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(54) **PHOSPHATE SUBSTITUTES FOR MEMBRANE-COMPATIBLE CLEANING AND/OR DETERGENT COMPOSITIONS**

PHOSPHATSUBSTITUTE FÜR MEMBRANKOMPATIBLE REINIGUNGS- UND/ODER WASCHMITTELZUSAMMENSETZUNGEN

PRODUITS DE REMPLACEMENT DE PHOSPHATE POUR DES COMPOSITIONS DE DÉTERGENT ET/OU DE NETTOYAGE COMPATIBLES AVEC DES MEMBRANES

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Description

[0001] The present invention relates to a cleaning or detergent composition as defined in claim 1 comprising 5 to 30 wt.-% of a phosphate substitute, said phosphate substitute comprising a water-soluble copolymer and a multidentate chelating agent, the composition being free from any phosphates, silicates and cellulose-based compounds.

[0002] Many cleaning or detergent compositions present on the market are phosphate-based. In particular, detergents traditionally comprise a high amount of phosphate as a builder, as phosphates combine many useful properties required in cleaning and washing processes. Phosphates bind calcium and magnesium ions and are able to disperse insoluble salts of these ions, e.g. calcium carbonate causing water hardness and leading to spotting on hard surfaces and graying in textiles. Phosphates furthermore can act as alkalinity source for the cleaning or detergent composition, while at the same time being able to buffer the wash liquor above pH 9 in combination with further additives.

[0003] On the other hand the environmental profile of phosphate is not favorable, phosphates being associated with eutrophication. For this reason in many countries phosphate-based laundry detergent compositions are nowadays almost completely banned from the market by legislation. Accordingly, a need for environmentally friendly phosphate substitutes for various applications exists. These phosphate substitutes should nevertheless fulfill the different functions of phosphate in cleaning and/or detergent compositions mentioned above, namely (1) complexing of magnesium and calcium ions, (2) dispersing capacity for insoluble salts of these ions, for example calcium carbonate, (3) providing alkalinity, and (4) buffering capacity.

[0004] Various compounds and mixtures of compounds have been tested for this purpose in the past. Like phosphates, zeolites (being alumino silicates) have a high binding constant for magnesium and calcium ions and are able to sequester free magnesium and calcium cations. However, zeolites are insoluble in water and their incorporation in cleaning and detergent compositions can lead to undesirable residues being deposited on the surfaces/fabrics to be cleaned. In addition, cleaning and detergent compositions comprising high levels of zeolite builders form undesirable cloudy wash liquors upon contact with water. For this reason zeolites are commonly used in combination with further additives in order to improve their performance and activity.

[0005] While these phosphate substitute builders based on zeolites or mixtures of zeolites with further compounds are suitable for various household applications, they are not for institutional and industrial processes, as in these processes, the wastewater generated in the automatic cleaning/washing process is usually cleaned and purified using a membrane filtration step. The purified water obtained from this membrane filtration step can afterwards be reused in further washing cycles, thus reducing the need of fresh water required to be added in the washing cycle, saving resources and reducing costs.

[0006] Such membrane-cleaning processes on the other hand can only be applied to wastewater which does not contain components blocking the membrane of the filtration unit. This is in particular true for the highly efficient, but rather sensitive ultra-fine reverse osmosis membranes. Water-insoluble compounds such as zeolites block the membranes used in membrane filtration processes, in turn lowering the permeate production, thus disturbing or even impeding waste water recycling and shortening the membrane's lifetime.

[0007] WO 2005/118760 and WO 2008/110205 A1 both describe a membrane-friendly pasty soap composition comprising a combination of an acrylic/maleic copolymer and the trisodium salt of nitrilotriacetic acid (NTA) as a builder system. Nowadays, however, NTA is suspected to cause cancer, and thus an NTA-free phosphate substitute would be highly desirable.

[0008] WO 2007/101470 A1 describes a liquid membrane-compatible detergent composition comprising a mixture of an acrylic-maleic copolymer and the sodium salt of methyl glycine diacetic acid (MGDA) in a ratio of 1:1. While the specific detergents and cleaning compositions described in this application show a good washing performance even in hard water, it is explicitly stated in WO 2007/101470 A1 that fatty acid soaps must not be present in such compositions as they tend to form lime soaps in the presence of hard water which block the membranes of the membrane filtration unit.

[0009] It was therefore an object of the present invention to provide a phosphate substitute as a builder for cleaning and/or detergent compositions, in particular for membrane-friendly cleaning and/or detergent compositions compatible with the hyperfiltration membranes used in reverse osmosis filtration.

[0010] It has now surprisingly been found that this object can be met by a cleaning or detergent composition as defined in claim 1.

[0011] The substitute exhibits an improved membrane compatibility in comparison to the phosphate substitutes known in the art, in particular with respect to membrane capacity and membrane cleaning results, even in the presence of fatty acids or the soaps derived therefrom. Detergent compositions comprising this substitute showed good cleaning properties as well.

[0012] The amount of 5 to 30 wt.-% relates to the amount of the complete phosphate substitute mixture, i.e. to the amount of the mixture of the water-soluble copolymer and the chelating agent. For example, if the cleaning/detergent composition comprises 15 wt.-% of a phosphate substitute comprising the copolymer and the chelating agent in a ratio of 2:1, then the cleaning/detergent composition comprises 10 wt.-% of the copolymer and 5 wt.-% of the chelating agent,

based on the whole composition.

