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(54) **Stable nonaqueous bleaching detergent composition dispersion**

(57) The invention pertains to a nonaqueous bleaching detergent composition comprising a dispersion of:

- a) from 20% to 85% by weight of a solid bleaching agent,
- b) from 0.1 to 10% by weight of a thickening agent,
- c) from 0 to 0.3% by weight of a thickening agent activator,
- d) from 0 to 23% by weight of an auxiliary compound, and
- e) at least 14.9% by weight up to a total of 100% by weight of a nonaqueous liquid, which is chemically inert to the bleaching agent and wherein the solubility

of the bleaching agent is less than 10 mg/l.

The composition is effective for washing machines, dishwashing and cleaning in place applications in removing coffee, tea, and wine stains and the like. The composition can be made in substantially higher concentrations than prior art compositions, and is nevertheless stable under storage conditions.

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Description

BACKGROUND OF THE INVENTION

1. Field of the invention

[0001] The present invention pertains to a nonaqueous bleaching detergent composition comprising a dispersion, a method of manufacturing said composition, and to a closed package containing the same.

2. Description of the prior art

[0002] Commercially available detergents for washing machines and dishwashing applications provided in powder dispersion or slurry, or in liquid form have the disadvantage of not being stable in high concentrations.

[0003] Stable nonaqueous bleaching detergent composition have been developed, for instance the composition of US patent No. 5,164,106, wherein a dishwasher detergent composition having improved cleaning performance against difficult to remove soils was disclosed. The disclosure of this patent was directed to a stable nonaqueous liquid composition containing a dual bleach system for use in an automatic dishwasher to clean dishware, glassware, cookware, and the like. It discloses a nonaqueous bleaching detergent composition comprising a dispersion of a carrier liquid, a bleaching agent selected from a hypochlorite-liberating compound, a nonaqueous builder salt, sodium silicate, alkali metal carbonate, and a bromine compound. Typical bleaching compositions contain an amount to provide 0.5 to 10% chlorine, corresponding to the use of hypochlorite-liberating compounds of 1 to 18 wt.%, and preferably of 2 to 12 wt.%. According to the examples concentrations of the bleaching agent of 2.5 to 5.36% by weight could be obtained.

[0004] Aqueous bleach compositions are known in the art, for instance in US patent No. 4,992,194. This patent describes a method wherein a nonaqueous peroxide acid is kept water insoluble by using a low pH. At higher pH the peroxide acid dissolves and thereby becomes inactivated. The disadvantage of this method is the restricted numbers of suitable peroxide acids. In fact one of the few acids that can be used according to this prior art method are compounds of the group PAP (phthaloyl aminoperoxocaproic acids). This method therefore is certainly not generally applicable.

SUMMARY OF THE INVENTION

[0005] It was found that compositions of US patent No. 5,164,106 are not stable at amounts of bleaching agent above 18% by weight. This is a considerable problem because there is a need for more concentrated bleaching compositions, which are effective in removing proteinaceous and starchy carbohydrate soils in dishwashing and stubborn stains in laundry washing, and which are also

effective in cleaning hard surfaces in CIP (cleaning in place) applications, such as in the food and beverage industry. For economic reasons it is particularly important to obtain compositions that are stable enough to be stored for longer periods of time at higher temperatures. The latter is of particular importance when using oxygen-generating bleaching agents because on decomposition they can release oxygen, or chlorine in the case of hypochlorite-releasing agents. In general, bleaching agents including peroxide- and hypochlorite-releasing agents, ultimately release oxygen, and decomposition of the bleaching agent will lead to decrease of activity and build up of oxygen pressure (in non-vented packages), which can lead to hazardous conditions when stored in (non-vented) bottles and other packaging types which are opened after decomposition has commenced.

[0006] Thus there is a need for stable dispersions containing much higher concentrations of bleaching agent than known in the art.

[0007] An object of the present invention is to obtain a stable dispersion containing at least 20% by weight, preferably about 40% by weight or higher of a bleaching agent, which can be selected from a large group of bleaching agents, particularly from oxygen-generating bleaching agents. It is further an object of the invention that such compositions can be packed and stored for long periods of time without decomposition or formation of oxygen.

