.g. 40 ppm) and catalyst. Record the absorbance spectrum of this solution Using a UV-Vis spectrophotometer according to procedures known to those skilled in the art. Add a given concentration of bleach (H2O2, oxone, percarbonate, perborate, activated bleach, etc.) and stir the solution containing the dye and catalyst. After stirring for 30 min, record again the absorbance spectrum of the solution. The amount of dye oxidation can then be determined from the change in the absorbance maximum for the dye. Keeping the experimental conditions the same, vary the amount of bleach so as to achieve the maximum dye oxidation.

(b) Reduction of dye transfer from fabric to another fabric

In either a washing machine or launderometer, add a known bleeding fabric and a known uncolored pick-up tracer (e.g. cotton) to the wash load. After simulating a wash cycle, determine the amount of dye that has been picked up by the tracer according to methods known to those skilled in the art. Now to separate washing machines, add the same amount of bleeding fabric and pick-up tracer, a fixed amount of catalyst and vary the bleach level. Determine the level of dye transfer onto the pick-up tracers and vary the amount of bleach as to minimize dye transfer. In this way the most optimal bleach concentration can be determined.

DETERGENT ADJUNCTS

A wide range of surfactants can be used in the detergent compositions. A typical listing of anionic, nonionic, ampholytic and zwitterionic classes, and species 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 C_{12}-C_{18} fatty source preferably from a C_{16}-C_{18} fatty source. In each instance the cation is an alkali 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 C_{14}-$_{15}$ alkyl sulphates. 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.

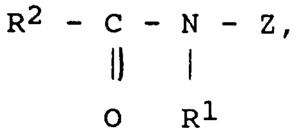
Especially preferred nonionic surfactants of this type are the C_9-C_{15} primary alcohol ethoxylates containing 3-8 moles of ethylene oxide per mole of alcohol, particularly the C_{14}-C_{15} primary alcohols containing 6-8 moles of ethylene oxide per mole of alcohol and the C_{12}-C_{14} primary alcohols containing 3-5 moles of ethylene oxide per mole of alcohol.

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

$$RO\ (C_nH_{2n}O)_tZ_x$$

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



$$R^2 - \underset{\displaystyle \overset{\|}{O}}{C} - \underset{\displaystyle \overset{|}{R^1}}{N} - Z,$$

wherein R^1 is H, or R^1 is 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 alkoxylated derivative thereof. Preferably, R^1 is methyl, R^2 is a straight C_{11-15} 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.

The compositions according to the present invention may further comprise a builder system. Any conventional builder system is suitable for use herein including aluminosilicate materials, silicates, polycarboxylates and fatty acids, materials such as ethylenediamine tetraacetate, metal ion sequestrants such as aminopolyphosphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine pentamethylenephosphonic acid. Though less preferred for obvious environmental reasons, phosphate builders can also be used herein.

Suitable 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 or HS.

Another suitable inorganic builder material is layered silicate, e.g. SKS-6 (Hoechst). SKS-6 is a crystalline layered silicate consisting of sodium silicate ($Na_2Si_2O_5$).

Suitable polycarboxylates 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.

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 phtalic 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.

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.

Especially for the liquid execution herein, suitable fatty acid builders for use herein are saturated or unsaturated C10-18 fatty acids, as well as the corresponding soaps. Preferred saturated species have from 12 to 16 carbon atoms in the alkyl chain. The preferred unsaturated fatty acid is oleic acid.

Preferred builder systems for use in granular compositions include a mixture of a water-insoluble aluminosilicate builder such as zeolite A, and a watersoluble carboxylate chelating agent such as citric acid.

Other builder materials that can form part of the builder system for use in granular compositions include inorganic materials such as alkali metal carbonates, bicarbonates, silicates, and organic materials such as the organic phosphonates, amiono polyalkylene phosphonates and amino polycarboxylates.

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.

Detergency builder salts are normally included in amounts of from 10% to 80% by weight of the composition preferably from 20% to 70% and most usually from 30% to 60% by weight.