[0013] The phosphate substitute comprises a water-soluble copolymer. According to the present invention, such a copolymer is regarded as being water-soluble if at least 100 g, more preferably at least 200 g of the polymer can be completely dissolved in one liter (1 L) of water at a temperature of 23°C.

[0014] In terms of the present invention, a multidentate chelating agent is a compound capable of donating two or more pairs of electrons from at least two different atoms of different functional groups (complexing groups) in a complexation reaction to form coordinate bonds. The multidentate chelating agent preferably comprises 3 to 6 complexing groups per molecule, which means that it preferably donates at least 3 to 6 pairs of electrons in a complexation reaction to form coordinate bonds. These multidentate chelating agents form water-soluble complexes with Ca^{2+} and/or Mg^{2+} magnesium ions, thus preventing the formation of insoluble precipitates, which otherwise would block the membrane. In terms of the present invention the calcium or magnesium complex is regarded as being water-soluble if at least 0.1 mol of this complex can be completely dissolved in one liter of water at a temperature of 23°C.

[0015] The composition is free from any phosphates, silicates, including zeolites, and cellulose-based compounds. Thus, the cleaning/detergent compositions of the present invention are not only environmentally friendly due to the lack of phosphates, but are also suitable for the application in machine dishwashing or laundry washing processes which employ membrane filtration techniques, including reverse osmosis membranes. The composition of the present invention can even be used as a cleaning agent for cleaning soiled, blocked and/or contaminated membranes, including reverse osmosis membranes.

[0016] Preferably, the composition of the present invention comprises 6 to 27.5 wt.-%, more preferably 7.5 to 25 wt.-%, and most preferably 9 to 20 wt.-% of the phosphate substitute. The amount of phosphate substitute may be adjusted to the water hardness in a particular region and to the aggregate state of the cleaning/detergent composition. If the composition of the present invention is provided in the form of a solid composition, the amount of phosphate substitute in the composition preferably is in the range of 14 to 25 wt.-%, more preferably in the range of 17 to 23 wt.-%, and even more preferably in the range of 18 to 20 wt.-%. If on the other hand the composition of the present invention is provided in the form of a liquid laundry detergent composition, the composition preferably comprises between 5 and 15 wt.-% of the phosphate substitute, more preferably between 7.5 and 12 wt.-% and most preferably 8.5 to 11 wt.-%.

[0017] The copolymer comprised in the phosphate substitute of the present invention has a calcium carbonate dispersing capacity of at least 150 mg $CaCO_3$/g copolymer, preferably of at least 175 mg $CaCO_3$/g, more preferably of at least 200 mg $CaCO_3$/g, even more preferably of at least 250 $CaCO_3$/g and most preferably the calcium carbonate dispersing capacity of the copolymer is in the range of 280 to 320 mg $CaCO_3$/g copolymer.

[0018] The calcium carbonate dispersing capacity referred to herein is determined according to F. Richter and E.W. Winkler, Tensides Surfactants Detergents 1987, 4, 213 - 216, by dissolving 1 gram of the substance (copolymer) in 100 mL deionized water, neutralizing the solution, if necessary, with 1M NaOH, adding 10 mL of a 10 % Na_2CO_3 solution, and adjusting to pH 10 by adding NaOH or HCl, as required. The solution is then titrated with a 0.25 M calcium acetate solution until the solution becomes turbid, while the pH and the temperature are kept constant during titration.

[0019] In terms of the present invention an aliphatic unsaturated monomer unit is an aliphatic organic molecule of low molecular weight, i.e. a molecule whose weight preferably is not exceeding 600 g/mol, which comprises at least one C-C double bond group -CR=CR'R" that can be polymerized to obtain polymers or copolymers. Herein, R, R' R"may be the same or different and are not particulary limited. Preferably, R, R' and R" represent hydrogen, C_1-C_6 alkyl groups or functional groups such as carboxylates, nitriles, and the like. Preferably the aliphatic unsaturated monomer units of the present invention further comprise acidic groups, preferably carboxylic groups, i.e. groups of the chemical formula -CO_2H or their salts -CO_2M, wherein M is an alkali metal cation. In a preferred embodiment the at least two different aliphatic unsaturated monomer units comprised in the water-soluble copolymer are selected from the group consisting of acrylic acid, methacrylic acid, maleic anhydride and fumaric acid, or salts thereof. In a preferred embodiment one aliphatic unsaturated monomer unit represents maleic acid or salts thereof and the second aliphatic unsaturated monomer unit represents acrylic acid or salts thereof. Preferably, the copolymer comprises 50 to 70 wt.-% acrylic acid and 50 to 10 % maleic acid. The relative molecular weight of the copolymer preferably is between 2,000 and 200,000, preferably between 3,000 and 150,000, more preferably between 4,000 and 125,000, even more preferably between 12,000 and 110,000, particularly preferred between 20,000 and 100,000, even more particularly preferred between 50,000 and 90,000, and most preferably between 65,000 and 75,000, based on free acid. It should be understood that even if the preferred molecular weights are given based on the free acid, in a particularly preferred embodiment at least partly neutralized copolymers are used, i.e. polymers comprising negatively charged carboxylate groups having a positively charged alkali metal counterion, wherein these counterions preferably are sodium or potassium ions. The copolymer preferably has a neutral or close to neutral pH (pH 6 to 8).

