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(54) STRUCTURED LIQUID DETERGENT COMPOSITION

STRUKTURIERTE FLÜSSIGE REINIGUNGSMITTELZUSAMMENSETZUNG

COMPOSITION DE DÉTERGENT LIQUIDE STRUCTURÉE

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Description

[0001] The present invention relates to an aqueous, phosphate-free, structured liquid detergent composition, in particular a heavy duty liquid detergent (HDL) that comprises a surfactant system comprising an alkyl ether sulfate, a builder system and water, wherein the detergent composition has a viscosity of between 1.000 and 10.000 mPas and is free of stabilizing and rheology modifying acrylate-containing polymers. The invention further relates to methods for washing of textiles using the detergents of the invention.

[0002] Liquid detergent compositions are well-known in the art and widely used. Over recent years, the have become more and more popular with the consumers because they offer a number of advantages over solid compositions, including, for example, the ease of dosing, dispensing and dissolving into a laundering liquor. In addition, they are perceived to be safer and less harsh to the textiles and environment compared to solid compositions. In particular for laundering colored fabrics they have gained popularity ever since their introduction on the market. Aqueous, structured liquid detergent compositions for laundering fabrics not according to the invention are known from the following documents of the prior art: EP 0530708 A2 and EP 2770044 A1.

[0003] Recently, for environmental and regulatory reasons the demand for phosphate-free liquid detergents has increased. However, liquid detergent compositions, in particular phosphate-free heavy duty liquid (HDL) detergents suffer from physical and chemical instability, such as phase separation, sedimentation, degradation of components and the like, and viscosity problems. This is particularly problematic for highly concentrated formulations. While HDL detergents have been introduced as early as the 1970's, the known stable formulations rely on the use of phosphates, in particular sodium tripolyphosphate (STPP), to form structured liquids containing high levels of builders and surfactants. In these built HDLs multilayered vesicles are formed that stabilize the formulation and prevent precipitation of the anionic surfactants by the builder components. These structures are stable and can be characterized by microscopic examination under polarized light and conductivity measurements. STPP was particularly suited to formation of vesicles with sodium alkylbenzene sulfonate (sodium LAS). In addition, STPP was well established as a builder in detergent powders and acts as a chelating agent, inhibits soil re-deposition during the wash and boosts overall detergency. The result of the use of STPP was the development of high performance and low cost HDL. However, as mentioned above, environmental concerns over the use of phosphates, including STPP, in laundry detergents have resulted in phosphate use being banned in some countries and a negative public image in most developed markets. While alternatives to STPP, such as zeolite, sodium citrate, and sodium carbonate, are known, these show poor performance relative to phosphate built HDL. In addition, these formulations suffer from stability problems and require the use of stabilizing and/or rheology modifying polymers, typically acrylates, that are undesirable for cost reasons and may still not suffice to ensure long term stability and the desired viscosity.

[0004] Therefore, there is still need in the art for phosphate-free, structured HDL detergents that overcome at least some of the known issues. Accordingly, it is an object of the present invention to meet this need by providing an aqueous, phosphate-free, structured liquid detergent composition, in particular a HDL detergent that exhibits the desired stability and viscosity.

[0005] It has surprisingly been found by the inventors that this object can be met by a composition that is free of known stabilizing and rheology modifying polymers and comprises a specific surfactant system, builder system and water. It has been demonstrated that such a detergent is stable over a period of 90 days at a temperature of 10-40°C, >12 months when stored between 15° and 30°C. Low temperature stability, for example at about 5°C, can be improved by modifying the system to include a nonionic surfactant.

[0006] In a first aspect, the present invention therefore relates to an aqueous, structured liquid detergent composition comprising a surfactant system, a builder system and water, as defined by claim 1.

[0007] In a further aspect, the invention relates to methods for cleaning textiles, wherein a washing liquor containing the liquid detergent composition of the present invention contacts the textile in at least one method step.

[0008] "At least one", as used herein, relates to one or more, i.e. 1, 2, 3, 4, 5, 6, 7, 8, 9, or more. If used in combination with a compound, the term does not relate to the absolute number of molecules but rather to the number of different types of said compound. "At least one alkyl ether sulfate" thus means that at least one type but that also 2 or more different alkyl ether sulfate types can be present.

[0009] If not indicated otherwise, all viscosities referred to herein are viscosities measured at 25°C by a Brookfield LVT, Spindle No. 3 at 12 rpm.

[0010] If not indicated otherwise, all percentages are by weight relative to the total weight of the composition.

[0011] "Free of", as used herein in relation to a specific type of component, means that the referenced composition does not contain more than 0.5 wt.%, preferably no more than 0.1 wt.%, more preferably no more than 0.05 wt.% of said component relative to the total weight of the composition. Most preferably, said component is not contained at all.

[0012] The detergent compositions of the present invention can be used as detergents for textiles, carpets or natural fibers. In preferred embodiments, the detergents disclosed herein are heavy duty liquid (HDL) detergents.

[0013] The present invention is based on the inventors' surprising finding, that by use of a surfactant system comprising

at least one alkyl ether sulfate in a certain amount structured liquid detergent compositions may be formed that have the desired viscosity and stability without the need for stabilizing or rheology modifying polymers.

[0014] Structured liquids are widely used in the field of detergents. They can either be internally structured by one or more of the primary ingredients, such as the surfactants, and/or by using secondary additives, such as certain salts, polymers and/or silicates. Structuring is used to endow the composition with properties such as a turbid appearance or certain flow properties. Such structured liquids may also contain suspended solids. While structured liquids provide more formulation flexibility compared to isotropic liquids, they often suffer from stability and viscosity problems. The presently disclosed formulations, however, overcome these stability and viscosity problems and provide for compositions that have the desired viscosities while at the same time showing good stability.

