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(54) **DETERGENT COMPOSITION**

REINIGUNGSMITTELZUSAMMENSETZUNG

COMPOSITION DETERGENTE

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(56) References cited:
EP-A- 0 523 956 **EP-A- 0 659 877**
WO-A-96/03486

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EP 0 901 512 B1

Description**Technical Field**

5 **[0001]** The present invention relates to fabric washing detergent compositions. In particular, the invention relates to fabric washing detergent compositions containing photofading inhibitors.

Background and prior art

10 **[0002]** The fading of coloured articles by sunlight is a major consumer problem in many parts of the world. Thus susceptible articles from temperate and low latitude regions in addition to those from the tropics can be severely faded during wear or whilst drying. Sun fading of fabrics is of specific concern to consumers because the contrast between exposed and unexposed areas makes it particularly noticeable. e.g on collars, inside versus outside of garments, and on wrap around garments such as saris.

15 **[0003]** The use of certain sunscreens has already been discussed in the literature. US 4 788 054 (Bernhardt) teaches the use of N-phenylphthalisomides as ultraviolet radiation absorbers for cotton, wool, polyester and rayon. The compositions require an aqueous sulphuric acid vehicle for deposition. Fabric care compositions comprising a water dispersible / water soluble copolymers which prevent photofading are disclosed in EP 0 523 956 (Unilever).

20 **[0004]** US 5 474 691 (Severns) also discloses the use of a tumble drier sheet to transfer photofading inhibitors to fabrics.

[0005] None of these systems is suitable for delivering photofading inhibitors to the fabric surface during washing.

[0006] However the major problem that needs to be overcome is how to deposit photofading inhibitors onto fabric during the wash using a detergent containing washing system, which is designed to suspend particulate materials and solubilise oils.

25 **[0007]** The present invention addresses these problems, and relates to an improved method of depositing photofading inhibitors to fabrics during the washing process. In addition the present invention also relates to a method of improving the perfume delivery of compositions.

Definition of the Invention

30 **[0008]** Thus according to one aspect of the invention there is provided a detergent composition comprising:

- i) a nonionic detergent surfactant;
- ii) a cationic quaternary ammonium compound material;
- 35 iii) a liquid photofading inhibitor having a log P value of at least 1.9 or a solid photofading inhibitor dissolved in a liquid the liquid having a log P of at least 1.9 or mixtures thereof; and
- iv) optionally, an anionic surfactant;

40 wherein the ratio of (i) nonionic surfactant to (ii) cationic material at least 1:1 by weight and in which (if anionic surfactant (iv) is present), the ratio of (ii) cationic material to (iv) anionic surfactant is at least 1:1, preferably at least 2:1 by weight.

[0009] The invention further relates to the use of a detergent composition as described above for the deposition of a photofading inhibitor onto a fabric.

Detailed Description of the Invention**The Photofading Inhibitor**

45 **[0010]** Without being bound by theory it is thought that the extent of individual dye fading is dependent on the light wavelength. Some dyes are photodegraded primarily by the UV component of solar radiation, for other dyes the visible component of solar radiation is the main cause of colour loss, whilst others are equally affected by both visible and UV radiation. Thus, in order to minimise photofading across the mix of dyes encountered in the home, it is essential to protect articles from the whole solar spectrum.

50 **[0011]** Protection against solar radiation can be achieved with UVA and UVB absorbing materials with high extinction coefficients. These compounds are commonly called sunscreens. However, the use of such materials is preferably limited for protection against UV radiation with a wavelength of 400nm or below as compounds with the whole or part of their spectra above 400nm will be coloured.

55 **[0012]** Protection from visible radiation with a wavelength of 400nm or greater is preferably achieved by using singlet oxygen quenchers, free radical traps and anti-oxidants.

[0013] It is therefore advantageous to deliver to the fabric surface both UV sunscreens and materials that will protect dyes from visible radiation and thus mixtures of sunscreens and antioxidants, singlet oxygen quenchers or free radical traps are used..

[0014] If liquid, the photofading inhibitors must have a log P value of at least 1.9, more preferably of at least 2.5, most preferably greater than 3.5.

[0015] If solid the photofading inhibitor must be dispersed in a liquid, the liquid having a log P value of at least 1.9, more preferably of at least 2.5, most preferably greater than 3.5. It is also beneficial if the liquid in which the solid photofading inhibitor is to be dissolved is immiscible in water or only sparingly soluble. By sparingly soluble a solubility of no more than 0.04 moles/litre is meant.

[0016] Log P is the octanol/water partition coefficient and can be used to measure the hydrophobicity of a molecule. Log P is determined experimentally. The procedure is described in Chemical Reviews Volume 71, number 5, pages 52-5-616(1971).

[0017] It is preferred that the photofading inhibitor or photofading inhibitor mixture is present at levels from 0.01 wt% to 10 wt% of the total weight of the composition. The more preferred level of sunscreen is from 0.025 wt% to 2.5 wt%, and most preferably 0.05 wt% to 0.5 wt%.

The Sunscreen

[0018] In the context of this invention a sunscreen is described as any material which absorbs UVA or UVB radiation. It is advantageous if the sunscreens have a molar extinction coefficient (E) of greater than $2,000 \text{ mol}^{-1} \text{ cm}^{-1}$.

[0019] The International Commission on Illumination (CIE) in 1970 defined the UV wavelength subdivisions as:-

UVA	315-400nm
UVB	280-315nm
UVC	100-280nm

[0020] The sunscreen can be an oily liquid with a logP of at least 1.9 or a solid organic material that can be dissolved in a water immiscible or sparingly water soluble liquid, the liquid having a logP of greater than 1.9.

[0021] Preferably the sunscreen absorbs light at a wavelength from about 280-400nm.

[0022] Suitable sunscreens are described in:

N.A. Saath, Cosmetics and Toiletries Vol 102 March 1987 page 21-39 Classifications given as table 2 on page 22,; N.A. Saath, Evolution of modern sunscreen chemicals pages 3-35; Cosmetics and Toiletries Vol 107 March 1992. Sunscreen use in cosmetic formulas, pages 45-47; Ultra violet absorbers by S.B. Miller, G.R. Lappin, and C.E. Tholstrup in 1968-1969 Modern Plastics Encyclopedia, pages 442-447 and; G.R. Lappin, Encyclopedia of polymer science and technology, vol 14, pages 125-148, Ultra violet radiation absorbers.