Other detergent ingredients that can be included are detersive enzymes which can be included in the detergent formulations for a wide variety of purposes including removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, and prevention of fugitive dye transfer. 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.

Enzymes are normally incorporated at levels sufficient to provide up to about 5 mg by weight, more typically about 0.05 mg to about 3 mg, of active enzyme per gram of the composition.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of B.subtilis and B.licheniformis. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames Alcalase , Savinase and Esperase by Novo Industries A/S (Denmark) and Maxatase and Maxacal by International Bio-Synthetics, Inc. (The Netherlands) and FN-base by Genencor, Optimase and Opticlean by MKC.

Of interest in the category of proteolytic enzymes, especially for liquid detergent compositions, are enzymes referred to herein as Protease A and Protease B. Protease A is described in European Patent Application 130,756. Protease B is described in European Patent Application Serial No. 87303761.8.

Amylases include, for example, α-amylases obtained from a special strain of B.licheniformis, described in more detail in British Patent Specification No. 1,296,839 (Novo). Amylolytic proteins include, for example, Rapidase, Maxamyl (International Bio-Synthetics, Inc.) and Termamyl,(Novo Industries).

The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 11. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, which discloses fungal cellulase produced from Humicola insolens. Suitable cellulases are also disclosed in GB-A-2.075.028 ; GB-A-2.095.275 and DE-OS-2.247.832.

Examples of such cellulases are cellulases produced by a strain of Humicola insolens (Humicola grisea var. thermoidea), particularly the Humicola strain DSM 1800, and cellulases produced by a fungus of Bacillus N or a cellulase 212-producing fungus belonging to the genus Aeromonas, and cellulase extracted from the hepatopancreas of a marine mollusc (Dolabella Auricula Solander).

Other suitable cellulases are cellulases originated from Humicola Insulens having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids. Such cellulase are described in Copending European patent application No. 93200811.3, filed March 19, 1993.

Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 Carezyme (Novo).

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 of 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 Internation Application WO 89/099813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991.

In liquid formulations, an enzyme stabilization system is preferably utilized. Enzyme stabilization techniques for aqueous detergent compositions are well known in the art. For example, one technique for enzyme stabilization in aqueous solutions involves the use of free calcium ions from sources such as calcium acetate, calcium formate and calcium propionate. Calcium ions can be used in combination with short chain carboxylic acid salts, preferably formates. See, for example, U.S. patent 4,318,818. It has also been proposed to use polyols like glycerol and sorbitol. Alkoxy-alcohols, dialkylglycoethers, mixtures of polyvalent alcohols with polyfunctional aliphatic amines (e.g., such as diethanolamine, triethanolamine, di-isopropanolamime, etc.), and boric acid or alkali metal borate. Enzyme stabilization techniques are additionally disclosed and exemplified in U.S. patent 4,261,868, U.S. Patent 3,600,319, and European Patent Application Publication No. 0 199 405, Application No. 86200586.5. Non-boric acid and borate stabilizers are preferred. Enzyme stabilization systems are also described, for example, in U.S. Patents 4,261,868, 3,600,319 and 3,519,570.

Other suitable detergent ingredients that can be added are enzyme oxidation scavengers which are described in Copending European Patent aplication N 92870018.6 filed on January 31, 1992. Examples of such enzyme oxidation scavengers are ethoxylated tetraethylene polyamines.

Especially preferred detergent ingredients are combinations with technologies which also provide a type of color care benefit. Examples of these technologies are polyvinylpyrrolidone polymers and other polymers which have dye transfer inhibiting properties. Other examples are cellulase and/or peroxidases and/or metallo catalysts for color maintance rejuvenation. Such metallo catalysts are described in copending European Patent Application No. 92870181.2.

In addition, it has been found that the polyamine-N-oxide containing polymers eliminate or reduce the deposition of the metallo-catalyst onto the fabrics resulting in improved whiteness benefit.

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.