[0015] In various embodiments, the liquid detergent compositions of the invention are internally structured in that the surfactant system leads to formation of multilayered vesicles. "Structured", as used herein, therefore means that the compositions are preferably internally structured by formation of multilayered vesicles. "Multilayered vesicles" preferably relates to essentially spherical vesicles that have a multilayered, typically double-layered, shell formed of molecules comprising hydrophobic moieties, with said hydrophobic moieties arranged such that they face each other while the more hydrophilic parts of the molecules face outwards. Said shell can form a vesicle lumen.

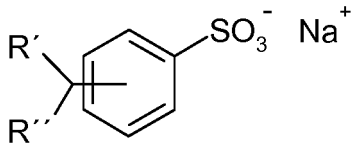
[0016] The detergent compositions of the current invention comprise sodium lauryl ether sulfate with 2 EO, as it is advantageous for achieving the desired viscosity ranges.

[0017] The level of ethoxylation is an average value and can, for a specific compound, be an integer or fractional number.

[0018] The sodium lauryl ether sulfate with 2 EO is contained in the compositions of the invention in an amount of 3.2 to 7.0 wt.% relative to the total weight of the composition, preferably 4.0 to 7.0 wt.%, more preferably 4.5 to 7.0 wt.%, most preferably 5.0 to 6.0 wt.%.

[0019] In various embodiments, the surfactant system further comprises at least one additional anionic surfactant, preferably an alkyl benzene sulfonate.

[0020] Exemplary alkyl benzene sulfonates include, but are not limited to linear and branched alkyl benzene sulfonates, preferably linear alkyl benzene sulfonates. Exemplary compounds are those of formula (III)



(III),

wherein R' and R" are independently H or alkyl and combined comprise 9 to 19, preferably 9 to 15 and more preferably 9 to 13 carbon atoms. Particularly preferred are dodecyl and tridecyl benzene sulfonates, in particular the sodium salts thereof. Preferred contents range from 6.8 to 19.0 wt.%, preferably 9.0 to 17.0 wt.%, more preferably 10.0 to 15.0 wt.% relative to the total weight of the composition.

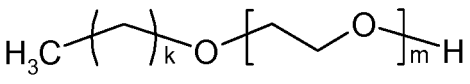
[0021] In addition, the compositions of the invention may further comprise one or more nonionic surfactants. Preferred nonionic surfactants are those of formula (IV)

$$R^2\text{-O-(AO)}_m\text{-H} \qquad \text{(IV)},$$

wherein R^2 represents a linear or branched substituted or unsubstituted alkyl moiety, AO represents an ethylene oxide (EO) or propylene oxide (PO) group and m is an integer from 1 to 50. In formula (IV) R^2 preferably represents a linear or branched, substituted or unsubstited alkyl group, preferably a linear, unsubstituted alkyl group, particularly preferred a fatty alcohol group. Preferred groups are R^2 are selected from decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl groups and combinations thereof, wherein those groups with an even number of carbon atoms are preferred. Particularly preferred are R^2 groups derived from C_{12}-C_{18} fatty alcohols, such as coconut oil alcohol, tallow oil alcohol, lauryl, myristyl, cetyl or stearyl alcohol or from C_{10}-C_{20} oxoalcohols.

[0022] AO represents an ethyleneoxide (EO) or propyleneoxide (PO) group, preferably an ethyleneoxide group. The index m represents an integer from 1 to 50, preferably from 1 to 20 and more preferably from 1 to 6. Particularly preferably, m is 1, 2, 3, 4 or 5, most preferably 3-5, as higher degrees of ethoxylation may negatively influence viscosity and stability.

[0023] In various preferred embodiments, the detergent compositions comprise an alkyl ether selected from fatty alcohol ethers of formula (V)



(V)

wherein k = 11 to 19, m = 1, 2, 3, 4, 5, 6, 7 or 8. Preferred are C_{12-18} fatty alcohols with 1-6 EO (k = 11-17, m = 1-5 in formula (V)). More preferred are C_{12-14} alcohols having 1-5 EO, most preferred are C_{12-14} alkyl ethers with 3-5 EO, in particular lauryl ether with 5 EO.

[0024] Such nonionic alkyl ethers may be contained in the formulation in amounts of 0.0 to 10 wt.%, preferably 0.5 to 8.0 wt.%, more preferably 2.0 to 6.0 wt.%. It has been found that the addition of such nonionic alkyl ether surfactants positively influences physical stability of the composition at low temperatures, i.e. temperatures around or below 10°C, particularly below 4°C, in that they prevent formation of solid particles or crystals in the liquid composition.

[0025] The detergents may further include other nonionic surfactants, such as alkyl glucosides of the general formula $RO(G)_x$, where R is a primary linear or 2-methyl-branched aliphatic radical containing 8 to 22 and preferably 12 to 18 carbon atoms and G stands for a glucose unit. The degree of oligomerization x, which indicates the distribution of monoglucosides and oligoglucosides, is a number of 1 to 10 and preferably a number of 1.2 to 1.4. However, in preferred embodiments, the compositions do not include such alkyl glucosides.

[0026] In various embodiments, the surfactant system therefore comprises at least two anionic surfactants, namely the at least one alkyl ether sulfate and preferably at least one alkyl benzene sulfonate, and optionally at least one alkyl ether.

[0027] The compositions may preferably comprise 15.0 to 20.0 wt.% of the surfactant system. Said surfactant system preferably comprise 9.0 to 17.0 wt.%, more preferably 10.0 to 15.0 wt.% of a linear alkyl benzene sulfonate, preferably dodecyl or tridecyl benzene sulfonate, and (3) 0.0 to 10 wt.%, preferably 0.5 to 8.0 wt.%, more preferably 2.0 to 6.0 wt.% C_{12-18} alkyl ethers with 1-6 EO, preferably C_{12-14} alkyl ethers having 1-5 EO, most preferably lauryl ether with 5 EO. All afore-mentioned percentages relate to the total weight of the composition. To avoid formation of solid particles at low temperatures, as described above, it may be advantageous to include the above-described alkyl ethers.