[0023] Examples of typical sunscreens but not meant to be exclusive are:

Cinnamates

[0024]

2-Ethylhexyl-4-methoxy cinnamate (Parsol MCX)

2-Ethoxyethyl-4-methoxy cinnamate

Propyl-4-methoxy cinnamate

i-Amyl-4-methoxy cinnamate

Cyclohexyl-4-methoxy cinnamate

i-Propyl-4-methoxy cinnamate

Octyl cinnamate

Ethyl-4-iso-propyl cinnamate

Ethyl-di-iso-propyl cinnamate and methyl ester

Ethyl-a-cyano-b-phenyl cinnamate

2-Ethylhexyl-a-cyano-b-phenyl-cinnamate

Salicylates**[0025]**

- 5 2-Ethylhexyl salicylate (Sunarome WMO)
 3,3,5-Trimethyl cyclohexyl-2-hydroxy benzoate
 3,3,5-Trimethyl cyclohexyl-2-acetamido benzoate
 2-Ethylhexyl-2-(4-phenylbenzoyl)benzoate
 4-Isopropylbenzyl salicylate
 10 Amyl salicylate
 Menthyl salicylate
 Homomenthyl salicylate
 Phenyl salicylate
 Benzyl salicylate
 15 i-Decyl salicylate

Aminobenzoates**[0026]**

- 20 Ethyl 4-bis(hydroxypropyl)amino benzoate (Amerscheen P)
 2,3-Dihydroxypropyl-4-amino benzoate (Nipa GMPA)
 Menthyl-2-aminobenzoate (Sunarome UVA)
 2-Ethylhexyl-4-dimethylamino benzoate (Escalol 507)
 25 Amyl-4-dimethylamino benzoate
 Ethyl-4-dimethylaminobenzoate
 Butyl-4-dimethylaminobenzoate
 4-bis(polyethoxy)-4-aminobenzoic acid polyethoxyethyl ester (Uvinul P-25)
 N-propoxylated ethyl-4-amino benzoate
 30

Benzophenones**[0027]**

- 35 2-hydroxy-4-methoxy benzophenone (Uvinul M40)
 2,2'-Dihydroxy-4-methoxybenzophenone (Spectra-Sorb UV-24)
 2,4-Dihydroxybenzophenone (Uvinul 400)
 2,2',4,4'-Tetrahydroxybenzophenone (Uvinul D-50)
 2,2'-Dihydroxy-4,4'-dimethoxybenzophenone (Uvinul D-49)
 40 2-Hydroxy-4-(2-ethylhexyloxy)benzophenone (Uvinul408)
 2-Hydroxy-4-methoxy-4'-methylbenzophenone (Mexenone)
 4-Phenyl-benzophenone
 2-Ethylhexyl-4'-phenyl-benzophenone-2-carboxylate 2-Hydroxy-4-n-octoxybenzophenone
 2-Hydroxy-3-carboxybenzophenone
 45

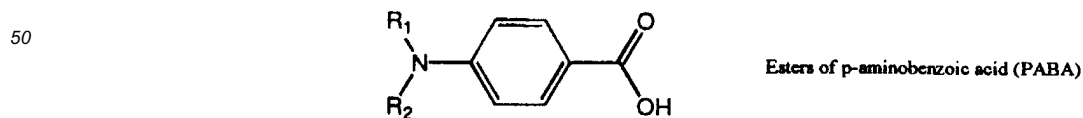
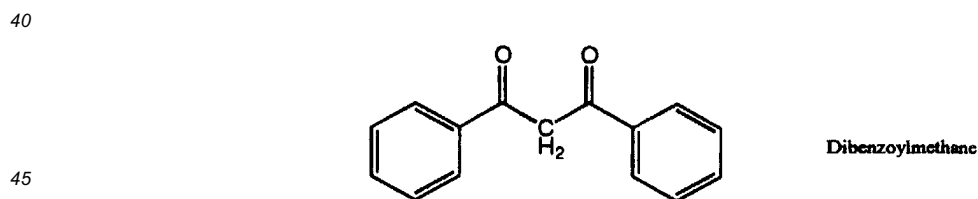
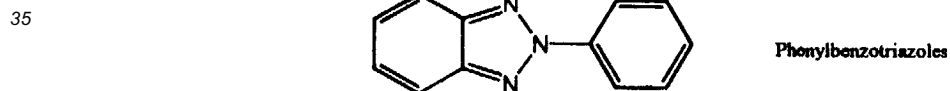
Acrylates**[0028]**

- 50 2-Ethylhexyl-2-cyano-3,3'-diphenylacrylate (Uvinul N-539)
 Ethyl-2-cyano-3,3'-diphenylacrylate (Uvinul N-35)
 3-Imidazol-4yl acrylic acid and ethyl ester
 2-Cyano-3-(4-methoxyphenyl)acrylate and hexyl ester
 55