[0008] The problem to be solved is to formulate a concentrated nonaqueous liquid detergent composition that is stable in storage and effective as bleach in automatic dishwashing, laundering and other bleaching applications. In particular, the composition should easily remove coffee, tea, and wine stains. Typical stains, such as originating from blood, starch and proteins should also be easily removed. The composition should be made at substantially higher concentrations than compositions known from the prior art, while maintaining stability under long term storage conditions.

[0009] Another object of the invention is to provide a nonaqueous liquid detergent concentrate composition which is stable under storage conditions, does not degrade or decompose (even at elevated temperatures), is easily pourable, and is readily dispersible in the wash water.

[0010] The present invention is directed to a nonaqueous bleaching detergent composition comprising a dispersion of:

- a) from 20% to 85% by weight of a solid bleaching agent,
- b) from 0.1 to 10% by weight of a thickening agent,
- c) from 0 to 0.3% by weight of a thickening agent activator,
- d) from 0 to 23% by weight of an auxiliary compound, and
- e) at least 14.9% by weight up to a total of 100% by weight of a nonaqueous liquid, which is chemically

inert to the bleaching agent and wherein the solubility of the bleaching agent is less than 10 mg/l.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0011] It was found that the compositions according to this invention are stable for at least 6 months, usually for at least 1 year, and in most cases even for an unlimited time period, and nevertheless contain very concentrated bleaching agent. It is possible to obtain stable compositions having 25 to 50%, preferably 35 to 45% by weight of the bleaching agent. Compositions within the most preferred range, i.e. containing 35 to 45% by weight of the bleaching agent, can be used in conventional washing machines, dishwashers, and the like. At higher concentrations, particularly those close to 85% by weight, the compositions become more viscous but can be used in adapted machines that use higher pressures to pump the bleaching composition. Concentrations higher than 85% by weight are possible, but due to the substantial increase of viscosity they are not commercially useful.

[0012] Surprisingly, the compositions of this invention can be used for liquid automatic dishwasher detergent composition having improved cleaning performance on protein and carbohydrate soils in automatic dishwashing, and on coffee, tea, and wine stains in textile laundering. They can also be used in food and beverage industries for cleaning hard surfaces. More generally, the bleach can be used as destainer but also for sanitizing purposes in dish wash and laundry. The liquid detergent composition contains an bleach source, particularly an oxygen-generating bleach source. The detergent composition more particularly contains a source of hypochlorite ion or peroxide.

[0013] The present invention specifically relates to liquid automatic dishwashing detergent concentrate compositions having improved cleaning performance against proteinaceous and starchy carbohydrate soils on dishware, glassware, cookware, and the like, particularly cooked on and baked on soils, and improved cleaning capacity for coffee, tea and wine stains. Such stains are removed in laundry applications.

[0014] The nonaqueous liquid compositions are stable in storage, do not settle, are preferably pourable and are readily dispersed in water.

[0015] The nonaqueous liquid detergent compositions of the present invention have the advantages of being stable, non-settling and non-gelling in storage, and are readily dispersible in (dish)washing machines. The preferred liquid compositions of the present invention are easily poured, easily measured, and easily put into (dish)washing machines and are readily dispersed in the wash water in the (dish)washing machines.

[0016] These and other objects of the invention will become more readily understood from the following detailed description of the invention and preferred embodiments thereof.

[0017] In accordance with the present invention there is provided a nonaqueous liquid automatic dishwasher detergent composition which includes at least a bleaching agent preferably selected from an oxygen-generating compound, a thickening agent, a nonaqueous liquid, and optionally a thickening agent activator, and auxiliary compound(s). The term "nonaqueous" throughout this invention means a composition or liquid containing less than 5% by weight of free water. Thus the compositions and liquids of the invention at the most only contain minor amounts of free water, and preferably do not contain any free water.

[0018] The present invention also provides a method for cleaning dishware, glassware, and cookware in a household or industrial automatic dishwashing machine and a method for cleaning laundry in a washing machine with an aqueous wash bath containing an effective amount of the nonaqueous liquid composition as described above. According to this aspect of the invention, the composition is stable in storage, is easily measured and can be readily poured or dispersed into automatic (dish)washing machines.