[0028] In various embodiments, the compositions of the invention have a conductivity of ≤15mS, preferably ≤11 mS, more preferably ≤10 mS. Conductivity can, for example, be measured by using an Oakton CON700 Conductivity meter, preferably standardized using a 12.88 milli-Siemens reference standard. Conductivity measurements can be carried out according to the EN ISO 7888:1985 standard. It has been found that compositions having a low conductivity are more stable and less prone to a viscosity decrease over extended periods of storage. Accordingly, "stable" or "stability" in the sense of the present invention refers to the property of a detergent composition to substantially maintain its viscosity, i.e. a viscosity decrease of no more than 10%, over extended periods of storage, for example more than 60 days at temperatures of about 20°C. In addition, said term means that the composition remains homogeneous, i.e. without any visible phase separation over the same period.

[0029] It has surprisingly been found that said stability can be achieved without the presence of any stabilizing or rheology modifying (thickening) polymers. To the contrary, it has been found that said polymers adversely affect stability of the liquid compositions disclosed herein in that such compositions are much more susceptible to loss of viscosity over extended periods of storage. Said polymers include all polymers known and used for said purposes in the art, in particular polyacrylates and polyacrylic acids as well as all homo- and copolymers including monomeric units derived from acrylates and/or acrylic acid. If reference is herein made to "acrylates" or "acrylic acid" and derivatives thereof, said terms include "methacrylates" and "methacrylic acid" as well as the various acrylic acid esters known in the art, such as methyl(meth)acrylate, ethyl(meth)acrylate, etc.. Examples of such acrylate polymers that are not contained in the liquid detergent compositions comprise, but are not limited to, polymers of the Acusol® series (Dow Chemicals, Midland, USA), Alcosperse® series, Aquatreat® series (both Akzo Nobel, Amsterdam, The Netherlands), Good-rite® series (Emerald Performance Materials, Cuyahoga Falls, USA), Junlon® series, Jurymer® series, Rheogic® series, Aron® series (all Toagosei Co., Ltd., Tokyo, Japan), Glascol® series (BASF, Ludwigshafen, Germany), Aqualic® series (Nippon Shokubai Co., Ltd., Osaka, Japan), Carbopol® series and Carboset® series (both The Lubrizol Corporation, Wickliffe, USA).

[0030] The compositions of the invention further comprise a builder system as defined in claim 1. The builder system is a phosphate-free builder system, as the composition is free of phosphates. However, although not preferred, the composition may comprise phosphonates. Accordingly, the term "phosphate-free", as used herein does not refer to phosphonates. In preferred embodiments, the compositions are phosphate- and phosphonate-free.

[0031] If the compositions comprise phosphonates, the phosphonates are preferably hydroxyalkane and/or amino alkane phosphonates, such as 1-hydroxyethane-1,1-diphosphonate (HEDP), ethylenediamine tetramethylene phosphonate (EDTMP), diethylenetriamine pentamethylene phosphonate (DTPMP), and lysine tetramethylene phosphonate (LTMP). If present, phosphonates are used in amounts of 0.1 to 10.0 wt.%, preferably 0.5 to 8.0 Gew.-%, more preferably 0.1 to 1.5 wt.%. The total phosphorus content of the detergents is preferably less than 0.5% by weight.

[0032] Suitable builders include, without limitation, inorganic builders, such as silicates, aluminosilicates (particularly

zeolite), and carbonates, as well as organic builders, such as organic di- and polycarboxylic acids, aminocarboxylic acids and combinations thereof. Preferred in the liquid compositions of the invention are carbonates, di- and polycarboxylic acids and aminocarboxylic acids. Also suitable are alkali metal hydroxides, in particular sodium hydroxide, but these are, besides their use for pH control, not preferred.

[0033] Suitable carbonates include alkali metal carbonates, hydrogen carbonates and sesquicarbonates, with alkali metal carbonates, in particular sodium carbonate being preferred.

[0034] In the current invention, inorganic builders, in particular water-soluble inorganic builders, preferably carbonates, are used in amounts of up to 5 wt.% relative to the total weight of the composition. In preferred embodiments, carbonate, preferably sodium carbonate, is used in amounts of 1.0 to 5.0 wt.%, preferably 2.0 to 4.0 wt.%. It has been found that amounts higher than 5 wt.% adversely affect the stability of the composition.

[0035] Suitable organic builders include polycarboxylic acids which can be used as free acids or in form of their salts, including, but not limited to, citric acid, adipic acid, succinic acid, glutaric acid, malic acid, tartric acid, maleic acid, fumaric acid, and sugar acids. In addition to their builder properties, the free acids can also be used for pH control. Preferred are citric acid, succinic acid, glutaric acid, adipic acid and gluconic acid, and combinations thereof.

[0036] Particularly preferred are citric acid and their salts, i.e. citrates. In various embodiments, the polycarboxylic acids, in particular citric acid/citrate, are contained in the compositions of the invention in amounts of 3.5 to 25.0 wt.%, preferably 4.0 to 10.0 wt.%.

[0037] In addition to the afore-mentioned builders, the compositions preferably also include aminocarboxylic acids or salts thereof, i.e. aminocarboxylates. In various embodiments, the aminocarboxylic acids/aminocarboxylates are selected from the group consisting of L-glutamic acid N,N-diacetic acid (GLDA), methyl glycine diacetic acid (MGDA), imino disuccinic acid (IDS), ethylenediamine N,N'-disuccinic acid (EDDS), diethylenetriamine pentaacetic acid (DTPA), beta-alanine N,N-diacetic acid, hydroxyethylenediamine triacetic acid (HEDTA), and alkali metal salts thereof as well as combinations of any one of more of the afore-mentioned, preferably GLDA tetrasodium salt.

[0038] The aminocarboxylates are preferably used in amounts of 0.5 to 5.0 wt.%, preferably 1.0 to 4.0 wt.%.

[0039] In various embodiments, the detergent compositions comprise a builder system comprising relative to the total weight of the composition:

(1) 0.5 to 5.0 wt.-%, preferably 1.0 to 4.0 wt.-% of an aminocarboxylate, preferably GLDA tetrasodium salt;
(2) 1.0 to 5.0 wt.-%, preferably 2.0 to 4.0 wt.-% carbonate, preferably sodium carbonate; and
(3) 3.5 to 25.0 wt.-%, preferably 4 to 10 wt.-% citrate, preferably sodium citrate.