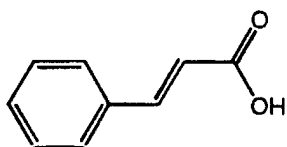
Dibenzoylmethanes**[0029]**

- 5 1-(4-Isopropyl phenyl)-3-phenyl propan-1,3-dione (Eusolex 8020)
 1-(4-t-Butylphenyl)-3-(4-methoxyphenyl)propan-1,3-dione
 1,3-bis(4-Methoxyphenyl)propane-1,3-dione
- 10 3-(4-Methylbenzylidene)-bornan-2-one (Eusolex 6300)
 5-(3,3-Dimethyl-2-norbonylidene)-3-penten-2-one
 3-Benzylidene bornan-2-one
 Digalloyl trioleate
 2-Hydroxy-1,4-naphthalenedione
 5-Methyl-2-phenylbenzoxazole
- 15 2,4,6-Trianiino-4-(carbo-2'-ethylhexyl-1'-oxy)-1,3,5-triazine (Uvinul T-150)
 2,2'-hydroxy-5-methylphenyl-benzotriazol
 2,2'-hydroxy-5-t-octylphenyl-benzotriazol
 Dibenzaldehydeamine
 Dianisoyl methane
- 20 Methyl eugenol
 2-Amino-6-hydroxypurin
 N-(4-Ethoxycarbonylphenyl)-N'-methyl-N'-phenylformamidine (Givosorb UV1)
 N-(4-Ethoxycarbonylphenyl)-N'-ethyl-N'-phenylformamidine (Givosorb UV2)
- 25 2-(2H-benzotriazol-2-yl)-4-methylphenol (Tinuvin P)
 2-(6-Chloro-2H-benzotriazol-2-yl)-4-methyl-6-t-butyl phenol (Tinuvin 326)
 2-(6-Chloro-2H-benzotriazol-2-yl)-4,6-di-t-butyl phenol (Tinuvin 327)
 2-(2H-benzotriazol-2-yl)-4,6-di-t-pentyl phenol (Tinuvin 328)
 3-(4'-Methylbenzylidene)-Camphor

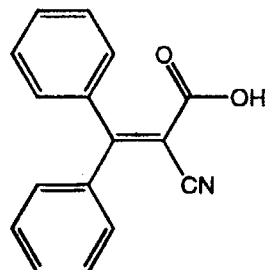
- 30 **[0030]** Preferred sunscreen compounds contain at least one chromophore selected from the following groups and mixtures thereof.



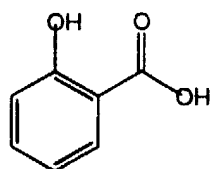
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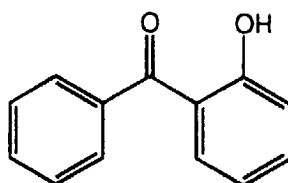
Esters of cinnamic acid



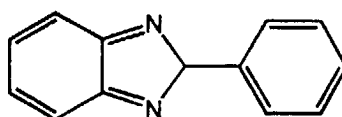
Esters of 2-cyano 3- diphenyl 2-propanoic acid



Esters of salicylic acid



2-Hydroxybenzophenones

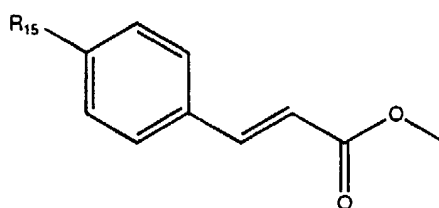
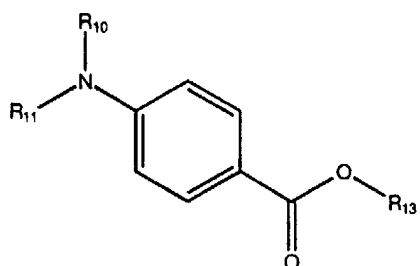
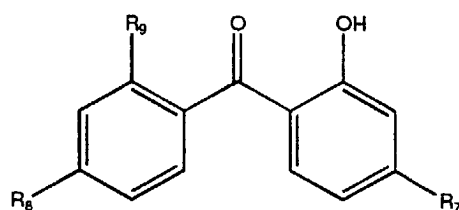
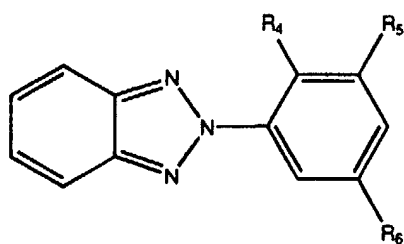


Phenylbenzimidazole

[0031] Wherein R1 and R2 is a hydrogen, methyl, ethyl, C₁-C₂₂ branched or straight chain alkyl group; and mixtures thereof, preferably a methyl group.

[0032] Preferably the sunscreen compound containing at least one chromophore is selected from the group consisting of phenylbenzotriazoles, esters of cinnamic acid, benzophenones, esters of para aminobenzoic acid, esters of salicylic acid, dibenzoyl methane and mixtures thereof.

[0033] Most preferably the sunscreen is selected from the following groups and mixtures thereof.



[0034] Where R_4 is a hydrogen, a hydroxy group, a C_1 - C_{22} alkyl group, preferably a hydrogen or a hydroxy group and most preferably a hydroxy group.

[0035] Where R_5 is a hydrogen, a hydroxy group, a C_1 - C_{22} alkyl group, more preferably a C_1 - C_8 alkyl group and most preferably a tertiary amyl group or tertiary butyl group.

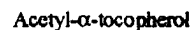
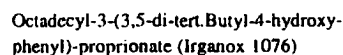
[0036] Where R_6 is a hydrogen, a hydroxy group, a C_1 - C_{22} alkyl group, more preferably a C_1 - C_8 alkyl group and most preferably a tertiary amyl group or tertiary butyl group.

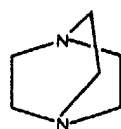
An example where R_4 is hydroxyl and R_5 and R_6 are tertiary amyl groups is the commercial sunscreen Tinuvin 328, and where R_4 is hydroxyl and R_5 and R_6 are tertiary butyl groups is Tinuvin 327. Both these sunscreens are manufactured by Ciba.

The antioxidants, singlet oxygen quenchers or free radical trap

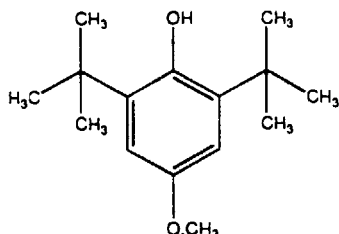
[0046] Examples of anti-oxidants meeting these requirements can be found in Kirk-Othmer Encyclopaedia of Chemical Technology, fourth edition, volume 3, pages 424-447.

[0048] Preferred materials include

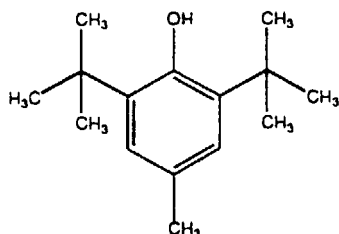




Diazobicyclo[2.2.2]octane



2,6-di-tert.-butyl-4-methoxyphenol



2,6-di-tert.-butyl-4-methylphenol

The nonionic surfactant

[0049] The composition of the invention requires the presence of a nonionic surfactant.