[0020] Suitable, but less preferred compounds of this class are copolymers of acrylic acid or methacrylic acid with vinyl ethers, such as vinyl methyl ethers, vinyl esters, ethylene, propylene and styrene, in which the acid makes up at least 50% by weight. Other suitable polymer carboxylates or carboxylic acids are water-soluble terpolymers which contain two unsaturated acids and/or salts thereof as monomers and vinyl alcohol and/or a vinyl alcohol derivative or a carbo-

hydrate as the third monomer. The first acidic monomer or its salt is derived from a monoethylenically unsaturated C_3-C_8-carboxylic acid and preferably from a C_3-C_4-monocarboxylic acid, more preferably from (meth)acrylic acid. The second acidic monomer or its salt may be a derivative of C_4-C_8-dicarboxylic acid, maleic acid being particularly preferred. The third monomer unit in this case will be formed from a vinyl alcohol and/or preferably an esterified vinyl alcohol. Especially preferred are vinyl alcohol esters formed form a short chain carboxylic acids, like C_1-C_4-carboxylic acids, with vinyl alcohol. Preferred terpolymers contain 60 to 95 wt-%, particularly 70 to 90 wt.-% (meth)acrylic acid or (meth)acrylate, respectively, more particular acrylic acid or acrylate, respectively, and maleic acid or maleinate and 5 to 40 wt.-%, preferably 10 to 30 wt.-% vinyl alcohol and/or vinyl acetate. Especially preferred are terpolymers with a weight ratio of (meth)acrylic acid and maleic acid or maleinate of between 1:1 and 4:1, preferably between 2:1 and 3:1 and especially 2:1 and 2.5:1, with the amounts as well as the weight ratios being based on the acid.

[0021] The second monomer or its salt may also be a derivative of an allyl sulfonic acid substituted in the 2-position by an alkyl group, preferably a C_1-C_4 alkyl group, or an aryl group which is preferably derived from benzene or a benzene derivative. Preferred terpolymers contain 40 to 60 wt.-%, in particular 45 to 55 wt.-% (meth)acrylic acid or (meth)acrylate, more preferred acrylic acid or acrylate, 10 to 30 wt.-%, particularly 15 to 25 wt.-% methallyl sulfonic acid or methallyl sulfonate and as third monomer 15 to 40 wt.-%, preferably 20 to 40 wt.-% of a carbohydrate. Said carbohydrate, for example, may be a mono-, di-, oligo- or polysaccharide, with mono-, di- or oligosaccharide being preferred. Saccharose is most preferred.

[0022] By applying the third monomer breaking points are implemented into the polymer which probably result in the good biodegradability properties of said polymers. Polymers which are completely or at least in part neutralized, particularly to more than 50% based on the carboxylic groups which are present, are especially preferred.

[0023] Most preferred polymeric polycarboxylates may be produced by the method described in German patent DE 42 21 381 and German patent application DE 43 00 772. The polyacetal carboxylic acids described, for example, in U.S. Pat. Nos. 4,144,226 and 4,146,495, which are obtained by polymerization of esters of glycolic acid, introduction of stable terminal groups and saponification to the sodium or potassium salts are also suitable, as are polymeric acids obtained by polymeriziation of acrolein and Cannizzaro disproportionation of the polymer with strong alkalis. They are essentially made of acrylic acid units and vinyl alcohol units or acrolein units.

[0024] The chelating agent of the present invention preferably is a so-called "polycarboxylic acid" comprising 3 to 6 carboxylic groups per molecule, either in the protonated or in the neutralized state, preferably selected from the group consisting of hydroxyethylenediaminetriacetic acid (HEDTA), diethylenetriaminepentaacetic acid (DTPA), methylglycinediacetic acid (MGDA), glutamic acid-*N*,*N*-diacetic acid (GLDA), iminodisuccinic acid (IDSA), hydroxyiminodisuccinic acid (HIDS), ethylenediaminodisuccinic acid (EDDS), aspartic acid-*N*,*N*-diacetic acid (ASDA), salts thereof, and mixtures thereof.

[0025] These ligands are able to form water-soluble complexes with Ca^{2+}-ions, said complexes preferably having a logarithmic stability constant (log K_{CaZ}) of at least 6.5, when measured at an ionic strength of 0.1 and a temperature of 25°C, wherein

$$K_{CaZ} = \frac{[CaZ^{(m-2)-}]}{[Ca^{2+}][Z^{m-}]} \ .$$

[0026] Herein $[CaZ^{(m-2)-}]$ represents the concentration of the chelate complex, $[Ca^{2+}]$ represents the concentration of free calcium ions, $[Z^{m-}]$ represents the concentration of the chelating agent anion, and K_{CaZ} represents the stability constant of the chelate complex.

[0027] The stability constants can easily be determined by methods well known to a person skilled in the art and are also mentioned in the product information sheet provided by the manufacturers of the aforementioned chelating agents, all of which are commercially available.

[0028] The composition of the present invention is free from any phosphates, silicates and/or cellulose-based compounds. In terms of the present invention, a composition is free from a compound if it contains less than 0.1 wt.-% of this compound, preferably less than 0.01 wt.-%, more preferably less than 0.001 wt.-% and preferably the composition does not contain a compound at all, i.e. the concentration of this compound is below the detection limit of the detection method typically used to detect the compound.