[0040] Further organic builders include polymeric polycarboxylates, polyacetals, dextrins and others. It is however preferred that the compositions are free of these other types of organic builders. It is particularly preferred that the compositions are free of polymeric organic builders, in particular (meth)acrylate-containing builders.

[0041] In the current invention, the builder system is comprised in the compositions in an amount of 5.0 to 25.0 wt.%, preferably 10.0 to 15.0 wt.%.

[0042] The detergent compositions of the invention are aqueous liquid compositions and as such comprise 50.0 to 85 wt.% water, preferably 65.0 to 75.0 wt.%.

[0043] The pH value of the detergents according to the invention is generally in the range of from 7 to 12, preferably in the range from 7 to 10.5. Relatively high pH values, for example above 9, may be adjusted by the use of small quantities of sodium hydroxide or alkaline salts, such as sodium carbonate. The liquid detergents are typically opaque, are flowable, and may be poured under the sole effect of gravity without any need for other shear forces to be applied. Their viscosity is generally greater than 1,000 mPas (Brookfield viscosimeter, spindle 3, 12 rpm, 25° C), namely in the range of between 1,000 and 10,000 mPas, preferably between 2,000 and 6,000 mPas.

[0044] In addition to the ingredients mentioned above, however, the detergents may commonly contain at least one, preferably two or more other substances selected from the group consisting of soaps, pH adjusting agents, perfumes, fluorescing agents (optical brighteners), dyes, colorants, antimicrobial active substances, germicides, fungicides, anti-oxidants, preservatives, and softening compounds.

[0045] Further possible ingredients include silicone oils, anti-redeposition agents, anti-greying agents, shrinkage preventers, wrinkle protection agents, dye transfer inhibitors, corrosion inhibitors, antistatic agents, bittering agents, ironing adjuvants, proofing and impregnation agents, swelling and anti-slip agents, complexing agents and UV absorbers.

[0046] Also included may be bleaching agents, bleach activators, bleach catalysts, and enzymes, however, in various embodiments, the compositions are free of those.

[0047] For cold wash properties, it can be beneficial to additionally include soaps. Accordingly, in some embodiments, the detergent compositions further comprise relative to their total weight 0.25 to 15 wt.%, preferably 0.5 to 12.5 wt.%, more preferably 1.0 to 10.0 wt.%, even more preferably 1.5 to 7.5 wt.% and most preferably 2.0 to 6.0 wt.% soaps. Preferred are soaps from C_{12}-C_{18} fatty acids, i.e. the salts of lauric acid, myristic acid, palmitic acid, stearic acid, or mixtures derived from natural fatty acids, for example coconut, palm kernel, olive oil, or tallow fatty acids.

[0048] Further ingredients that are commonly used include colorants, perfumes and optical brighteners, as well as pH adjusting agents. All of these ingredients are well-known in the art and readily available.

[0049] The present invention further relates to methods for cleaning textiles, wherein a washing liquor containing the liquid detergent composition of the present invention contacts the textile in at least one method step. The methods are preferably carried out in an automatic washing machine.

[0050] Methods for cleaning of textiles are generally characterized by the fact that in several different process steps various cleaning-active substances are applied to the textiles and after the contact time said cleaning-active substances are washed off, or that the textiles are treated in any other way with a detergent or a solution of said substance.

[0051] All embodiments described herein in relation to the compositions of the invention are similarly applicable to the methods of the invention and vice versa.

Examples

Example 1:

[0052] The following formulations were made:

Table 1: 35ml Dose and 45ml Dose Formulations (not according to the invention)

Ingredient	grams per wash	35mL Dose Formula (wt.%)	45mL Dose Formula (wt.%)	Addition Order	Oberservations during manufacture
Deionised Water	24.127	58.420%	67.990%	1	Clear liquid
Optical brightener	0.074	0.180%	0.140%	2	Clear vellow liquid
Sodium LAS	6.608	16.000%	12.440%	3	Clear vellow liquid
Citric Acid	3.098	7.500%	5.540%	4	Grainy suspension
Sodium Hydroxide	0.516	1.250%	0.935%	5	Grainy suspension
Tetrasodium GLDA	1.652	4.000%	3.110%	6	Grainy suspension
Sodium Carbonate	2.065	5.000%	3.890%	7	Grainy suspension
Sodium Laureth-2 Sulfate	1.652	4.000%	3.110%	8	Grainy suspension
Fragrance	0.372	0.900%	0.700%	9	Grainy suspension
Colorant	0.002	0.006%	0.006%	10	Grainy suspension
Polymeric builder (polyacrylate)	0.537	1.300%	1.040%	11	Smoother but grainy
Polymeric stabilizer (polyacrylate)	0.083	0.200%	0.160%	12	Smooth and stable

[0053] In the market context, historical dosage of laundry liquids was approximately 100 mLs. Thus a 3X concentrate formula would have a dosage range of 30 to 35mLs while a 2X concentrate would have a dosage of 45 to 55mLs. Initial work was to develop a 3X Concentrate formula which equated to a 35mL dose. A 45mL dose formula was then prepared by dilution of the 35mL dose formula with water to achieve the same grams/wash of ingredients. It was observed that the diluted formula had a very low viscosity <1000 mPas (Brookfield LVT No 3 spindle, 12 rpm measured at 25°C) which was below the desired range of 2000 to 6000 mPas. Despite the low viscosity, the formula was still stable. These formulations demonstrate the need to include a polymeric stabilizer to achieve stable formulations.

[0054] In order to increase viscosity, the concentration of SLES was increased from 3.2 wt.-% to wt.-% 6.1%. The resultant viscosity was >10,000 mPas. This viscosity was unacceptably high. While the batch was very thick there was a surprising observation that after SLES was added the appearance changed from a grainy suspension to very smooth and stable formula.