1 Bleaching agents

[0019] Oxygen-generating compounds suitable for use in the compositions of the present invention are those water soluble solid materials which generate oxygen on contact with, or dissolution in water. Such oxygen release can be obtained by direct oxygen release or release via hypochlorite, hypobromite, or hypoiodite ions, ozone, perhydroxy ions, or halodioxide, such as chlorodioxide. Examples of solid bleaching agents are particulate heterocyclic N-haloimides such as trihalocyanuric acid, dihalorocyanuric acid and salts thereof such as sodium dihalocyanurate and potassium dihalocyanurate, wherein the term "halo" stands for chloro, bromo, or iodo. The preferred halo group is chloro. The corresponding dihaloisocyanuric and trihaloisocyanuric acid salts can also be used. Other N-halimides may be used such as N-halosuccinimide, N-halomalonimide, N-halophthalimide and N-halonaphthalimide. Additional suitable N-haloroimides are the hydantoins such as 1,3-dihalo-5,5-dimethylhydantoin; N-monohalo-C,C-dimethylhydantoin; methylene-bis(N-halo-C,C-dimethylhydantoin) 1,3-dihalo-5-methyl-5-isobutylhydantoin; 1,3-dihalo-5-methyl-5-ethylhydantoin; 1,3-dihalo-5,5-diisobutylhydantoin; 1,3-dihalo-5-methyl-5-n-amylyhydantoin; and the like.

[0020] Useful hypochlorite-liberating agents are trichloromelamine and dry, particulate, water soluble anhydrous inorganic salts such as calcium and lithium hypochlorite. The hypochlorite-liberating agent may, if desired, be a stable, solid complex or hydrate such as sodium p-toluene-sulfo-chloramine-trihydrate (chloramine-T), sodium benzene-sulfo-chloramine-dihydrate, calcium hypochlorite tetrahydrate, or chlorinated trisodium phosphate containing 0.5 to 4% available chlorine produced by combining trisodium phosphate in its normal

Na₃PO₄·12H₂O form and an alkali metal hypochlorite (e.g., sodium hypochlorite). Apart for potassium, sodium and calcium, also other salts may be used, such as lithium, magnesium, and ammonium salts.

[0021] In compositions in which the alkali and alkaline earth metal hypochlorites are used as the chlorine source, these compounds can be used in the form of anhydrous dispersed solids in order to prevent deterioration of the nonionic surfactants in the composition.

[0022] The preferred sources of hypochlorite are dichloro- and trichloroisocyanurates and chloramine-T (p-toluenesulfochloramine).

[0023] Source of hydrogen peroxide is selected from the group percarbonate, persulfate, persulfate, perborate, peroxyacids, dialkyl peroxides, diacyl peroxides, preformed percarboxylic acids, nonaqueous peroxides, inorganic peroxides, hydroperoxides, and mixtures thereof. Specific examples include peroxyformic acid, peroxyacetic acid, monoperphthalate, monoperoxysuccinate, monoperoxysulfate, monoperoxy phosphate, peroxyoctanoic acid, peroxybenzoic acid, ethylperoxy-carbonic acid, phthalimidoperoxyhexanoic acid, sodium perborate, and sodium percarbonate.

[0024] Typically, the oxygen-generating agents are employed in a proportion of about 20 to 85% by weight of the composition, preferably about 25 to 50%, and more preferably 35 to 45% by weight.

[0025] It was found that the best dispersions were obtained with solid bleaching agents having a particle size less than 400 μm, preferably 10 to 200 μm, most preferably 30-110 μm. According to the examples the bleaching particles have a particle size of about 70 μm.

2. Thickening agents

[0026] The composition also includes conventional thickening agents in amounts from 0.1 up to 10% by weight to obtain a product consistency of a cream or a paste.

[0027] The thickening agents, i.e. thickeners or suspending agents which provide thickening properties, are known in the art and may be water soluble or insoluble, dispersible or colloid-forming, and monomeric or polymeric, and should of course be stable in these compositions, e.g., stable to alkalinity and bleaching agents, such as sodium hypochlorite and peroxide. The preferred thickeners generally comprise the inorganic, colloid-forming clays of smectite and/or attapulgite types. These materials are generally used in amounts of about 1.5 to 10 wt.%, preferably 2 to 5 wt.%, to confer the desired thickening properties to the formulation.