[0029] Cellulose-based compounds commonly found in detergent composition, which, however, are not present in the composition of the present invention are, for example, greying inhibitors such as cellulose ethers, e.g. carboxymethyl cellulose, methyl cellulose, hydroxyalkyl cellulose, methylhydroxyethyl cellulose, methylhydroxypropyl cellulose, and methylcarboxymethyl cellulose.

[0030] In a particularly preferred embodiment the composition is free from ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), and/or any silicon-containing compounds.

[0031] Using the composition of the present invention foam inhibitors/antifoaming agents on a silicon basis such as, for example, polysiloxanes or silicon oil defoamers, commonly used in membrane-friendly laundry detergent compositions known in the state of the art do not have to be included in the composition of the present invention. The composition of the present invention can be free from any of these compounds, while still having desirable foaming properties.

[0032] The fatty acids of the general formula (II) and their salts can be exemplified by the fatty acids octanoic acid, pelargonic acid, decanoic acid, lauric acid, lauroleic acid, myristic acid, myristoleic acid, palmitic acid, palmitoleic acid, stearic acid, petroselinic acid, petroselaidic acid, oleic acid, linoleic acid, linolaidic acid, linolenis acid, eleostearic acid, arachic acid, gadoleic acid, arachidonic acid, behenic acid, erucic acid, brassidic acid, clupanodonic acid.

[0033] The composition comprises two different alkoxylated fatty alcohols of the formulas $R^{1a}O(C_2H_4O)_{5-7}H$ and $R^{1b}O(C_2H_4O)_{12-16}H$, wherein R^{1a} and R^{1b} may be the same or different and represent a linear or branched alkyl or alkenyl residue with 15 to 20 carbon atoms, preferably with 16 to 18 carbon atoms.

[0034] The composition of the present invention optionally comprises an anionic surfactant in an amount of from 0.1 to 15 wt.-%, preferably of from 1 to 5 wt.-%, and more preferably of from 1.2 to 2 wt.-%. The anionic surfactant preferably is selected from from the group consisting of C_8-C_{18} alkyl sulfates, C_8-C_{18} alkyl ether sulfates, C_8-C_{18} alkyl sulfonates, C_8-C_{18} α-olefinsulfonates, sulfonated C_8-C_{18} fatty acids, C_8-C_{18} alkylbenzenesulfonates, sulfosuccinic mono- and di-C_1-C_{12} esters, C_8-C_{18} alkyl polyglycol ether carboxylates, C_8-C_{18} N-acyl taurides, C_8-C_{18} N-sarconisates, C_8-C_{18} alkyl isethionates, and mixtures thereof.

[0035] The composition furthermore preferably comprises one or more alkalinity sources in a total amount of 3 to 90 wt.-%, more preferably in an amount of 5 to 50 wt.-%, based on the whole composition.

[0036] The compositions of the present invention may be provided as a liquid, a gel, an emulsion, a paste or a solid, including tablets, granules, powders, blocks. If the composition is in a solid form or, in the case of a pasty composition, has a solid phase, the solid phase is formed from the alkalinity source (and the phosphate substitute). Accordingly, a solid or paste-like composition comprises a higher amount of alkalinity sources than a liquid or a gel composition. For example, a powdered laundry detergent composition according to the present invention preferably comprises 20 to 60 wt.-% of one or more alkalinity sources according to the present invention, more preferably between 30 and 50 wt.-%, whereas a liquid laundry detergent composition according to the present invention preferably comprises 3 to 15 wt.-%, more preferably 4 to 10 wt.-%.

[0037] The alkalinity source preferably is selected from the group consisting of sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, or mixtures thereof.

[0038] The composition additionally may comprise additives commonly used in cleaning and/or detergent compositions, preferably selected from the group consisting of pH modifiers, antimicrobial agents, viscosity modifying agents, optical brighteners, organic solvents, bleaching agents, bleach activators, dyes, perfume, membrane-compatible antifoaming agents, corrosion inhibition agents, enzymes, and mixtures thereof.

[0039] The present invention furthermore provides a method for washing textiles using the composition of the present invention. The method preferably is an automatic machine washing process, wherein waste water accumulated during the whole washing process or parts thereof is purified in a filtration process using one or more membrane filtration units, said filtration process preferably comprising one or more reverse osmosis steps.

[0040] In a particularly preferred embodiment, the above-mentioned compositions are used in commercial laundries. However, the compositions may as well be used in private washing machines, as a cleaning agent in general and/or a warewashing agent. As mentioned above, the inventive composition is membrane-friendly, i.e. it does not cause blocking of the membrane or other damages when it is contained in the waste water which is accumulated during the whole washing process or parts thereof and purified using membrane filtration units. It is even possible that the filtration comprises one or more reverse osmosis steps, which means that the permeation of the wastewater to purify generally remains stable. The obtained purified water may then be reused in another washing cycle, which results in a decrease in the amount of fresh water required to be added to the washing cycle and, accordingly, in a reduction of expenses and in saving resources.