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. Especially preferred suds controlling agent are the suds suppressor system comprising a mixture of silicone oils and 2-alkyl-alcanols. Suitable 2-alkyl-alcanols are 2-butyl-octanol which are commercially available under the trade name Isofol 12 R.

Such suds suppressor system are described in Copending European Patent application N 92870174.7 filed 10 November, 1992.

Especially preferred silicone suds controlling agents are described in Copending European Patent application N° 92201649.8 Said compositions can comprise a silicone/silica mixture in combination with fumed nonporous silica such as Aerosil^R.

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.

Other components used in detergent compositions may be employed, such as soil-suspending agents, soil-release agents, optical brighteners, fabric softening clays, abrasives, bactericides, tarnish inhibitors, coloring agents, and/or encapsulated or non encapsulated perfumes.

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 $4,4^1$-bis-(2-diethanolamino-4-anilino -s- triazin-6-ylamino)stilbene-$2:2^1$ disulphonate, disodium 4, - 4^1-bis-(2-morpholino-4-anilino-s-triazin-6-ylaminostilbene-$2:2^1$ - disulphonate, disodium $4,4^1$ - bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-$2:2^1$ - disulphonate, monosodium $4^1,4^{11}$ -bis-(2,4-dianilino-s-triazin-6 ylamino)stilbene-2-sulphonate, disodium $4,4^1$ -bis-(2-anilino-4-(N-methyl-N-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-$2,2^1$ - disulphonate, disodium $4,4^1$ -bis-(4-phenyl-2,1,3-triazol-2-yl)-stilbene-$2,2^1$ disulphonate, disodium $4,4^1$bis(2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-$2,2^1$disulphonate and sodium 2(stilbyl-4^{11}-(naphtho-$1^1,2^1$:4,5)-1,2,3 - triazole-2^{11}-sulphonate.

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 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

$$(CH_3(PEG)_{43})_{0.75}(POH)_{0.25}[T\text{-}PO)_{2.8}(T\text{-}PEG)_{0.4}]T(PO\text{-}H)_{0.25}((PEG)_{43}CH_3)_{0.75}$$

where PEG is -$(OC_2H_4)O$-,PO is (OC_3H_6O) and T is $(pcOC_6H_4CO)$.

Also very useful are modified polyesters as random copolymers of dimethyl terephtalate, dimethyl sulfoisophtalate, 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 terephtalic 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 sulfoisophtalic 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.

The detergent compositions according to the invention can be in liquid, paste, gels or granular forms. Granular compositions according to the present invention can also be in "compact form", i.e. they may have a relatively higher density than conventional granular detergents, i.e. from 550 to 950 g/l; in such case, the granular detergent compositions according to the present invention will contain a lower amount of "inorganic filler salt", compared to conventional granular detergents; typical filler salts are alkaline earth metal salts of sulphates and chlorides, typically sodium sulphate; "compact" detergents typically comprise not more than 10% filler salt. The liquid compositions according to the present invention can also be in "concentrated form", in such case, the liquid detergent compositions according to the present invention will contain a lower amount of water,compared to conventional liquid detergents. Typically, the water content of the concentrated liquid detergent is less than 30%, more preferably less than 20%, most preferably less than 10% by weight of the detergent compositions. Other examples of liquid compositions are anhydrous compositions containing substantially no water.

Both aqueous and non-aqueous liquid compositions can be structured or non-structured.

The present invention also relates to a process for inhibiting dye transfer from one fabric to another of solubilized and suspended dyes encountered during fabric laundering operations involving colored fabrics.

The process comprises contacting fabrics with a laundering solution as hereinbefore described.

The process of the invention is conveniently carried out in the course of the washing process. The washing process is preferably carried out at 5 °C to 75 °C, especially 20 to 60, but the polymers are effective at up to 95 °C and higher temperatures. The pH of the treatment solution is preferably from 7 to 11, especially from 7.5 to 10.5.

The process and compositions of the invention can also be used as detergent additive products.

Such additive products are intended to supplement or boost the performance of conventional detergent compositions.