[0028] Smectite clays include montmorillonite (bentonite), hectorite, attapulgite, smectite, saponite, and the like. Montmorillonite clays are preferred and are available under trade names such as Tixogel® MP100, Tixogel® VP, Tixogel® MIO from Sud-chemie, Bentone® 34, Bentone® Gel, Bentone® SD-1 from Water Ingredients, Thixogel® No. 1 and Gelwhite® GP, H, etc., from Georgia

Kaolin Company; and ECCAGUM® GP, H, etc., from Georgia Kaolin Company; and ECCAGUM® GP, H, etc., from Luthern Clay Products. Attapulgite clays include the materials commercially available under the trade name Attagel®, i.e. Attagel® 40, Attagel® 50 and Attagel® 150 from Engelhard Minerals and Chemicals Corporation. Mixtures of smectite and attapulgite types in weight ratios of 4:1 to 1:5 are also useful. Thickening or suspending agents of the foregoing types are well known in the art, being described, for example in U.S. Pat. No. 3,985,668, which is incorporated herein by reference.

[0029] The conventionally used organic polymeric thickening agents, such as the polyacrylates, e.g. powdered polyacrylates having a molecular weight of 1,000-20,000 can be used. Suitable polyacrylates, e.g. sodium, are Alcosperse® 130D, MW 15,000, available from Alco Chem. Co. Alcosperse® 149D, MW 2000, available from Alco Chem. Co., and Alcrysol® 45N, MW 4500, available from Rohm & Haas Co., Polymer WSP 10 (butene copolymer), WSP 01 (blockcopolymer S-E/P), WSP 52 (triblockcopolymer styrene-ethylene/butylene), WSP 50 (triblockcopolymer styrene-ethylene/butylene-styrene), WSP 22 (polybutene), PEO-1 (polyethyleneoxide) from Water Ingredients.

[0030] The composition preferably comprises 0.1 to 6%, preferably 1 to 4%, more preferably 2 to 3% by weight of thickening agent.

[0031] It was further found that apart from the chemical stability as obtained with these compositions, also a high physical stability could be obtained (i.e. stabile dispersions without phase separation) when a mixture of both a clay and a polymer was used as thickening agent. Such mixtures are effective for increasing the physical stability when the ratio clay: polymer is 1 : 10 to 10 : 1, preferably 1 : 3 to 2 : 1. Most preferably, these mixtures are used in combination with paraffin oil as nonaqueous liquid (see herein below).

3. Thickening agent activator

[0032] The compositions may contain up to 0.3% by weight of a thickening agent activator. Such activators improve the dispersing properties of the clay thickening agents, and are well known in the art. Suitable activators for use with clays include lower alcohols, such as ethanol, and propylene carbonate.

4. Auxiliary compounds

[0033] The composition may further contain up to 23% by weight of an auxiliary compound. Auxiliary compounds are for instance surfactant detergents, builder salts such as phosphates, silicates, and carbonates, foam inhibitors, perfumes, gloss enhancers, colorants, sequestering agents, and the like.

[0034] Surfactants that can be used linear or branched alkali metal mono- and/or di-(C8-14)alkyl diphenyl oxide mono- and/or disulfonates, which are commercially avail-

able for example as DOWFAX® 3B-2 and DOWFAX® 2A-1. Other suitable surfactants include the primary alkyl sulfates, alkyl sulfonates, alkylaryl sulfates, sec-alkyl sulfates, alkyl phosphonates. Examples include sodium (C10-18)alkyl sulfates such as sodium dodecyl sulfate; sodium (C10-18)alkyl sulfonates such as sodium hexadecyl-1-sulfonate and sodium (C12-18)alkylbenzene sulfonates, such as sodium dodecylbenzene sulfonates. The corresponding potassium salts may also be employed.

[0035] Sodium carbonate can be added as a builder salt to act as a buffer to maintain the desired pH level. The compositions of the present invention can also contain inorganic builder salts such as NaTPP or organic builder salts such as the alkali metal salts of polycarboxylic acids.

[0036] A preferred inorganic builder salt is an alkali metal polyphosphate such as sodium tripolyphosphate (TPP). In place of all or part of the alkali metal polyphosphate one or more other detergent builder salts can be used. Suitable other builder salts are alkali metal borates, phosphates and hydrogencarbonates. Specific examples of such builders are sodium tetraborate, sodium pyrophosphate, potassium pyrophosphate, sodium bicarbonate, sodium hexametaphosphate, sodium sesquicarbonate, sodium mono- and diorthophosphate, potassium bicarbonate, and sodium or potassium zeolites.