List of figures

[0041]

Fig. 1a and b show the results of screening membrane capacity with different cleaning composition in pure soft water determined as described in example 2, the cleaning compositions containing either 26 wt.-% of a phosphate builder (reference example 1) or phosphate substitutes, namely 26 wt.-% of Na_3-MGDA (reference example 2), 12 wt.-% of the sodium salt of a copolymer of maleic acid and acrylic acid (reference example 3), a combination of 12 wt.-% of the sodium salt of a copolymer of maleic acid and acrylic acid and 3.4 wt.-% of Na_3-MGDA (ratio 3.5:1, reference example 4), a combination of 12 wt.-% of the sodium salt of a copolymer of maleic acid and acrylic acid and 7.2 wt.-% of Na_3-MGDA (ratio 1.7:1, inventive example 1), a combination of 8 wt.-% of the sodium salt of a

copolymer of maleic acid and acrylic acid, 4 wt.-% Na_3-MGDA and 1.5 wt.-% of Na_4-GLDA, (ratio of copolymer to combined chelating agents 1.45:1, inventive example 2), a combination of 3 wt.-% of the sodium salt of a copolymer of maleic acid and acrylic acid and 3 wt.-% of Na_3-MGDA (ratio 1:1, reference example 5) and a combination of 3 wt.-% of the sodium salt of a copolymer of maleic acid and acrylic acid and 3.2 wt.-% of Na_3-MGDA (ratio 1:1.1, reference example 6), respectively.

Fig. 2 and 3 each show a comparison of the membrane capacity using reference composition 1 and the inventive composition in a waste water test on two different commercially available reverse osmosis membranes according to example 3.

Fig. 4 shows the soil removal performance of the inventive composition in comparison to the phosphate-based reference composition 1 with respect to the removal of fat pigments soiling on fabrics made of cotton (CO), polyester (PES), or mixtures thereof (see example 4).

Examples

Example 1: Preparation of detergent compositions

[0042] Detergent composition were prepared by mixing the compounds listed in table 1 with phosphate or phosphate substitute, respectively, according to table 2.

Table 1: Basic Detergent Composition

Compound	Amount [wt.-%]
C_{16}-C_{18} fatty alcohol with 14 EO[1]	2
C_{16}-C_{18} fatty alcohol with 6 EO[1]	2
C_{12}-C_{18} coconut fatty acid	3
Alkylbenzene sulfonic acid	2
Hydroxyethylidene diphosphonic acid	1
Sodium hydroxide	2
Sodium carbonate	38
Builder	see table 2
Mixture of optical brighteners	0.3
Salts and water	remaining
In total	**100 wt.-%**
[1]EO: mol ethylene oxides per molecule	

Table 2: Builder

Composition	Builder [Amount in wt.-% based on the whole composition]
Reference composition 1	26 wt.-% Na_3PO_4
Reference composition 2	26 wt.-% Na_3-MGDA
Reference composition 3	12 wt.-% sodium salt of a copolymer of maleic acid and acrylic acid
Reference composition 4	12 wt.-% sodium salt of a copolymer of maleic acid and acrylic acid + 3.4 wt.-% Na_3-MGDA
Reference composition 5	3 wt.-% sodium salt of a copolymer of maleic acid and acrylic acid + 3 wt.-% of Na_3-MGDA
Reference composition 6	3 wt.-% sodium salt of a copolymer of maleic acid and acrylic acid + 3.2 wt.-% Na_3-MGDA

(continued)

Composition	Builder [Amount in wt.-% based on the whole composition]
Inventive composition 1	12 wt.-% sodium salt of a copolymer of maleic acid and acrylic acid
	+ 7.2 wt.-% Na_3-MGDA
Inventive composition 2	6 wt.-% sodium salt of a copolymer of maleic acid and acrylic acid + 2.3 wt.-% Na_3-MGDA + 1.5 wt.-% of Na_4-GLDA
[1]EO: mol ethylene oxides per molecule	

[0043] Inventive composition 1 is a solid powdered composition. However, the composition of the present invention may also be in the form of a liquid composition and table 2 refers to a liquid composition according to the present invention (inventive composition 3).

Table 2

Compound	Amount [wt.-%]
sodium salt of a copolymer of maleic acid and acrylic acid	6
Na_3-MGDA	3
C_{16}-C_{18} fatty alcohol with 14 EO[1]	2
C_{16}-C_{18} fatty alcohol with 6 EO[1]	2
C_{12}-C_{18} coconut fatty acid	3
Alkylbenzene sulfonic acid	2
Hydroxyethylidene diphosphonic acid	0.2
Sodium hydroxide	5
Triethanolamine	2
Propylene Glycol	10
Isopropanol	3
Water	61
Mixture of optical brighteners	0.4
In total	**100 wt.-%**
[1]EO: mol ethylene oxides per molecule	

Example 2: Membrane capacity using soft water

[0044]

a) Using reference composition 1 - 6 and inventive composition 1, respectively, preliminary test on the membrane capacity were carried out in a membrane-stress test using soft water to which increasing amounts of the aforementioned compositions were added.
At the beginning, the permeate flow was determined on two different commercially available membrane packages, each containing three membrane plates, while circulating 20 L pure soft water at a temperature of 55 °C and a flux rate of 500 L/h under a pressure of 16 bar. The measured permeate flow equals the water value at the beginning (WV at beginning).
10 g of the respective composition were then added, and the resoluting mixture was circulated over the membranes for another 20 min over the two different membrane packages under the conditions described above. After 20 min the actual permeate flow was determined (SV value). Another 10 g of the product composition were then added and circulated over the membranes for 20 min, before determining the permeate flow. This procedure was repeated twelve times in total, until a final product concentration of 0.6 wt-% was reached. The permeate flow measured at this concentration equals the end value (EV).

The results are presented in Fig. 1a. It can bee seen that among all the composition not comprising phosphate, the composition of the present invention afforded the highest amount of permeate, almost as much as the phosphate-based detergent.

b) In a further experiment the membrane capacity using the inventive composition 2 and reference compositions 1 and 3 were determined as described under item a). The results are presented in Fig. 1b, showing that excellent results are obtained as well, when a combination of two different chelating agents in combinations with a water-soluble copolymer is used.