[0050] Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C8-C20 aliphatic alcohols ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C10-C15 primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkylpolyglycosides, glycerol monoethers, and polyhydroxyamides (glucamide).

[0051] It is preferred if the level of nonionic surfactant is from 2 wt% to 40 wt%, preferably from 10 wt% to 30 wt% of the total product.

[0052] The choice of detergent-active compound (surfactant), and the amount present, will depend on the intended use of the detergent composition. In fabric washing compositions, different surfactant systems may be chosen, as is well known to the skilled formulator, for handwashing products and for products intended for use in different types of washing machine.

The Anionic Surfactant

[0053] Although an anionic surfactant may be present in compositions of the invention it is preferred if it is absent.

[0054] If present it is preferred if the ratio of cationic material to anionic material is at least 2:1.

[0055] If present suitable anionic surfactants are well-known to those skilled in the art and include alkylbenzene sulphonate primary and secondary alkyl sulphates, particularly C₈-C₁₅ primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulphosuccinates; ethercarboxylates; isothionates; sarcosinates and fatty acid ester sulphonates, Sodium salts are generally preferred.

[0056] Detergent compositions suitable for use in most automatic fabric washing machines generally contain anionic non-soap surfactant, or nonionic surfactant, or combinations of the two in any ratio, optionally together with soap.

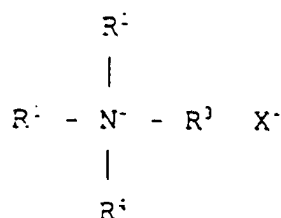
[0057] For compositions in solid form, especially powder, the detergent surfactant is advantageously solid at room temperature as this provides crisp composition particles.

The Cationic Compound

[0058] The compositions of the invention must contain a quaternary ammonium compound cationic compound.

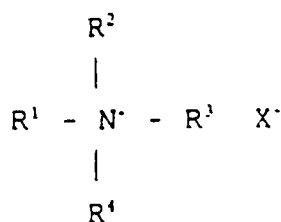
[0059] It is advantageous if the quaternary ammonium compound is a quaternary ammonium compound having at least one C₁₂-C₂₂ alkyl chain.

[0060] It is preferred if the quaternary ammonium compound has the following formula:



in which R¹ is a C₁₂ to C₂₂ alkyl or alkenyl chain, R², R³ and R⁴ are independently selected from C₁-C₄ alkyl chains and X⁻ is a compatible anion. A preferred compound of this type is the quaternary ammonium compound cetyl trimethyl quaternary ammonium bromide.

[0061] A second class of materials for use with the present invention are the quaternary ammonium compound having the following formula:



in which R¹ and R² are independently selected from C₁₂ to C₂₂ alkyl or alkenyl chain; R³ and R⁴ are independently selected from C₁-C₄ alkyl chains and X⁻ is compatible anion.

[0062] Other suitable quaternary ammonium compounds are disclosed in EP 0 239 910 (Procter and Gamble).

[0063] It is preferred if the ratio of cationic to nonionic surfactant is from 1:100 to 50:50, more preferably 1:50 to 20:50.

[0064] The cationic compound may be present from 0.02 wt% to 20 wt% of the total weight of the composition.

[0065] Preferably the cationic compound may be present from 0.05 wt% to 15 wt%, a more preferred composition range is from 0.2 wt% to 5 wt%, and most preferably the composition range is from 0.4 wt% to 2.5 wt% of the total weight of the composition.

[0066] If the product is a liquid it is preferred if the level of cationic surfactant is from 0.05wt% to 10wt% of the total weight of the composition. Preferably the cationic compound may be present from 0.2wt% to 5 wt%, and most preferably from 0.4 wt% to 2.5 wt% of the total weight of the composition.

[0067] If the product is a solid it is preferred if the level of cationic surfactant is 0.05 wt% to 15 wt% of the total weight of the composition. A more preferred composition range is from 0.2 wt% to 10 wt%, and the most preferred composition range is from 0.9 wt% to 3.0 wt% of the total weight of the composition.

Detergency Builder

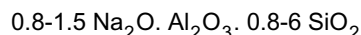
[0068] The detergent compositions of the invention will generally also contain one or more detergency builders. The total amount of detergency builder in the compositions will suitably range from 5 to 80 wt%, preferably from 10 to 60 wt%.

[0069] Inorganic builders that may be present include sodium carbonate, if desired in combination with a crystallisation seed for calcium carbonate, as disclosed in GB 1 437 950 (Unilever); crystalline and amorphous aluminosilicates, for example, zeolites as disclosed in GB 1 473 201 (Henkel), amorphous aluminosilicates as disclosed in GB 1 473 202 (Henkel) and mixed crystalline/amorphous aluminosilicates as disclosed in GB 1 470 250 (Procter & Gamble); and layered silicates as disclosed in EP 164 514B (Hoechst). Inorganic phosphate builders, for example, sodium ortho-

phosphate, pyrophosphate and tripolyphosphate are also suitable for use with this invention.

[0070] The detergent compositions of the invention preferably contain an alkali metal, preferably sodium, aluminosilicate builder. Sodium aluminosilicates may generally be incorporated in amounts of from 10 to 70% by weight (anhydrous basis), preferably from 25 to 50 wt%.

[0071] The alkali metal aluminosilicate may be either crystalline or amorphous or mixtures thereof, having the general formula:



[0072] These materials contain some bound water and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO₂ units (in the formula above). Both the amorphous and the crystalline materials can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply described in the literature.

[0073] Suitable crystalline sodium aluminosilicate ion-exchange detergency builders are described, for example, in GB 1 429 143 (Procter & Gamble). The preferred sodium aluminosilicates of this type are the well-known commercially available zeolites A and X, and mixtures thereof.

[0074] The zeolite may be the commercially available zeolite 4A now widely used in laundry detergent powders. However, according to a preferred embodiment of the invention, the zeolite builder incorporated in the compositions of the invention is maximum aluminium zeolite P (zeolite MAP) as described and claimed in EP 384 070A (Unilever). Zeolite MAP is defined as an alkali metal aluminosilicate of the zeolite P type having a silicon to aluminium ratio not exceeding 1.33, preferably within the range of from 0.90 to 1.33, and more preferably within the range of from 0.90 to 1.20.