[0037] Since the compositions of this invention are generally highly concentrated, and therefore may be used at relatively low dosages, it is desirable to supplement any phosphate builder (such as sodium tripolyphosphate) with an auxiliary builder such as an alkali metal polycarboxylic acid. Suitable alkali metal polycarboxylic acids are alkali metal salts of citric and tartaric acid, e.g., monosodium and disodium citrate (anhydrous). The sodium salts of citric and tartaric acids are preferred.

[0038] Addition of foam inhibitors is important to increase dishwasher machine efficiency and minimize destabilizing effects which might occur due to the presence of excess foam within the washer during use. Foam may be sufficiently reduced by suitable selection of the type and/or amount of detergent active material, the main foam-producing component. The degree of foam is also somewhat dependent on the hardness of the wash water in the machine whereby suitable adjustment of the proportions of NaTPP which has a water softening effect may aid in providing the desired degree of foam inhibition. However, it is generally preferred to include a chlorine bleach stable foam depressant or inhibitor. Particularly effective are alkyl phosphonic acid esters which are available, for example, from BASF-Wyandotte (PCUK-PAE), and alkyl acid phosphate esters which are available, for example, from Hooker (SAP) and Knapsack (LPKN-158). Other foam inhibitors which may be used include, for example, the known silicones such as Dow Corning 1400 and 1500, which are polysiloxanes mixed with dispersed silica.

[0039] Alkali metal silicates, e.g. sodium silicate, which

provide alkalinity and protection of hard surfaces, such as fine china, may be employed. Sodium silicate also protects the washing machine from corrosion. The preferred silicates are sodium disilicate and sodium metasilicate.

[0040] Most of the components of the composition can be added to the nonaqueous liquid composition in the form of dry powders or nonaqueous dispersions or solutions.

[0041] Sequestering agents can be employed in higher quantities when necessary. Preferred sequestering agents are compounds that have a strong complexation with or bonding to calcium and magnesium. Most preferred are sodium or potassium salts of NTA (nitrilotriacetic acid), MGDA (methylglycinediacetic acid), EDTA (ethylenediamine tetraacetic acid), and (S,S)-EDDS (ethylenediamine-N,N'-disuccinic acid), or mixtures thereof. Preferred amounts of the sequestering agent amount to 10-23 wt.%.

[0042] Various other conventional ingredients may be included in these compositions in small amounts, generally less than about 4 wt.%, such as perfume and hydro-tropic agents, preservatives, gloss enhancers, dyestuffs, and pigments and the like, all of course being stable to chlorine bleaching agent and high alkalinity (properties of many of the components). Especially preferred for coloring are the chlorinated phthalocyanines and polysulfides of aluminosilicate which provide, respectively, pleasing green and blue tints.

5. Nonaqueous liquids

[0043] The nonaqueous liquids that can be used in accordance with the present invention are in general vegetable oils, mineral oils, synthetic oils, or animal oils including fish oils. Specific but not exhaustive examples are paraffin oil, coconut oil, salad oil, and olive oil.

[0044] The above discussed nonaqueous liquids can be used alone or in admixture in order to obtain a desired viscosity and stability of the product liquid. It may be preferred to use a nonaqueous liquid that is a mixture of at least two liquids. Preferred mixtures contain in addition to the above liquids 0.1 to 5% by weight of a saturated or unsaturated fatty acid having 12 to 24 carbon atoms as co-liquid. Examples of such co-liquids are for instance silicone oil, low alkanes such as hexanes, heptanes, octanes, soybean oil methyl esters (e.g. Steposol® SB-W), methyl soyate/ethyl lactate blend (e.g. Steposol® SC), isobutyl ester (Rodiasolve® DIB, ex. Rhodia), and other types of liquids such as ethylene glycol ethers.

[0045] The component only partially dissolve or do not dissolve at all in the liquids and co-liquids, and form an emulsion, dispersion, or suspension in the liquid.

[0046] The compositions of the present invention have good viscosity and stability characteristics and remain stable at room temperature and higher, and are pourable at low temperatures. A particularly useful composition contained 35-45 wt.% of solid sodium dihaloisocyanuric

acid (NaDCCA) having a mean particle size of about 60-80 μm , 0.5-3 wt.% of a clay thickener such as Tixogel® MP100, 0.02 to 0.04 wt.% ethanol, and 64.48 to 51.96 wt.% up to 100 wt.% of paraffin oil. It was found that the stability was excellent in that no oxygen formation occurred. The stability of the compositions of the invention is expressed as less than 5% decrease of activity of the bleaching agent after 6 months storage at 40° C, as measured by thiosulfate titration according to ASTM D 2022. For that reason the composition can be stored in close packages for months under normal storage conditions between 0 and 40° C. It is therefore also an object of the invention to obtain storage stable packages (or containers) containing the composition of the invention.