Example 3: Membrane capacity using waste water

[0045] Even more important than the performance using pure water described in example 1 is the membrane capacity using waste water formed during the washing process. To evaluate the long-term capacity of membranes used for treating waste water comprising the composition of the present invention, the following experiment was carried out:
For producing waste water, polluted and heavily polluted clothes from hospital area and nursing homes were washed on a laboratory washing machine using reference composition 1 and inventive composition 1, respectively. 10 g of powdered detergent composition supplemented with 2.5 g of a commercially available alkali booster and 5.5 g of a commercially available bleach booster per kg clothes was used. The clothes (7.5 kg) were washed for 5 min at 30 °C, then for 20 min at 75 °C, using a liquor ratio of 1:5, i.e. 5 L of water per 1 kg of laundry, and finally were rinsed for 5 min at 60 °C. 20 L of the drain from each, the main wash and the rinse, were collected and filtered.
[0046] At a temperature of 55 °C and a flux rate of 500 L/h under a pressure of 16 bar 20 L of this waste water was then circulated over two different membrane packages, each containing three membrane plates, for 90 min. Afterwards the membranes were rinsed for 5 min using soft water. This cycle was then repeated for five days in total while monitoring the permeate flow. After five days, the membranes were cleaned using commercially available chemical cleaning agents for membranes and rinsed using soft water.
The results are presented in figures 2 and 3, respectively: Both membranes exhibit a better membrane capacity when treated with waste water comprising the composition of the present invention in comparision to waste water comprising a phosphate-based composition.

Example 4: Soil removal

[0047] Using reference composition 1 and the inventive composition 1 removal of different fat pigment soil (lanolin, sebum, olive oil, mineral oil, motor oil, make up, and lipstick, respectively) from fabrics made of cotton (CO) and polyester (PES), or a mixture thereof was evaluated. The soiled fabrics were washed for 10 min at 70 °C in a bath comprising 2 g/L of reference composition 1 and the inventive composition 1, respectively, using soft water (0° dH).
[0048] The results are presented in figure 4. It can be seen that reference composition 1 and the inventive composition 1 are more or less equal regarding soil removal. (Note that the LSD value given in figure 4 is the lowest significant difference, and only differences greater than that value can be considered as being significant.)

Claims

1. A cleaning or detergent composition comprising

a) alkoxylated fatty alcohols of the general formula (I) $R^1O(C_nH2_nO)_xH$ (I), wherein the composition comprises two different alkoxylated fatty alcohols, a mixture of $R^{1a}O(C_2H_4O)_{5-7}H$ and $R^{1b}O(C_2H_4O)_{12-16}H$, wherein R^{1a} and R^{1b} may be the same or different and represent a linear or branched alkyl or alkenyl residue with 15 to 20 carbon atoms, preferably with 16 to 18 carbon atoms,
and optionally one or more surfactant components selected from the group consisting of: (i) fatty acids of the general formula (II) R^2CO_2M (II) and (ii) anionic surfactants, or mixtures thereof, wherein R^1 and R^2 independently represent a linear or branched alkyl or alkenyl residue with 8 to 22 carbon atoms, n ranges from 1 to 5 and preferably is 2 or 3, x represents a degree of alkoxylation ranging from 5 to 25, and M represents hydrogen or an alkali metal ion;
b) one or more alkalinity sources,
c) water, and
d) 5 to 30 wt.-%, based on the whole composition, of a phosphate substitute comprising:

i) a water-soluble copolymer comprising at least two different aliphatic unsaturated monomer units and

having a calcium carbonate dispersing capacity of at least 150 mg $CaCO_3$/g copolymer and
ii) a multidentate chelating agent comprising three to six complexing groups per molecule and forming water-soluble complexes with Ca^{2+}-ions, wherein the ratio of the copolymer to the chelating agent is in the range of greater than 1:1 to 3:1 (wt.-%/wt.-% based on the whole composition) and the composition is free from any phosphates, silicates and cellulose-based compounds.

2. The composition according to claim 1, comprising 6 to 27.5 wt.-%, preferably 7.5 to 25 wt.-%, and more preferably 9 to 20 wt.-% of the phosphate substitute.

3. The composition according to claim 1 or 2, wherein the calcium carbonate dispersing capacity of the copolymer is at least 175 mg $CaCO_3$/g copolymer, preferably at least 200 mg $CaCO_3$/g, more preferably at least 250 mg $CaCO_3$/g and most preferably is in the range of 280 to 320 mg $CaCO_3$/g.

4. The composition according to any of claims 1 to 3, wherein the at least two different aliphatic unsaturated monomer units are selected from the group consisting of acrylic acid, methacrylic acid, maleic acid, maleic anhydride and fumaric acid, or salts thereof, one aliphatic unsaturated monomer unit preferably being maleic acid or salts thereof and the second aliphatic unsaturated monomer unit preferably being acrylic acid or salts thereof.

5. The composition according to any of claims 1 to 4, wherein the chelating agent is a polycarboxylic acid or a salt thereof, preferably selected from the group consisting of hydroxyethylenediaminetriacetic acid (HEDTA), diethylenetriaminepentaacetic acid (DTPA), methylglycinediacetic acid (MGDA), glutamic-*N,N*-diacetic acid (GLDA), iminodisuccinic acid (IDSA), hydroxyiminodisuccinic acid (HIDS), ethylenediaminodisuccinic acid (EDDS), aspartic-*N,N*-diacetic acid (ASDA), salts thereof, and mixtures thereof.