[0075] Especially preferred is zeolite MAP having a silicon to aluminium ratio not exceeding 1.07, more preferably about 1.00. The calcium binding capacity of zeolite MAP is generally at least 150 mg CaO per g of anhydrous material.

[0076] Organic builders that may be present include polycarboxylate polymers such as polyacrylates, acrylic/maleic copolymers, and acrylic phosphinates; monomeric polycarboxylates such as citrates, gluconates, oxydisuccinates, glycerol mono-, di- and trisuccinates, carboxymethyloxysuccinates, carboxymethyloxymalonates, dipicolinates, hydroxyethyliminodiacetates, alkyl- and alkenylmalonates and succinates; and sulphonated fatty acid salts. This list is not intended to be exhaustive.

[0077] Especially preferred organic builders are citrates, suitably used in amounts of from 5 to 30 wt%, preferably from 10 to 25 wt%; and acrylic polymers, more especially acrylic/maleic copolymers, suitably used in amounts of from 0.5 to 15 wt%, preferably from 1 to 10 wt%.

[0078] Builders, both inorganic and organic, are preferably present in alkali metal salt, especially sodium salt, form.

Bleach Components

[0079] Detergent compositions according to the invention may also suitably contain a bleach system. Fabric washing compositions may desirably contain peroxy bleach compounds, for example, inorganic persalts or organic peroxyacids, capable of yielding hydrogen peroxide in aqueous solution.

[0080] Suitable peroxy bleach compounds include organic peroxides such as urea peroxide, and inorganic persalts such as the alkali metal perborates, percarbonates, perphosphates, persilicates and persulphates. Preferred inorganic persalts are sodium perborate monohydrate and tetrahydrate, and sodium percarbonate.

[0081] Especially preferred is sodium percarbonate having a protective coating against destabilisation by moisture. Sodium percarbonate having a protective coating comprising sodium metaborate and sodium silicate is disclosed in GB 2 123 044B (Kao).

[0082] The peroxy bleach compound is suitably present in an amount of from 0.1 to 35 wt%, preferably from 0.5 to 25 wt%.

[0083] The peroxy bleach compound may be used in conjunction with a bleach activator (bleach precursor) to improve bleaching action at low wash temperatures. The bleach precursor is suitably present in an amount of from 0.1 to 8 wt%, preferably from 0.5 to 5 wt%.

[0084] Preferred bleach precursors are peroxycarboxylic acid precursors, more especially peracetic acid precursors and pernoanoic acid precursors. Especially preferred bleach precursors suitable for use in the present invention are N,N,N',N'-tetracetyl ethylenediamine (TAED) and sodium noanoyloxybenzene sulphonate (SNOBS). The novel quaternary ammonium and phosphonium bleach precursors disclosed in US 4 751 015 and US 4 818 426 (Lever Brothers Company) and EP 402 971A (Unilever), and the cationic bleach precursors disclosed in EP 284 292A and EP 303 520A (Kao) are also of interest.

[0085] The bleach system can be either supplemented with or replaced by a peroxyacid. Examples of such peracids

can be found in US 4 686 063 and US 5 397 501 (patent on TPCAP - Unilever). A preferred example is the imido peroxy-carboxylic class of peracids described in EP A 325 288, EP A 349 940, DE 382 3172 and EP 325 289. A particularly preferred example is phthalimido peroxy caproic acid (PAP). Such peracids are suitably present at 0.1 - 12%, preferably 0.5 - 10%.

[0086] A bleach stabiliser (heavy metal sequestrant) may also be present. Suitable bleach stabilisers include ethylenediamine tetraacetate (EDTA), the polyphosphonates such as Dequest (Trade Mark) and non-phosphate stabilisers such as EDDS (ethylene diamine di-succinic acid). These Bleach stabilisers are also useful for stain removal, especially in products containing low levels of bleaching species or no bleaching species.

[0087] An especially preferred bleach system comprises a peroxy bleach compound (preferably sodium percarbonate optionally together with a bleach activator), and a transition metal bleach catalyst as described and claimed in EP 458 397A, EP 458 398A and EP 509 787A (Unilever).

The Enzyme

[0088] Suitable enzymes include the proteases, amylases, cellulases, oxidases, peroxidases and lipases usable for incorporation in detergent compositions.

[0089] Preferred proteolytic enzymes (proteases) are, catalytically active protein materials which degrade or alter protein types of stains when present as in fabric stains in a hydrolysis reaction. They may be of any suitable origin, such as vegetable, animal, bacterial or yeast origin.

[0090] Proteolytic enzymes or proteases of various qualities and origins and having activity in various pH ranges of from 4-12 are available and can be used in the instant invention. Examples of suitable proteolytic enzymes are the subtilisins, which are obtained from particular strains of *B. subtilis* and *B. licheniformis*, such as the commercially available subtilisins Maxatase (Trade Mark), as supplied by Gist-Brocades N.V., Delft, Holland, and Alcalase (Trade Mark), as supplied by Novo Industri A/S, Copenhagen, Denmark.

[0091] Particularly suitable is a protease obtained from a strain of *Bacillus* having maximum activity throughout the pH range of 8-12, being commercially available, e.g. from Novo Industri A/S under the registered trade-names Esperase (Trade Mark) and Savinase (Trade-Mark). The preparation of these and analogous enzymes is described in GB 1 243 785. Other commercial proteases are Kazusase (Trade Mark) (obtainable from Showa-Denko of Japan), Optimase (Trade Mark) (from Miles Kali-Chemie, Hannover, West Germany), and Superase (Trade Mark) (obtainable from Pfizer of U.S.A.).

[0092] Detergency enzymes are commonly employed in granular form in amounts of from about 0.1 to about 3.0 wt%.

Perfumes

[0093] Any perfume is suitable for use with the present invention. However we have found that the presence of a photofading inhibitor aids the deposition of perfume, this affect is especially pronounced with non-volatile perfume ingredients. The converse of this is also true, in that the presence of perfume aids the deposition of the photofading inhibitor.