[0055] To investigate the structure and stability of the formulations, a polarizing light microscope and conductivity meter were used.

[0056] Microscopy was carried out using a Nikon Eclipse Ci-L optical microscope with polarizing light filter. A sample

was placed on a glass slide and spread to a thin layer and observed under 40X magnification.

[0057] Minitab® statistical software was used to design a set of experiments to identify the optimum formula in terms of stability and viscosity. A series of laboratory batches were prepared with varying levels of sodium carbonate, SLES and a polymeric thickener (Acusol® 810A). The results of this study were:

- conductivity >11 milli-Siemens leads to instability with respect to maintenance of the desired viscosity; Conductivity was measured using an Oakton CON700 Conductivity meter. The meter was standardized daily using a 12.88 milli-Siemens reference standard.
- >5 wt.-% soda ash causes instability (crystal formation) below 10°C;
- all variations showed viscosity decrease over time; and
- all variations showed conductivity increase over time.

[0058] There was a clear trend that samples without polymers, in particular acrylates, had conductivities <10 and displayed higher viscosity stability over time. Accordingly, the following batch was made:

Table 2: Formulations with and without polymers (formulations 13-154C and 13-154H are not according to the invention)

Ingredient	13-154C	13-154H	13-397
Deionised Water	67.564%	67.294%	66.104%
Optical brightener	0.140%	0.140%	0.140%
Sodium LAS	12.440%	12.440%	12.440%
Citric Acid	5.540%	5.540%	5.540%
Sodium Hydroxide	2.400%	2.400%	2.400%
Tetrasodium GLDA	3.110%	3.110%	3.110%
Sodium Carbonate	3.890%	3.890%	3.890%
Fragrance	0.470%	0.470%	0.470%
Colorant	0.006%	0.006%	0.006%
Sodium Laureth-2 Sulfate	3.110%	3.110%	5.900%
Polymeric builder (polyacrylate)	1.040%	1.040%	0.000%
Polymeric stabilizer (polyacrylate)	0.200%	0.200%	0.000%
Acusol 810A	0.090%	0.360%	0.000%
All % are wt.%.			

[0059] Surprisingly, formula 13-397 was found to be stable. Based on the success further laboratory batches were prepared with a variety of fragrances as well as an unfragranced variant. All showed excellent stability. Manufacture of 13-397 was scaled up to 200kg.

[0060] Data comparing conductivity and viscosity changes over time are presented in Figures 1 and 2. Formulations 13-154C and 13-154H were the most stable formulations found that contain polymeric builders and stabilizers (Acusol® 420N and Alcosperse® 325) as well as polxmeric thickeners (Acusol® 810A) to increase viscosity. Formula 13-397 does not contain said polymers and is as described in Table 2. The data shows that formula 13-397 has a stable conductivity and viscosity over time, while reference formulations with polymer increase in conductivity and decrease in viscosity.

[0061] A further enhancement was to include a nonionic surfactant to improve stability with respect to phase separation and solid particle agglomeration, particularly with respect to the optical brightener at low temperatures (<4°C). Refer to Table 3.

Table 3 - Example Formulation with Nonionic Surfactant

Ingredient	**wt.%**
Water	65.583
Optical Brightener	0.124

(continued)

Ingredient	wt.%
Sodium LAS	11.000
Silicone Antifoam	0.100
Tetrasodium GLDA	3.100
Sodium Hydroxide	3.160
Citric Acid	5.500
Sodium Cabronate	3.900
Laureth-5	2.500
Dye	0.003
Sodium Laureth-2 Sulfate	4.560
Fragrance	0.470

Claims

1. Aqueous, structured liquid detergent composition comprising a surfactant system, a builder system and water and not more than 0.5 wt.% phosphate, wherein

- the composition comprises relative to the total weight of the composition

  (a) 10.0 to 25.0 wt.-%. preferably 15.0 to 20.0 wt.-% of the surfactant system,
  (b) 5.0 to 25.0 wt.-%. preferably 10.0 to 15.0 wt.-% of the builder system,
  (c) 50.0 to 85.0 wt.-%. preferably 65.0 to 75.0 wt.-% water

- wherein the builder system comprises

  (1) at least two organic builders, preferably selected from aminocarboxylates, citrate and combinations thereof; and
  (2) at least one inorganic builder, preferably water-soluble inorganic builder, more preferably carbonate; wherein the amount of inorganic builder is ≤5 wt.-% relative to the total weight of the composition.

- and wherein

  (A) the surfactant system comprises sodium lauryl ether sulfate with 2 EO in an amount of between 3.2 and 7.0 wt.-% relative to the total weight of the composition;
  (B) the composition has a viscosity of between 1,000 and 10,000 mPas at 25°C (Brookfield LVT, Spindle No. 3, 12 rpm), preferably 2,000 to 6,000 mPas; and
  (C) the composition is free of acrylate-containing polymers.

2. The detergent composition according to claim 1, wherein the conductivity of the composition is ≤15 mS, preferably ≤11 mS, more preferably ≤10 mS.

3. The detergent composition according to claim 1 or 2, wherein

(2) the surfactant system further comprises an alkyl benzene sulfonate, preferably a linear alkyl benzene sulfonate (LAS), more preferably a C_{9-13} alkyl benzene sulfonate, most preferably a linear C_{12-13} alkyl benzene sulfonate; and/or
(3) the surfactant system further comprises a nonionic surfactant, preferably a C_{12-18} alkyl ether with 1-6 EO, more preferably a C_{12-14} alkyl ether with 3-5 EO, most preferably a C_{12} alkyl ether with 5 EO.

4. The detergent composition according to claim 1, wherein the aminocarboxylate is selected from the group consisting

of L-glutamic acid N,N-diacetic acid (GLDA), methyl glycine diacetic acid (MGDA), imino disuccinic acid (IDS), ethylenediamine N,N'-disuccinic acid (EDDS), diethylenetriamine pentaacetic acid (DTPA), beta-alanine N,N-diacetic acid, hydroxyethylenediamine triacetic acid (HEDTA), and alkali metal salts thereof, preferably GLDA tetrasodium salt.