METHOD OF PREPARATION OF LIQUID COMPOSITION

[0047] The compositions of the present invention can be prepared by conventional means. In a suitable manner to make the compositions of the invention the method comprising the steps:

- i) making at elevated temperature a pre-gel of a polymer and a nonaqueous liquid, which is chemically inert to the bleaching agent and wherein the solubility of the bleaching agent is less than 10 mg/l;
- ii) making a pre-gel of a clay and the nonaqueous liquid using a high-shear mixer.
- iii) adding under stirring the pre-gel of ii) to the pre-gel of i), and
- iv) optionally, adding a thickening agent activator and/or auxiliary compound.

[0048] Suitable elevated temperatures as used in step i) are above 100° C, preferably about 150° C. High-shear mixers as used in step ii) are known in the art and comprise mixtures such as Silverson, ULTRA TURRAX T25, and Heidolph DIAX 600.

[0049] The invention may be put into practice in various ways and a number of specific embodiments will be described to illustrate the invention.

[0050] The viscosity profile was determined for a structured liquid containing 55% of paraffin oil, 3% of fractionated coconut oil, 2% of Tixogel® MP100, and 40% of sodium dichloroisocyanuric acid (NaDCCA).

[0051] The following examples of formulations according to the invention illustrate the invention and are not intended to restrict the invention

PRE-GELS

[0052] Pre-gel polymer (WSP01):

A mixture of 96 wt.% paraffin oil and 4 wt.% WSP®01 (blockcopolymer styrene-ethylene/propylene, ex Water Ingredients, Zeist, The Netherlands) was stirred and heated above 160° C for about 60 min.

After WSP01 was completely dissolved it was slowly cooled down under stirring.

Pre-gel WSP 50 was made according to the above procedure wherein 99 wt.% paraffin oil and 1 wt.% WSP®50 (triblock polymer styrene-ethylene/butylene-styrene, ex Water Ingredients, Zeist, The Netherlands) solution was stirred and heated above 160° C for about 60 min. When WSP50 was dissolved it was slowly cooled down under stirring.

[0053] Pre-gel clay:

A mixture of 88 wt.% paraffin oil and 10 wt.% Tixogel® MP 100 (ex Süd-Chemie, Munich, Germany) was brought into a plastic beaker and stirred with a high shear mixer (Ultra Turrax) during 5 to 10 min (speed: 16000 rpm), after which 2 wt.% ethanol were added to the blend and stirred with a high shear mixer for another 10 min at 16000 rpm.

PROCEDURE

[0054] Paraffin oil (32.5%) and the pre-gel clay (15%) were mixed for 5 min, after which the pre-gel polymer (12.5%) was added and mixing was continued for 20 min. Then NaDCCA powder (40%) (ex. Clearon, Terneuzen, The Netherlands) was added and the mixture was stirred for another 30 min.

FORMULATIONS

[0055] The following formulations according to the invention were prepared.

A) 50% Pre-gel WSP 01 + 10% Pre-gel MP 100 + 40% NaDCCA

B) 45% Pre-gel WSP 01 + 15% Pre-gel MP 100 + 40% NaDCCA

C) 32.5% Paraffin oil + 15% Pre-gel MP 100 + 12.5% Pre-gel WSP 01 + 40% NaDCCA

D) 42.5% Paraffin oil + 15% Pre-gel MP 100 + 12.5% Pre-gel WSP 01 + 30% NaDCCA

E) 57% Paraffin oil + 2% Pre-gel WSP 01 + 1% Pre-gel MP 100 + 40% NaDCCA

F) 58% Paraffin oil + 0.5% Pre-gel WSP 50 + 1.5% Pre-gel MP 100 + 40% NaDCCA.

[0056] The above compositions were tested for their stability by measuring the phase separation as follows. The products were brought into a measuring cylinder and kept at 40° C for 40 days. The volume of the separated oil was read out from the measuring bars and expressed

as percentage of the total volume. None of the compositions of the invention showed phase separation (oil volume 0%), whereas comparison compositions made of the pre-gel of the clay only, showed substantial phase separation (oil volume in the range from 5 to 15%).