Other ingredients

[0094] The compositions of the invention may contain alkali metal, preferably sodium carbonate, in order to increase detergency and ease processing. Sodium carbonate may suitably be present in amounts ranging from 1 to 60 wt%, preferably from 2 to 40 wt%. However, compositions containing little or no sodium carbonate are also within the scope of the invention.

[0095] Powder flow may be improved by the incorporation of a small amount of a powder structurant, for example, a fatty acid (or fatty acid soap), a sugar, an acrylate or acrylate/maleate polymer, or sodium silicate.

[0096] One preferred powder structurant is fatty acid soap, suitably present in an amount of from 1 to 5 wt%.

[0097] Other materials that may be present in detergent compositions of the invention include sodium silicate; antire-deposition agents such as cellulosic polymers; inorganic salts such as sodium sulphate; lather control agents or lather boosters as appropriate; proteolytic and lipolytic enzymes; dyes; coloured speckles; foam controllers; fabric softening compounds, soil release polymers, fluorescers and decoupling polymers. This list is not intended to be exhaustive.

[0098] The detergent composition when diluted in the wash liquor (during a typical wash cycle) will give a pH of the wash liquor from 7 to 10.5.

[0099] The detergent components of the present invention may be incorporated in detergent compositions of all physical types, for example, powders, liquids, gels and solid bars.

[0100] Detergent compositions of the invention may be prepared by any suitable method.

[0101] Particulate detergent compositions are suitably prepared by spray-drying a slurry of compatible heat-insen-

sitive ingredients, and then spraying on or postdosing those ingredients unsuitable for processing via the slurry. The skilled detergent formulator will have no difficulty in deciding which ingredients should be included in the slurry and which should not.

[0102] Particulate detergent compositions of the invention preferably have a bulk density of at least 400 g/l, more preferably at least 500 g/l.

[0103] Especially preferred compositions have bulk densities of at least 650 g/litre, more preferably at least 700 g/litre.

[0104] Such powders may be prepared either by post-tower densification of spray-dried powder, or by wholly non-tower methods such as dry mixing and granulation; in both cases a high-speed mixer/granulator may advantageously be used.

[0105] Processes using high-speed mixer/granulators are disclosed, for example, in EP 340 013A, EP 367 339A, EP 390 251A and EP 420 317A (Unilever).

[0106] Liquid detergent compositions can be prepared by admixing the essential and optional ingredients thereof in any desired order to provide compositions containing components in the requisite concentrations. Liquid compositions according to the present invention can also be in compact form which means it will contain a lower level of water compared to a conventional liquid detergent.

[0107] The invention will now be illustrated with reference to the following non-limiting Examples.

[0108] Comparative examples are illustrated by a letter and examples of the invention are illustrated by a number.

Examples

Examples A-D and 1-3

Testing Methods

[0109] Five sequential washes were carried out in a Tergotometer under the following conditions.

Initial wash volume 1200ml

[0110] Washes with systems were carried out in distilled water at a total surfactant concentration of 1 g/l.

Water	Demineralised
Load	40 g of knitted cotton
Liquor to Cloth ratio	30:1
Temperature	30°C isothermal
Wash time	30 minutes
Paddle Speed	75 rpm
Rinsing	3 rinses at 40:1 L/C, short (2 minute) agitation times
Drying	Fabric pieces were dried in the dark in an oven set at 60°C

[0111] Fabrics were removed at the end of each wash, and the liquor volume for subsequent washes adjusted to 30:1

Determination of Sunscreen Level on Cotton

[0112] The Parsol MCX present on the dry fabric was recovered by solvent extraction. A 3g piece of knitted cotton was placed in a 20 ml screw top vial, and 15 ml of high purity isopropyl alcohol added. The vial was roller mixed for 3 hours on a Luckham Multimix Major, before sonicating for 30 minutes in a small sonic bath. The concentration of Parsol MCX present in the extract was then determined by GC/MS analysis (Finnigan Magnum fitted with a 25 metre SGE BPX-5 (non-polar) glass capillary column of internal diameter 0.22mm with a film thickness of 0.25µm). UV/visible absorbance procedures were also employed as a check of sunscreen deposition level. A Perkin Elmer λ2 spectrometer was used to measure the absorbance of the isopropyl alcohol extract solutions at the $\lambda_{\max}$ of the sunscreen. The amount of sunscreen deposited was determined using a calibration plot obtained from measurement of the absorbance of standard sunscreen solutions.

TABLE 1

Composition of test formulations					
Component	Example A	Example B	Example C	Example 1	Example 2
Coco PAS	0.85%	-	-	-	-
Synperonic 7EO	-	-	-	-	-
1:1 mix of Coco 3EO and 7EO NRE	16.15%	17.0%	15.0%	15.0%	16.15%
CTAB	-	-	1.5%	1.5%	0.85%
Ethanol	5%	5%	5%	5%	5%
Borax	1.5%	1.5%	1.5%	1.5%	1.5%
EDTA	0.08%	0.08%	0.08%	0.08%	0.08%
Perfume (PWG3345)	-	-	0.5%	0.5%	-
Parsol MCX	0.1%	0.1%	-	0.1%	0.1%
Distilled water	to 100%	to 100%	to 100%	to 100%	to 100%

Table 2:

Composition of test formulations		
Component	Example 3	Example D
Arquad 2T	0.85%	-
Synperonic A7	16.15%	9.0%
PAS	-	8.0%
Ethanol	5.0%	5.0%
Borax	1.5%	1.5%
EDTA	0.08%	0.08%
Parsol MCX	0.1%	0.1%
Water	to 100%	to 100%
Coco PAS = Coconut primary alcohol sulphate Coco 7EO NRE = C ₁₂₋₁₄ alcohol ethoxylate with a mean ethylene oxide chain length of 7. Coco 3EO NRE = C ₁₂₋₁₄ alcohol ethoxylate with a mean ethylene oxide chain length of 3. NRE = Narrow range ethoxylate CTAB = Cetyl trimethyl ammonium bromide. ARQUAD 2T = dimethyl ditallow ammonium chloride (non-hardened) Synperonic A7 = C ₁₁₋₁₃ alcohol ethoxylate with a mean ethylene oxide chain length of 7		

[0113] Parsol MCX is 2-Ethylhexyl 4-methoxycinnamate with a log P value of 5.2.