6. The composition according to any of claims 1 to 5, wherein the composition is free of ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA) and any silicon-containing compounds.

7. A composition according to claim 1, wherein the anionic surfactant is selected from the group consisting of C_8-C_{18} alkyl sulfates, C_8-C_{18} alkyl ether sulfates, C_8-C_{18} alkyl sulfonates, C_8-C_{18} α-olefinsulfonates, sulfonated C_8-C_{18} fatty acids, C_8-C_{18} alkylbenzenesulfonates, sulfosuccinic mono- and di-C_1-C_{12} esters, C_8-C_{18} alkyl polyglycol ether carboxylates, C_8-C_{18} N-acyl taurides, C_8-C_{18} N-sarconisates, C_8-C_{18} alkyl isethionates, and mixtures thereof.

8. A composition according to claim 1 or 7, wherein the alkalinity source is selected from the group consisting of sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, or mixtures thereof, and preferably is present in an amount of 3 to 90 wt.-%, more preferably in an amount of 5 to 50 wt.%, based on the whole composition.

9. A composition according to any of claims 1 to 8, wherein the composition additionally comprises additives selected from the group consisting of pH modifiers, antimicrobial agents, viscosity modifying agents, optical brighteners, organic solvents, bleaching agents, bleach activators, dyes, perfume, membrane-compatible antifoaming agents, corrosion inhibition agents, enzymes and mixtures thereof.

10. A method for washing textiles using a composition according to any of claims 1 to 9.

11. A method according to claim 10, wherein the waste water accumulated during the whole washing process or parts thereof is purified in a filtration process using one or more membrane filtration units, said filtration process preferably comprising one or more reverse osmosis steps.

12. Use of a composition according to any of claims 1 to 9 as a detergent in commercial laundry and/or private washing machines, as cleansing and/or warewashing agent.

Patentansprüche

1. Reinigungs- oder Waschmittelzusammensetzung, umfassend:

a) alkoxylierte Fettalkohole der allgemeinen Formel (I) $R^1O(C_nH2_nO)_xH$ (I), wobei die Zusammensetzung zwei verschiedene alkoxylierte Fettalkohole umfasst, eine Mischung aus $R^{1a}O(C_2H_4O)_{5\text{-}7}H$ und $R^{1b}O(C_2H_4O)_{12\text{-}16}H$, wobei R^{1a} und R^{1b} gleich oder verschieden sein können und einen linearen oder verzweigten Alkyl- oder

Alkenylrest mit 15 bis 20 Kohlenstoffatomen, vorzugsweise mit 16 bis 18 Kohlenstoffatomen, und gegebenenfalls eine oder mehrere Tensidkomponenten darstellen, ausgewählt aus der Gruppe bestehend aus: (i) Fettsäuren der allgemeinen Formel (II) R^2CO_2M (II) und (ii) anionischen Tensiden oder Mischungen davon, wobei R^1 und R^2 unabhängig voneinander einen linearen oder verzweigten Alkyl- oder Alkenylrest mit 8 bis 22 Kohlenstoffatomen darstellen, n im Bereich von 1 bis 5 liegt und vorzugsweise 2 oder 3 ist, x einen Alkoxylierungsgrad im Bereich von 5 bis 25 darstellt, und M Wasserstoff oder ein Alkalimetallion darstellt;
b) eine oder mehrere Alkalinitätsquellen,
c) Wasser, und
d) 5 bis 30 Gew.-%, bezogen auf die gesamte Zusammensetzung, eines Phosphatersatzes, umfassend:

i) ein wasserlösliches Copolymer, das mindestens zwei verschiedene aliphatische ungesättigte Monomereinheiten umfasst und eine Calciumcarbonatdispersionskapazität von mindestens 150 mg $CaCO_3$/g Copolymer aufweist, und
ii) einen mehrzähnigen Chelatbildner, der drei bis sechs komplexbildende Gruppen pro Molekül umfasst und mit Ca^{2+}-Ionen wasserlösliche Komplexe bildet, wobei das Verhältnis des Copolymers zu dem Chelatbildner im Bereich von mehr als 1:1 bis 3:1 liegt (Gew.-%/Gew.-% bezogen auf die gesamte Zusammensetzung) und die Zusammensetzung frei ist von jeglichen Phosphaten, Silikaten und Verbindungen auf Cellulosebasis.

2. Zusammensetzung nach Anspruch 1, umfassend 6 bis 27,5 Gew.-%, bevorzugt 7,5 bis 25 Gew.-% und stärker bevorzugt 9 bis 20 Gew.-% des Phosphatersatzes.

3. Zusammensetzung nach Anspruch 1 oder 2, wobei die Calciumcarbonatdispispergierkapazität des Copolymers mindestens 175 mg $CaCO_3$/g Copolymer beträgt, bevorzugt mindestens 200 mg $CaCO_3$/g, stärker bevorzugt mindestens 250 mg $CaCO_3$/g und am stärksten bevorzugt im Bereich von 280 bis 320 mg $CaCO_3$/g liegt.