5. The detergent composition according to any one of claims 1 to 4, wherein the surfactant system comprises relative to the total weight of the detergent composition:

(a1) 3.2 to 7.0 wt.%, preferably 4.5 to 7.0 wt.% C_{10-16} alkyl ether sulfates with 1 to 7 EO, preferably C_{12-14} fatty alcohol ether sulfates with 1-3 EO, more preferably lauryl ether sulfate with 2 EO;
(a2) 6.8 to 19.0, preferably 9.0 to 17.0 wt.%, more preferably 10.0 to 15.0 wt.% of a linear C_{9-13} alkyl benzene sulfonate, preferably dodecyl or tridecyl benzene sulfonate; and
(a3) 0.0 to 10 wt.%, preferably 0.5 to 8.0 wt.%, more preferably 2.0 to 6.0 wt.% C_{12-18} alkyl ethers with 1-6 EO, preferably C_{12-14} alkyl ethers having 3-5 EO, most preferably lauryl ether with 5 EO.

6. The detergent composition according to any one of claims 1 to 5, wherein the builder system comprises relative to the total weight of the detergent composition:

(b1) 0.5 to 5.0 wt.-%, preferably 1.0 to 4.0 wt.-% of an aminocarboxylate, preferably GLDA tetrasodium salt;
(b2) 1.0 to 5.0 wt.-%, preferably 2.0 to 4.0 wt.-% carbonate, preferably sodium carbonate; and
(b3) 3.5 to 25.0 wt.-%, preferably 4 to 10 wt.-% citrate, preferably sodium citrate.

7. The detergent composition according to any one of claims 1 to 6, wherein the detergent composition further comprises at least one, preferably two or more other substances selected from the group consisting of soaps, pH adjusting agents, perfumes, fluorescing agents (optical brighteners), dyes, colorants, antimicrobial active substances, germicides, fungicides, antioxidants, preservatives, and softening compounds.

8. Method for cleaning textiles, wherein a washing liquor containing the detergent composition according to any one of claims 1 to 7 contacts the textile in at least one method step.

Patentansprüche

1. Wässrige, strukturierte Flüssigwaschmittelzusammensetzung, umfassend ein Tensidsystem, ein Buildersystem und Wasser und nicht mehr als 0,5 Gew.-% Phosphat, wobei

- die Zusammensetzung relativ zu dem Gesamtgewicht der Zusammensetzung umfasst

(a) 10,0 bis 25,0 Gew.-%, bevorzugt 15,0 bis 20,0 Gew.-%, des Tensidsystems,
(b) 5,0 bis 25,0 Gew.-%, bevorzugt 10,0 bis 15,0 Gew.-%, des Buildersystems,
(c) 50,0 bis 85,0 Gew.-%, bevorzugt 65,0 bis 75,0 Gew.-%, Wasser

- wobei das Buildersystem umfasst

(1) mindestens zwei organische Builder, die bevorzugt aus Aminocarboxylaten, Citraten und Kombinationen davon ausgewählt sind; und
(2) mindestens einen anorganischen Builder, bevorzugt wasserlösliche anorganische Builder, weiter bevorzugt Carbonat;
wobei die Menge an anorganischem Builder $\leq$5 Gew.-% relativ zu dem Gesamtgewicht der Zusammensetzung ist.

- und wobei

(A) das Tensidsystem Natriumlaurylethersulfat mit 2 EO in einer Menge zwischen 3,2 und 7,0 Gew.-% relativ zu dem Gesamtgewicht der Zusammensetzung umfasst;
(B) die Zusammensetzung eine Viskosität zwischen 1.000 und 10.000 mPas bei 25 °C (Brookfield LVT, Spindel Nr. 3, 12 U/min), bevorzugt 2.000 bis 6.000 mPas aufweist; und
(C) die Zusammensetzung frei von acrylathaltigen Polymeren ist.

2. Waschmittelzusammensetzung nach Anspruch 1, wobei die Leitfähigkeit der Zusammensetzung ≦15 mS, bevorzugt ≤11 mS, weiter bevorzugt ≤10 mS, ist.

3. Waschmittelzusammensetzung nach Anspruch 1 oder 2, wobei

(2) Tensidsystem ferner ein Alkylbenzolsulfonat, bevorzugt ein lineares Alkylbenzolsulfonat (LAS), weiter bevorzugt ein C_{9-13}-Alkylbenzolsulfonat, am meisten bevorzugt ein lineares C_{12-13}-Alkylbenzolsulfonat, umfasst; und/oder
(3) das Tensidsystem ferner ein nichtionisches Tensid, bevorzugt ein C_{12-18}-Alkylether mit 1-6 EO, weiter bevorzugt ein C_{12-14}-Alkylether mit 3-5 EO, am meisten bevorzugt ein C_{12}-Alkylether mit 5 EO umfasst.

4. Waschmittelzusammensetzung nach Anspruch 1, wobei das Aminocarboxylat aus der Gruppe ausgewählt ist, die aus L-Glutaminsäure-N,N-Diessigsäure (GLDA), Methylglycindiessigsäure (MGDA), Iminodibernsteinsäure (IDS), Ethylendiamin-N,N'-Dibernsteinsäure (EDDS), Diethylentriaminpentaessigsäure (DTPA), Beta-Alanin-N,N-diessigsäure, Hydroxyethylendiamintriessigsäure (HEDTA) und Alkalimetallsalzen davon, bevorzugt GLDA-Tetranatriumsalz besteht;

5. Waschmittelzusammensetzung nach einem der Ansprüche 1 bis 4, wobei das Tensidsystem relativ zu dem Gesamtgewicht der Waschmittelzusammensetzung umfasst:

(a1) 3,2 bis 7,0 Gew.-%, bevorzugt 4,5 bis 7,0 Gew.-% C_{10-16}-Alkylethersulfate mit 1 bis 7 EO, bevorzugt C_{12-14}-Fettalkoholethersulfate mit 1-3 EO, weiter bevorzugt Laurylethersulfat mit 2 EO;
(a2) 6,8 bis 19,0, bevorzugt 9,0 bis 17,0 Gew.-%, weiter bevorzugt 10,0 bis 15,0 Gew.-% eines linearen C_{9-13}-Alkylbenzolsulfonat, bevorzugt Dodecyl- oder Tridecylbenzolsulfonat; und
(a3) 0,0 bis 10 Gew.-%, bevorzugt 0,5 bis 8,0 Gew.-%, weiter bevorzugt 2,0 bis 6,0 Gew.-% C_{12-18}-Alkylether mit 1-6 EO, bevorzugt C_{12-14}-Alkylether mit 3-5 EO, am meisten bevorzugt Laurylether mit 5 EO.