TABLE 3:

Deposition of Parsol MCX on cotton from duplicate washes containing Examples 2 and 3, 5, 6 and Example B and D. Deposition monitored as ppm of Parsol MCX in iso-propyl alcohol extract. Level determined by GC/MS.		
Product	Duplicate experiment 1	Duplicate experiment 2
Example B	1.28	1.22
Example D	1.6	1.52
Example 3	10.35	11.23
Example 2	18.1	17.8

TABLE 4 :

Deposition of Parsol MCX on cotton from duplicate washes containing Example B and Example 1. Deposition monitored as ppm of Parsol MCX in iso-propyl alcohol extract. Level determined by GC/MS.

Number of Wash Cycles	Example A		Example 1	
	Duplicate Experiment 1	Duplicate Experiment 2	Duplicate Experiment 1	Duplicate Experiment 2
1	5.46	4.64	17.3	17.2
2	6.8	6.6	36.8	40.0
3	7.1	6.7	56.4	55.9
4	6.5	6.8	5.9	66.9
5	4.5	5.0	5.6	118.0

Table 5:

Deposition of Parsol MCX on cotton from duplicate washes containing Example A and Example 1. Deposition monitored as ppm of Parsol MCX in iso-propyl alcohol extract. Level determined by measurement of the optical density at the $\lambda_{\max}$ of Parsol MCX.

Number of Wash Cycles	Example A		Example 1	
	Experiment 3	Experiment 4	Experiment 3	Experiment 4
1	2.8	2.7	23.0	21.5
2	3.6	3.3	57.8	50.3
3	4.0	-	88.9	-
4	4.15	3.5	97.5	103.6
5	2.3	2.5	115.5	118.0

[0114] The results show better deposition when the nonionic/cationic ratio of the invention is used.

Example C and Example 1

[0115] Table 6 shows the comparison of perfume components delivered to cotton fabric from a CTAB/nonionic (10/90) liquid product containing 17% total active. The perfume components are quoted as concentration (ppm) in a solvent extract from the washed and dried fabric.

[0116] Two products were compared, one containing 0.5% perfume, the other containing 0.5% and 0.1% Parsol MCX. The perfume has twenty components, each component of the perfume being present at equal concentration.

TABLE 6:

Level of perfume on fabric		
Perfume Component	Example C (ppm)	Example 2 (ppm)
Limonene	0.0074	0.0088
Tetrahydrolinalol	0.022	0.026
Linalol	nd	nd
Benzyl Acetate	nd	nd
Inonyl Acetate	0.00	0.019
Dimethylbenzyl cyclohexyl acetate	0.027	0.056

TABLE 6: (continued)

Level of perfume on fabric		
Perfume Component	Example C (ppm)	Example 2 (ppm)
Anther	0.117	0.279
Cyclamen aldehyde	0.782	1.339
Bourgeonal	0.921	1.696
Florocyclene	0.456	1.704
Lilial	1.081	2.019
Amyl cinnamic aldehyde	1.800	3.513
Celestolide	1.799	3.122
Hexyl cinnamic aldehyde	2.232	4.681
Tonalid	1.963	3.611
Phenylethylphenyl acetate	1.111	1.921
Musk Ketone	1.778	3.308
Ethylene Brassylate	1.255	1.931

[0117] Table 6 shows the level of perfume deposited onto fabric.

Examples 4 and Example E

[0118] Two non-ionic cationic liquids were prepared containing the solid sunscreen Tinuvin 328 (2-(2-hydroxy-3,5-di-tertiaryamyl-phenyl)-2H-benzotriazole ex Ciba Geigy). Examples 4 and E are listed in Table 7. The only difference between the two formulations is the solvent used to dissolve the Tinuvin 328 sunscreen. Example 4 contains diethylphthalate which has a logP of 2.15, and Example E contains 2-butoxyethanol which is water soluble and has a logP of 0.84.

Table 7:

Component	Example 4 (wt%)	Example E (wt%)
Coconut 5EO narrow range ethoxylate	15.3	15.3
CTAB	1.7	1.7
Ethyl alcohol	10	10
Tinuvin 328	0.1	0.1
Diethylphthalate	1.0	-
2-Butoxy ethanol	-	1.0
Water	to 100%	to 100%

[0119] Washes were carried out in a Tergotometer at 20°C using 6g/l of each product over a period of 20 minutes in the presence of 1.14g/l of borax buffer. An initial liquor volume of 1200ml was selected for the first wash. Fabrics were removed after each wash to determine the level of sunscreen deposited on the fabric. The wash liquor volume was reduced in the second and third washes to maintain the liquor to cloth ratio at 30:1. At the end of each wash the fabrics were squeezed to remove excess liquor and rinsed three times at a liquor to cloth ratio of 40:1, before air drying in the dark. Dry white cotton pieces measuring 5.08 cm x 11.43 cm (2" x 4.5") taken from each wash were each placed in a glass sample vial and 15ml of ethylacetate added. The vials were rolled on a roller mixer (Luckham Multimix Major) for a minimum period of 2 hours. The optical density of the extracts were then measured at 303nm, the $\lambda_{\max}$ of Tinuvin 328. The results in table 8 show that delivery of Tinuvin 328 to cotton was achieved in the presence of diethyl phthalate. Whereas in the presence of 2-butoxyethanol readings were close to those obtained with a sunscreen free control.

Table 8:

Deposition of Tinuvin 328 on cotton from washes containing Example E and Example 4. Deposition monitored as optical density at $\lambda_{\max}$ of Tinuvin 328.

Wash cycle	Example 4	Example E
1	0.48	0.025
2	0.63	0.05
3	0.78	0.08

Claims

1. A detergent composition comprising:

- i) a nonionic detergent surfactant;
- ii) a quaternary ammonium compound cationic material;
- iii) a liquid photofading inhibitor having a log P value of at least 1.9 or a solid photofading inhibitor dissolved in a liquid the liquid having a log P of at least 1.9 or mixtures thereof; and
- iv) optionally, an anionic surfactant;

wherein the ratio of (i) nonionic surfactant to (ii) cationic material at least 1:1 by weight and in which (if anionic surfactant (iv) is present), the ratio of (ii) cationic material to (iv) anionic surfactant is at least 1:1 by weight.