The detergent compositions according to the present invention include compositions which are to be used for cleaning substrates, such as fabrics, fibers, hard surfaces, skin etc., for example hard surface cleaning compositions (with or without abrasives), laundry detergent compositions, automatic and non automatic dishwashing compositions.

The following examples are meant to exemplify compositions of the present invention , but are not necessarily meant to limit or otherwise define the scope of the invention, said scope being determined according to claims which follow.

The stability of the various lipases in the presence of metallo catalysts were measured as follows :

Detergent solutions (6.6 g/l) according to compositions as given in examples I, II or III are adjusted to pH 10.0 and heated to 40 °C after which lipase is added.

The stability of the lipases were determined by measuring the residual activity of the various lipases.

The residual activity is the activity which is measured after 15 minutes and is expressed as a percentage of the activity measured after 30 seconds. The measurements were made by using the pH-stat method. (pH 9/ 40 °C)

Example I :

A granular detergent composition according to the present invention is prepared, having the following compositions :

% by weight of the total detergent composition	
Linear alkyl benzene sulphonate	11.40
Tallow alkyl sulphate	1.80
C_{45} alkyl sulphate	3.00
C_{45} alcohol 7 times ethoxylated	5.00
Tallow alcohol 11 times ethoxylated	2.00
Dispersant	0.07
Silicone fluid	0.80
Trisodium citrate	14.00
Sodium carbonate	3.00
Zeolite	38.00
Maleic acid actylic acid copolymer	5.00
Sodium silicate	2.00
Sodium sulphate	3.50
Mn-Phthalocyanine tetrasulfonated	0.14
Perborate monohydrate	0.60
Savinase 4T®	1.2
H_2O + minors	Balance to 100

Table I

The above composition of table I was supplemented with various lipases.

Example I 1-6

	Residual activity
- Lipolase ®	79%
- Lipase Amano AKG	33%
- Lipase 1, ex Pseudomonas	15%
- Lipase 2, ex Pseudomonas	0%
- Lipase M1 (IBIS)	19%
- Lipase SDL 195 (Showa Denko)	8%

Example II :

A granular detergent composition according to the present invention is prepared, having the following compositions :

% by weight of the total detergent composition	
Linear alkyl benzene sulphonate	11.40
Tallow alkyl sulphate	1.80
C_{45} alkyl sulphate	3.00
C_{45} alcohol 7 times ethoxylated	5.00
Tallow alcohol 11 times ethoxylated	2.00
Dispersant	0.07
Silicone fluid	0.80
Trisodium citrate	14.00
Sodium carbonate	3.00
Zeolite	38.00
Maleic acid actylic acid copolymer	5.00
Sodium silicate	2.00
Sodium sulphate	3.50
Fe tetrasulfonated tetraphenylporphine	0.07
Perborate monohydrate	0.3
Savinase 4T®	1.2
H_2O + minors	Balance to 100

Table II

The above composition of table II was supplemented with various lipases.

Example II 1-2

	Residual activity
- Lipolase ®	88%
- Lipase M1 (IBIS)	18%

Example III :

A granular detergent composition according to the present invention is prepared, having the following compositions :

% by weight of the total detergent composition	
Linear alkyl benzene sulphonate	7.00
Tallow alkyl sulphate	2.00
C_{45} alcohol 7 times ethoxylated	5.00
Tallow alcohol 11 times ethoxylated	2.00
Dispersant	0.07
Silicone fluid	0.80
Trisodium citrate	6.00
Sodium carbonate	15.00
Zeolite	20.00
Maleic acid actylic acid copolymer	5.00
Sodium silicate	2.00
Sodium sulphate	3.50
Mn-Phthalocyanine tetrasulfonated	0.14
Perborate monohydrate	16
TAED	5
Savinase 4T®	1.8
H_2O + minors	Balance to 100

Table III

The above composition of table III was supplemented with various lipases.