Claims

1. A nonaqueous bleaching detergent composition comprising a dispersion of:
 - a) from 20% to 85% by weight of a solid bleaching agent,
 - b) from 0.1 to 10% by weight of a thickening agent,
 - c) from 0 to 0.3% by weight of a thickening agent activator,
 - d) from 0 to 23% by weight of an auxiliary compound, and
 - e) at least 14.9% by weight up to a total of 100% by weight of a nonaqueous liquid, which is chemically inert to the bleaching agent and wherein the solubility of the bleaching agent is less than 10 mg/l.
2. The bleaching detergent composition of claim 1 wherein the bleaching agent is selected from a salt of dihaloisocyanurate, trihaloisocyanurate, chloramine-T, N-halosuccinimide, N-halomalonimide, N-halophthalimide, N-halonaphthalimide, 1,3-dihalo-5,5-dimethylhydantoin; N-monohalo-C,C-dimethylhydantoin; methylene-bis(N-halo-C,C-dimethylhydantoin); 1,3-dihalo-5-methyl-5-isobutyl-hydantoin; 1,3-dihalo-5-methyl-5-ethylhydantoin; 1,3-dihalo-5,5-diisobutylhydantoin; 1,3-dihalo-5-methyl-5-n-amylyhydantoin; trihalomelamine, perborate, percarbonate, and mixtures thereof, wherein halo stands for chloro, bromo, and/or iodo.
3. The bleaching detergent composition of claim 1 or 2 wherein the bleaching agent has a particle size less than 400 μ m, preferably 10 to 200 μ m, most preferably 30-110 μ m.
4. The bleaching detergent composition of any one of claims 1 to 3 wherein the thickening agent is clay or a polymer, preferably selected from a bentonite and a block(co)polymer, or mixtures thereof.
5. The bleaching detergent composition of any one of claims 1 to 4 wherein the auxiliary compound is selected from surfactant, bleach activator, enzyme, colorant, perfume, phosphate, anti-foam agent, inorganic carbonate or hydrogen carbonate, gloss enhancer, sequestering agent, and nonaqueous builder, or mixtures thereof.
6. The bleaching detergent composition of any one of claims 1 to 5 wherein the dispersion comprises 25 to 50%, preferably 35 to 45% by weight of the bleaching agent.
7. The bleaching detergent composition of any one of claims 1 to 6 wherein the dispersion comprises 0.1 to 6%, preferably 0.1 to 4%, more preferably 0.5 to 3% by weight of thickening agent.
8. The bleaching detergent composition of claim 7 wherein the thickening agent is a mixture of a clay and a polymer in a ratio clay : polymer is 1 : 10 to 10 : 1, preferably 1 : 3 to 2 : 1.
9. The bleaching detergent composition of any one of claims 1 to 8 wherein the nonaqueous liquid is paraffin oil.
10. A closed package comprising the bleaching detergent composition of any one of claims 1-9.
11. A method for preparing the bleaching detergent composition of any one of claims 1-9 at least containing a solid bleaching agent and a thickening agent, comprising the steps:
 - i) making at elevated temperature a pre-gel of a polymer and a nonaqueous liquid, which is chemically inert to the bleaching agent and wherein the solubility of the bleaching agent is less than 10 mg/l;
 - ii) making a pre-gel of a clay and the nonaqueous liquid in a high-shear mixer;
 - iii) adding under stirring the pre-gel of ii) to the pre-gel of i), and
 - iv) optionally, adding a thickening agent activator and/or auxiliary compound.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 04 10 3183