6. Waschmittelzusammensetzung nach einem der Ansprüche 1 bis 5, wobei das Buildersystem relativ zu dem Gesamtgewicht der Waschmittelzusammensetzung umfasst:

(b1) 0,5 bis 5,0 Gew.-%, bevorzugt 1,0 bis 4,0 Gew.-% eines Aminocarboxylats, bevorzugt GLDA-Tetranatriumsalz;
(b2) 1,0 bis 5,0 Gew.-%, bevorzugt 2,0 bis 4,0 Gew.-% Carbonat, bevorzugt Natriumcarbonat; und
(b3) 3,5 bis 25,0 Gew.-%, bevorzugt 4 bis 10 Gew.-% Citrat, bevorzugt Natriumcitrat.

7. Waschmittelzusammensetzung nach einem der Ansprüche 1 bis 6, wobei die Waschmittelzusammensetzung ferner mindestens einen, bevorzugt zwei oder mehr Stoffe umfasst, die aus der Gruppe ausgewählt sind, die aus Seifen, pH-Wert einstellenden Mitteln, Duftstoffen, fluoreszierenden Mitteln (optischen Aufhellern), Farbstoffen, Farbmitteln, antimikrobiellen Stoffen, Desinfektionsmitteln, Fungiziden, Antioxidantien, Konservierungsmitteln und Weichmacherverbindungen besteht.

8. Verfahren zum Reinigen von Textilien, wobei eine Waschflotte, die die Waschmittelzusammensetzung nach einem der Ansprüche 1 bis 7 enthält, das Textil in mindestens einem Verfahrensschritt berührt.

Revendications

1. Composition détergente liquide structurée aqueuse comprenant un système tensioactif, un système adjuvant et de l'eau et pas plus de 0,5% en poids de phosphate, dans laquelle

- la composition comprend, par rapport au poids total de la composition

(a) 10,0 à 25,0 % en poids, de préférence 15,0 à 20,0 % en poids du système tensioactif,
(b) 5,0 à 25,0 % en poids, de préférence 10,0 à 15,0 % en poids du système adjuvant,
(c) 50,0 à 85,0 % en poids, de préférence 65,0 à 75,0 % en poids d'eau

- le système adjuvant comprenant

(1) au moins deux adjuvants organiques, de préférence choisis parmi les aminocarboxylates, le citrate et leurs combinaisons ; et
(2) au moins un adjuvant inorganique, de préférence un adjuvant inorganique soluble dans l'eau, plus préférablement le carbonate ;
la quantité d'adjuvant inorganique étant de ≤ 5 % en poids par rapport au poids total de la composition.

- et

(A) le système tensioactif comprenant du lauryléthersulfate de sodium à 2 EO en une quantité comprise entre 3,2 et 7,0 % en poids par rapport au poids total de la composition ;
(B) la composition ayant une viscosité comprise entre 1000 et 10000 mPas à 25 °C (Brookfield LVT, broche n° 3, 12 tours par minute), de préférence de 2000 à 6000 mPas ; et
(C) la composition étant exempte de polymères contenant des acrylates.

2. Composition détergente selon la revendication 1, dans laquelle la conductivité de la composition est ≤ 15 mS, de préférence ≤ 11 mS, plus préférablement ≤ 10 mS.

3. Composition détergente selon la revendication 1 ou 2, dans laquelle

(2) le système tensioactif comprend en outre un sulfonate de benzène d'alkyle, de préférence un benzènesulfolnate d'alkyle à chaîne droite (LAS), plus préférablement un benzènesulfonate d'alkyle en C_9 à C_{13}, encore plus préférablement un benzènesulfonate d'alkyle à chaîne droite en C_{12} à C_{13} ; et/ou
(3) le système tensioactif comprend en outre un tensioactif non ionique, de préférence un éther d'alkyle en C_{12} à C_{18} ayant 1 à 6 EO, plus préférablement un éther d'alkyle en C_{12} à C_{14} ayant 3 à 5 EO, encore plus préférablement un éther d'alkyle en C_{12} ayant 5 EO.

4. Composition détergente selon la revendication 1, dans laquelle l'aminocarboxylate est choisi dans le groupe constitué par l'acide N, N-diacétique de l'acide L-glutamique (GLDA), l'acide méthyl glycine diacétique (MGDA), l'acide iminodisuccinique (IDS), l'acide éthylènediamine N, N'-disuccinique (EDDS), l'acide diéthylènetriaminepentaacétique(DTPA), la bêta-alanine, l'acide N, N-diacétique, l'acide hydroxyéthylènediamine triacétique (HEDTA) et leurs sels de métaux alcalins, de préférence le sel de tétrasodium GLDA.