Example III 1-2

	Residual activity
- Lipolase ®	91%
- Lipase M1 (IBIS)	6%

EXAMPLE IV (A/B/C)

A liquid detergent composition according to the present invention is prepared, having the following compositions :

% by weight of the total detergent composition			
	A	B	C
Linear alkylbenzene sulfonate	10	-	-
Polyhydroxy fatty acid amide	-	9	-
Alkyl alkoxylated sulfate	-	-	9
Alkyl sulphate	4	4	4
Fatty alcohol (C_{12}-C_{15}) ethoxylate	12	12	12
Fatty acid	10	10	10
Oleic acid	4	4	4
Citric acid	1	1	1
Diethylenetriaminepentamethylene Phosphonic acid	1.5	1.5	1.5
NaOH	3.4	3.4	3.4
Propanediol	1.5	1.5	1.5
Ethanol	10	10	10
Ethoxylated tetraethylene pentamine	0.7	0.7	0.7
Termamyl® 300 KNU/g	0.1	0.1	0.1
Carezyme® 5000 CEVU/g	0.02	0.02	0.02
Protease 40 mg/g	1.8	1.8	1.8
Lipolase® 100 KLU/g	0.14	0.14	0.14
Endoglucanase A 5000 CEVU/g	0.4	0.4	0.4
Suds supressor (ISOFOL^r)	2.5	2.5	2.5
H_2O_2	7.5	7.5	7.5
Metallo catalyst	0.1	0.1	0.1
Minors	up to 100		

EXAMPLE V (A/B/C)

A compact granular detergent composition according to the present invention is prepared, having the following formulation:

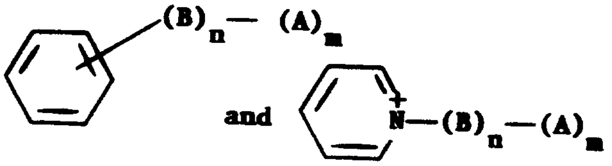
% by weight of the total detergent composition				
	A	B	C	D
Linear alkyl benzene sulphonate	11.40	-	-	-
Polyhydroxy fatty acid amide	-	10	-	-
Alkyl alkoxylated sulfate	-	-	9	-
Tallow alkyl sulphate	1.80	1.80	1.80	1.80
C_{45} alkyl sulphate	3.00	3.00	3.00	3.00
C_{45} alcohol 7 times ethoxylated	4.00	4.00	4.00	4.00
Tallow alcohol 11 times ethoxylated	1.80	1.80	1.80	1.80
Dispersant	0.07	0.07	0.07	0.07
Silicone fluid	0.80	0.80	0.80	0.80
Trisodium citrate	14.00	14.00	14.00	14.00
Citric acid	3.00	3.00	3.00	3.00
Zeolite	32.50	32.50	32.50	32.50
Maleic acid acrylic acid copolymer	5.00	5.00	5.00	5.00
Cellulase (active protein)	0.03	0.03	0.03	0.03
Savinase 4T®	0.60	0.60	0.60	0.60
Lipolase® 100T	0.36	0.36	0.36	0.36
Sodium silicate	2.00	2.00	2.00	2.00
Sodium sulphate	3.50	3.50	3.50	3.50
Metallo catalyst	0.1	0.1	0.1	0.1
Percarbonate			15	10
Perborate	15	15	-	-
TAED	5	-	5	-
H_2O + Minors	up to 100			

The above compositions (Example IV (A/B/C) and V (A/B/C/D)) were very good at displaying excellent cleaning and detergency performance with outstanding color-care performance on colored fabrics and mixed loads of colored and white fabrics.

Claims

1. A dye transfer inhibiting composition comprising:
    A. a metallo catalyst selected from
        a) metallo porphin and water-soluble or water-dispersable derivatives thereof;
        b) metallo porphyrin and water-soluble or water-dispersable derivatives thereof;
        c) metallo phthalocyanine and water-soluble or water-dispersable derivatives thereof;
    B. an efficient amount of a bleaching agent.
    C. a lipolytic enzyme which is characterized in that the aminoacid sequence contains no methionine.