2. A detergent composition according to claim 1, in which the ratio of (ii) cationic material to (iv) anionic surfactant is at least 2:1.

3. A detergent composition according to claim 1 or claim 2, which does not comprise anionic surfactant.

4. A detergent composition according to any preceding claim, in which the level of cationic material to nonionic surfactant is from 1:100 to 50:50.

5. A detergent composition according to any preceding claim, in which the quaternary ammonium compound has at least one C₁₂-C₂₂ alkyl or alkenyl chains.

6. A detergent composition according to any preceding claim, which is a liquid and in which the total level of cationic material is from 0.05 wt% to 10 wt% of the total weight of the composition.

7. A detergent composition according to any one of claims 1 to 5, in which the composition is in powdered or granular form and in which the level of cationic is from 0.05 wt% to 15 wt% of the total weight of the composition.

8. A detergent composition according to any preceding claim, in which the level of photofading inhibitor is from 0.01 wt% to 10 wt% of the total weight of the composition.

9. Use of a detergent composition according to claim 1, for the deposition of a sunscreen onto a fabric.

Patentansprüche

1. Waschmittelzusammensetzung, umfassend

- i) ein nichtionisches Waschmitteltensid;
- ii) ein kationisches Material einer quaternären Ammoniumverbindung;
- iii) einen flüssigen Lichtverblässungsinhibitor mit einem logP-Wert von mindestens 1,9 oder einen festen Lichtverblässungsinhibitor, gelöst in einer Flüssigkeit, wobei die Flüssigkeit einen logP-Wert von mindestens 1,9

aufweist, oder Gemische davon; und
iv) gegebenenfalls ein anionisches Tensid;

wobei das Verhältnis von (i) nichtionischem Tensid zu (ii) kationischem Material mindestens 1:1, auf das Gewicht, ist und wobei (falls anionisches Tensid (iv) vorliegt) das Verhältnis von (ii) kationischem Material zu (iv) anionischem Tensid mindestens 1:1, auf das Gewicht, ist.

2. Waschmittelzusammensetzung nach Anspruch 1, wobei das Verhältnis von (ii) kationischem Material zu (iv) anionischem Tensid mindestens 2:1 ist.

3. Waschmittelzusammensetzung nach Anspruch 1 oder Anspruch 2, die kein anionisches Tensid umfaßt.

4. Waschmittelzusammensetzung nach einem vorangehenden Anspruch, wobei der Anteil von kationischem Material zu nichtionischem Tensid 1:100 bis 50:50 ist.

5. Waschmittelzusammensetzung nach einem vorangehenden Anspruch, wobei die quaternäre Ammoniumverbindung mindestens eine C₁₂-C₂₂-Alkyl- oder Alkenylkette aufweist.

6. Waschmittelzusammensetzung nach einem vorangehenden Anspruch, die eine Flüssigkeit darstellt und in der der Gesamtanteil an kationischem Material 0,05 Gewichtsprozent bis 10 Gewichtsprozent des Gesamtgewichts der Zusammensetzung ist.

7. Waschmittelzusammensetzung nach einem der Ansprüche 1 bis 5, in der die Zusammensetzung in Pulver- oder granulärer Form vorliegt und in der der Anteil von kationischem Material 0,05 Gewichtsprozent bis 15 Gewichtsprozent des Gesamtgewichts der Zusammensetzung ist.

8. Waschmittelzusammensetzung nach einem vorangehenden Anspruch, in der der Anteil an Lichtverblässungsinhibitor 0,01 Gewichtsprozent bis 10 Gewichtsprozent des Gesamtgewichts der Zusammensetzung ist.

9. Verwendung einer Waschmittelzusammensetzung nach Anspruch 1 zur Abscheidung eines Sonnenschutzmittels auf einem Textil.

Revendications

1. Composition détergente comprenant :

- i) un tensioactif détergent non ionique,
- ii) un composé ammonium quaternaire cationique,
- iii) un inhibiteur de photodécoloration liquide ayant une valeur logP d'au moins 1,9 ou un inhibiteur de photodécoloration solide dissous dans un liquide, le liquide ayant un log P d'au moins 1,9 ou leurs mélanges, et
- iv) facultativement, un tensioactif anionique,

dans laquelle le rapport du tensioactif non ionique (i) au cationique (ii) est d'au moins 1:1 en poids et dans laquelle (si le tensioactif anionique (iv) est présent), le rapport du tensioactif cationique (ii) au tensioactif anionique (iv) est d'au moins 1:1 en poids.

2. Composition détergente selon la revendication 1, dans laquelle le rapport du tensioactif cationique (ii) au tensioactif anionique (iv) est d'au moins 2:1.

3. Composition détergente selon la revendication 1 ou 2, qui ne comprend pas de tensioactif anionique.

4. Composition détergente selon l'une quelconque des revendications précédentes, dans laquelle la quantité de matière cationique au tensioactif non ionique est de 1:100 à 50:50.

5. Composition détergente selon l'une quelconque des revendications précédentes, dans laquelle le composé ammonium quaternaire a au moins une chaîne alkyle ou alcényle en C₁₂₋₂₂.

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6. Composition détergente selon l'une quelconque des revendications précédentes, qui est un liquide et dans laquelle la quantité totale de cationique est de 0,05% en poids à 10% en poids du poids total de la composition.
7. Composition détergente selon l'une quelconque des revendications 1 à 5, dans laquelle la composition est sous forme de poudre ou granulaire et dans laquelle la quantité de cationique va de 0,05% en poids à 15% en poids du poids total de la composition.
8. Composition détergente selon l'une quelconque des revendications précédentes, dans laquelle la quantité d'inhibiteur de photodécoloration va de 0,01% à 10% en poids du poids total de la composition.
9. Utilisation d'une composition détergente selon la revendication 1, pour le dépôt d'un écran solaire sur un textile.