5. Composition détergente selon l'une quelconque des revendications 1 à 4, dans laquelle le système tensioactif comprend, par rapport au poids total de la composition détergente :

(a1) 3,2 à 7,0 % en poids, de préférence 4,5 à 7,0 % en poids d'alkyléthersulfates en C_{10} à C_{16} ayant 1 à 7 EO, de préférence d'éthersulfates d'alcools gras en C_{12} à $_{14}$ ayant 1 à 3 EO, plus préférablement de lauryléthersulfate avec 2 EO ;
(a2) de 6,8 à 19,0, de préférence de 9,0 à 17,0 % en poids, plus préférablement de 10,0 à 15,0 % en poids d'un benzènesulfonate d'alkyle à chaîne droite en Cg à C_{13}, de préférence de dodécylbenzènesulfonate ou de tridécylbenzènesulfonate ; et
(a3) 0,0 à 10 % en poids, de préférence 0,5 à 8,0 % en poids, plus préférablement 2,0 à 6,0 % en poids d'éthers d'alkyle en C_{12} à C_{18} ayant 1 à 6 EO, de préférence d'éthers d'alkyle en C_{12} à C_{14}, ayant 3 à 5 EO, encore plus préférablement l'éther de lauryle ayant 5 EO.

6. Composition détergente selon l'une quelconque des revendications 1 à 5, dans laquelle le système adjuvant comprend, par rapport au poids total de la composition détergente :

(b1) 0,5 à 5,0 % en poids, de préférence 1,0 à 4,0 % en poids d'un aminocarboxylate, de préférence le sel de GLDA tétrasodique ;
(b2) 1,0 à 5,0 % en poids, de préférence 2,0 à 4,0 % en poids de carbonate, de préférence de carbonate de sodium ; et
(b3) 3,5 à 25,0 % en poids, de préférence 4 à 10 % en poids de citrate, de préférence de citrate de sodium.

7. Composition détergente selon l'une quelconque des revendications 1 à 6, dans laquelle la composition détergente comprend en outre au moins une, de préférence deux ou plusieurs autres substances choisies dans le groupe constitué des savons, des correcteurs d'acidité, des parfums, des agents fluorescents (agents d'azurage optique), des teintures, des colorants, des substances actives antimicrobiennes, des germicides, des fongicides, des antioxy-

dants, des conservateurs et des composés adoucissants.

8. Procédé de nettoyage de textiles, dans lequel une liqueur de lavage contenant la composition détergente selon l'une quelconque des revendications 1 à 7 est en contact avec le textile lors d'au moins une étape du procédé.

Figure 1 – Conductivity Stability Data

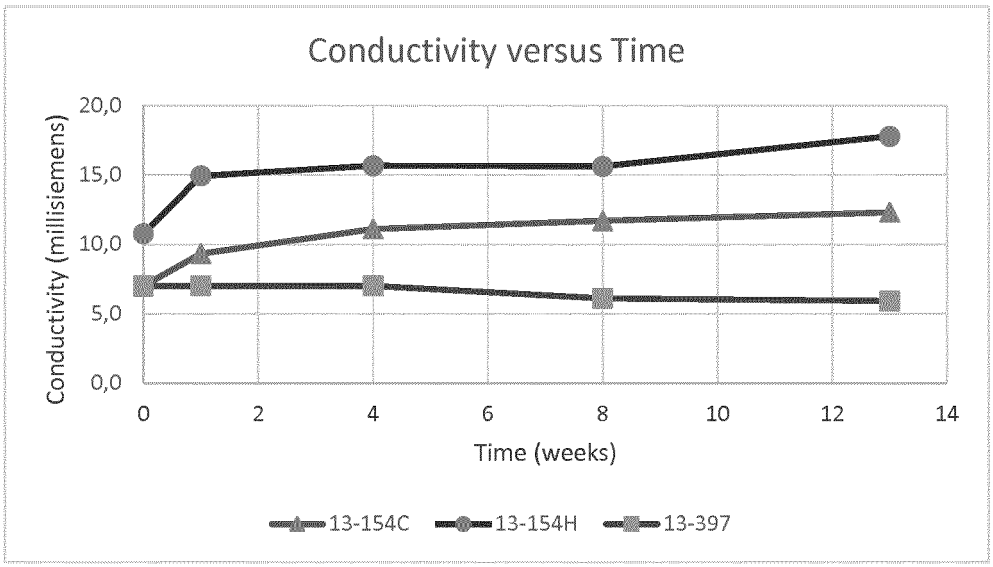
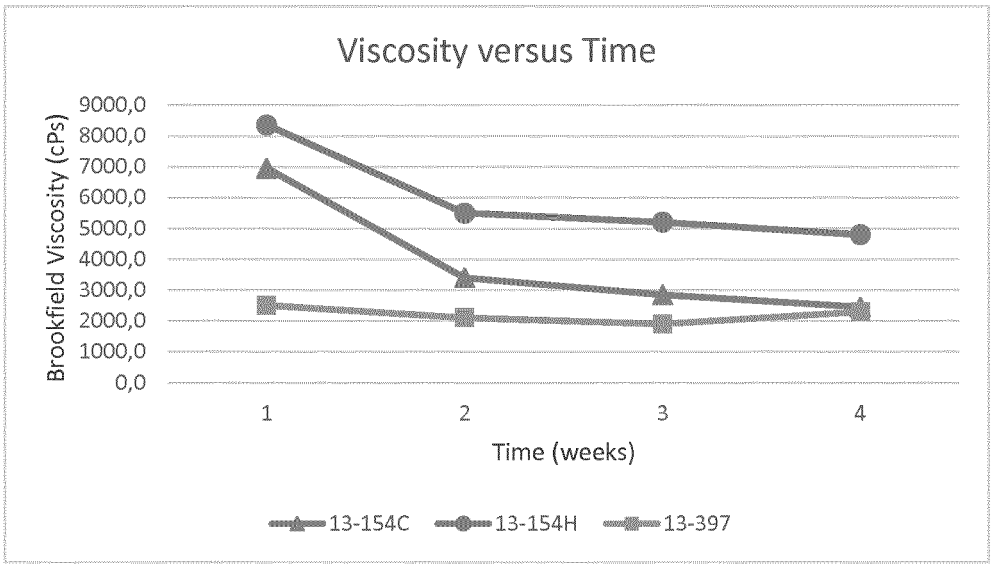


Figure 2 – Viscosity Stability Data



REFERENCES CITED IN THE DESCRIPTION

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