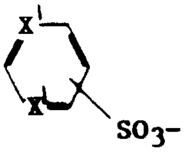
2. A dye transfer inhibiting composition according to claim 1 containing a metallo porphin derivative, wherein said porphin is substituted on at least one of its meso positions with a phenyl or pyridyl substituent selected from the group consisting of



wherein n and m may be 0 or 1, A is selected from the water-solubilizing group, e.g., sulfate, sulfonate, phosphate, and carboxylate groups, and B is selected from the group consisting of C_1-C_{10} alkyl, C_1-C_{10} polyethoxyalkyl and C_1-C_{10} hydroxyalkyl.

3. A dye transfer inhibiting composition according to claim 2 wherein the substituents on the phenyl or pyridyl groups are selected from the group consisitng of $-CH_3$, $-C_2H_5$, $-CH_2CH_2CH_2SO_3-$, $-CH_2COO-$, $-CH_2C-H(OH)CH_2SO_3-$, and $-SO_3$.

4. A dye transfer inhibiting composition according to claims 1-3, containing a metallo porphin derivative, wherein said metallo porphin is substituted on at least one of its meso positions with a phenyl substituent selected from the group consisting of



wherein X^1 is (=CY-) wherein each Y, independently, is hydrogen, chlorine, bromine or meso substituted alkyl, cycloalkyl, aralkyl, aryl, alkaryl or heteroaryl.

5. A dye transfer inhibiting composition according to claim 1 wherein the central atom is selected from Fe, Mn, Co, Rh, Cr, Ru, Mo or other transition metals.

6. A dye transfer inhibiting composition according to claims 1-5 wherein said lipase is a fungal lipase producible by Humicola lanuginosa.

7. A dye transfer inhibiting composition according to claims 1-6 wherein said lipase is producible by a host organism in which the DNA encoding for the lipase has been cloned and expressed.

8. A dye transfer inhibiting composition according to claims 7 wherein the lipase is producible by the host organism Aspergillus

9. A dye transfer inhibiting composition according to 8 wherein the host organism is Aspergillus oryzae.

10. A dye transfer inhibiting composition according to claim 6 wherein said lipase is Lipolase.

11. A dye transfer inhibiting composition according to claims 1-10 wherein said lipase is a lipase which shows a positive immunological cross-reaction with the antibody of said lipase.

12. A dye transfer inhibiting composition according to claim 1-11 wherein the wash concentration of metallo catalyst is from 10^{-8} to 10^{-3} molar, preferably from 10^{-6} to 10^{-4} molar.

13. A dye transfer inhibiting composition according to claims 1-12 wherein the lipolytic activity is from 10 to 10000 LU/g of the composition

14. A dye transfer inhibiting composition according to claim 1-13 wherein the bleaching agent is selected from an activated or a non-activated bleach.

15. A dye transfer inhibiting composition according to claims 1-14 which is a detergent additive, in the form of a non-dusting granule or a liquid.

16. A detergent composition which comprises a dye transfer inhibiting composition according to any of the preceding claims further comprising surfactants, builders, and other conventional detergent ingredients.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 87 0149

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
A	US-A-4 077 768 (J. P. JOHNSTON ET. AL.) * column 1, line 57 - column 6, line 35 *	1-5,12, 14-16	C11D3/00 C11D3/386 C11D3/39
A	EP-A-0 538 228 (THE PROCTER & GAMBLE COMPANY) * page 2, line 50 - page 5, line 25 *	1-5,12, 14-16	
A	EP-A-0 384 503 (UNILEVER NV ET AL) * page 2, line 1 - page 6, line 29 *	1-5, 14-16	
A	EP-A-0 271 152 (UNILEVER NV ET AL) * page 2, line 9 - page 7, line 30 *	1,6,7, 11,14-16	
A	HAPPI vol. 28, no. 10 , October 1991 , RAMSEY NJ, USA E. GORMSEN ET AL 'A NEW LIPASE FOR THE DETERGENT INDUSTRY' * page 122 * * page 124 - page 125 *	1,6-11	**TECHNICAL FIELDS SEARCHED (Int.Cl.5)** C11D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10 August 1994	Doolan, G

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document