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.7)
X	WO 93/22412 A (UNILEVER) 11 November 1993 (1993-11-11) * page 2, lines 34-39 * * page 12, line 19 - page 13, line 15 * * page 15, lines 15-36 * * claims; example 2 * -----	1-11	C11D3/395 C11D3/39 C11D3/12 C11D3/37 C11D3/18
X	GB 2 217 727 A (UNILEVER) 1 November 1989 (1989-11-01) * page 2, line 27 - page 3, line 11 * * page 15, lines 9-15 * * example 11 * -----	1-10	
X	WO 99/61571 A (HENKEL KGAA) 2 December 1999 (1999-12-02) * claims 1-13 * -----	1-7,10	
X	WO 01/66685 A (HENKEL KGAA) 13 September 2001 (2001-09-13) * page 2, last paragraph * * page 11, paragraph 2 - page 12, paragraph 1 * * examples E6,E8,E10 * * claims 1,8,9 * -----	1-10	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C11D
X	WO 98/00507 A (PROCTER & GAMBLE) 8 January 1998 (1998-01-08) * page 3, last paragraph * * page 30, paragraph 4 - page 31, paragraph 3 * * examples III-1; table II * -----	1-10	
X	US 4 655 954 A (BROZE GUY ET AL) 7 April 1987 (1987-04-07) * column 18, lines 24-40 * ----- -/--	1-10	
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 17 December 2004	Examiner Bertran Nadal, J
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			

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EPO FORM 1503 03.82 (P04C01)



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 04 10 3183

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
D,A	US 5 164 106 A (AHMED FAHIM U ET AL) 17 November 1992 (1992-11-17) * column 4, lines 38-51 * * column 7, line 63 - column 8, line 17 * -----	1-11	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 17 December 2004	Examiner Bertran Nadal, J
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			

1
EPO FORM 1503 03/82 (P04/C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 04 10 3183

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The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

17-12-2004

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9322412 A	11-11-1993	AU 4041093 A	29-11-1993
		WO 9322412 A1	11-11-1993
		EP 0672098 A1	20-09-1995
		ZA 9303069 A	30-10-1994
GB 2217727 A	01-11-1989	NONE	
WO 9961571 A	02-12-1999	DE 19822939 A1	25-11-1999
		WO 9961571 A1	02-12-1999
		EP 1080174 A1	07-03-2001
WO 0166685 A	13-09-2001	DE 10011273 A1	20-09-2001
		WO 0166685 A1	13-09-2001
WO 9800507 A	08-01-1998	BR 9710060 A	10-08-1999
		CA 2258626 A1	08-01-1998
		EP 0907707 A2	14-04-1999
		JP 11513068 T	09-11-1999
		JP 3267626 B2	18-03-2002
		WO 9800507 A2	08-01-1998
		US 6165959 A	26-12-2000
US 4655954 A	07-04-1987	AT 396113 B	25-06-1993
		AT 218486 A	15-10-1992
		AU 590781 B2	16-11-1989
		AU 6081086 A	26-02-1987
		BE 905290 A1	19-02-1987
		BR 8603960 A	31-03-1987
		CA 1285844 C	09-07-1991
		CH 671235 A5	15-08-1989
		DE 3626572 A1	26-02-1987
		DK 379486 A	21-02-1987
		EG 18069 A	30-11-1991
		ES 2001237 A6	01-05-1988
		FR 2586424 A1	27-02-1987
		GB 2179365 A ,B	04-03-1987
		GR 862159 A1	24-12-1986
		HK 68892 A	18-09-1992
		IN 170170 A1	22-02-1992
		IT 1196578 B	16-11-1988
		LU 86558 A1	06-03-1987
		MX 168222 B	13-05-1993
		NL 8602119 A	16-03-1987
		NO 863334 A ,B,	23-02-1987
		NZ 216987 A	29-09-1988
		PT 83191 A ,B	01-09-1986

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 04 10 3183

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

17-12-2004

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4655954	A		SE 468598 B	15-02-1993
			SE 8603447 A	21-02-1987
			SG 72792 G	02-10-1992
			ZW 15486 A1	01-07-1987

US 5164106	A	17-11-1992	AU 630689 B2	05-11-1992
			AU 5389590 A	01-11-1990
			BR 9002000 A	13-08-1991
			CA 2015603 A1	28-10-1990
			EP 0395186 A2	31-10-1990
			GR 90100318 A ,B	27-09-1991
			MX 173778 B	28-03-1994
			NO 901909 A	29-10-1990
			NZ 233357 A	28-04-1992
			PL 284965 A1	14-01-1991
			PT 93873 A	20-11-1990
			US 5076952 A	31-12-1991
			AT 120484 T	15-04-1995
			AU 635774 B2	01-04-1993
			AU 6325590 A	18-04-1991
			CA 2027199 A1	11-04-1991
			DE 69018190 D1	04-05-1995
			EP 0423014 A2	17-04-1991
			NZ 235491 A	28-04-1992
			US 5108641 A	28-04-1992