4. Zusammensetzung nach einem der Ansprüche 1 bis 3, wobei die mindestens zwei verschiedenen aliphatischen ungesättigten Monomereinheiten aus der Gruppe ausgewählt sind, die aus Acrylsäure, Methacrylsäure, Maleinsäure, Maleinsäureanhydrid und Fumarsäure oder Salzen davon besteht wobei eine aliphatische ungesättigte Monomereinheit vorzugsweise Maleinsäure oder Salze davon ist und die zweite aliphatische ungesättigte Monomereinheit Acrylsäure oder Salze davon ist.

5. Zusammensetzung nach einem der Ansprüche 1 bis 4, wobei der Chelatbildner eine Polycarbonsäure oder ein Salz davon ist, vorzugsweise ausgewählt aus der Gruppe bestehend aus Hydroxyethylendiamintriessigsäure (HEDTA), Diethylentriaminpentaessigsäure (DTPA) und Methylglycindiessigsäure (MGDA), Glutamin-N,N-diessigsäure (GLDA), Iminodisuccinsäure (IDSA), Hydroxyiminodisuccinsäure (HIDS), Ethylendiaminodisuccinsäure (EDDS), Asparagin-N,N-diessigsäure (ASDA), Salze davon, und Mischungen davon.

6. Zusammensetzung nach einem der Ansprüche 1 bis 5, wobei die Zusammensetzung frei von Ethylendiamintetraessigsäure (EDTA), Nitrilotriessigsäure (NTA) und jeglichen siliciumhaltigen Verbindungen ist.

7. Zusammensetzung nach Anspruch 1, wobei das anionische Tensid ausgewählt ist aus der Gruppe bestehend aus C_8-C_{18}-Alkylsulfaten, C_8-C_{18}-Alkylethersulfaten, C_8-C_{18}-Alkylsulfonaten, C_8-C_{18}-α-Olefinsulfonaten, sulfonierten C_8-C_{18}-Fettsäuren, C_8-C_{18}--Alkylbenzolsulfonaten, Sulfosuccinmono- und -di-C_1-C_{12}-Estern, C_8-C_{18}-Alkylpolyglycolethercarboxylaten, C_8-C_{18}-N-Acyltauriden, C_8-C_{18}-N-Sarconisaten, C_8-C_{18}-Alkylisethionaten und Mischungen davon.

8. Zusammensetzung nach Anspruch 1 oder 7, wobei die Alkalinitätsquelle aus der Gruppe bestehend aus Natriumhydroxid, Kaliumhydroxid, Natriumcarbonat, Kaliumcarbonat oder Mischungen davon ausgewählt ist, und vorzugsweise in einer Menge von 3 bis 90 Gew.-%, stärker bevorzugt in einer Menge von 5 bis 50 Gew.-%, bezogen auf die gesamte Zusammensetzung, vorliegt.

9. Zusammensetzung nach einem der Ansprüche 1 bis 8, wobei die Zusammensetzung zusätzlich Additive umfasst, die aus der Gruppe bestehend aus pH-Modifizierungsmitteln, antimikrobiellen Mitteln, Viskositätsmodifizierungsmitteln, optischen Aufhellern, organischen Lösungsmitteln, Bleichmitteln, Bleichaktivatoren, Farbstoffen, Duftstoff, membrankompatiblen Antischaummitteln, Korrosionsinhibitoren, Enzymen und Mischungen davon ausgewählt sind.

10. Verfahren zum Waschen von Textilien unter Verwendung einer Zusammensetzung nach einem der Ansprüche 1

bis 9.

11. Verfahren nach Anspruch 10, wobei das Abwasser, das sich während des gesamten Waschprozesses oder Teilen davon ansammelt, in einem Filtrationsprozess unter Verwendung einer oder mehrerer Membranfiltrationseinheiten gereinigt wird, wobei der Filtrationsprozess vorzugsweise einen oder mehrere Umkehrosmoseschritte umfasst.

12. Verwendung einer Zusammensetzung nach einem der Ansprüche 1 bis 9 als Waschmittel in kommerziellen und/oder privaten Waschmaschinen als Reinigungs- und/oder Spülmittel.

Revendications

1. Composition nettoyante ou détergente comprenant

a) des alcools gras alcoxylés de formule générale (I) $R^1O(C_nH2_nO)_xH$ (I), la composition comprenant deux alcools gras alcoxylés différents, un mélange de $R^{1a}O(C_2H_4O)_{5-7}H$ et $R^{1b}O(C_2H_4O)_{12-16}H$, R^{1a} et R^{1b} pouvant être identiques ou différents et représentant un résidu alkyle ou alcényle linéaire ou ramifié contenant 15 à 20 atomes de carbone, de préférence 16 à 18 atomes de carbone,
et facultativement un ou plusieurs composés tensioactifs choisis dans le groupe constitué par : (i) les acides gras de formule générale (II) R^2CO_2M (II) et (ii) les tensioactifs anioniques, ou des mélanges de ceux-ci, R^1 et R^2 représentant indépendamment un résidu alkyle ou alcényle linéaire ou ramifié contenant 8 à 22 atomes de carbone, n se situant entre 1 et 5 et de préférence valant 2 ou 3, x représentant un degré d'alcoxylation se situant entre 5 et 25, et M représentant l'hydrogène ou un ion métallique alcalin ;
b) une ou plusieurs sources d'alcalinité,
c) de l'eau, et
d) 5 à 30 % en poids, sur la base de la composition totale, d'un substitut du phosphate comprenant :

i) un copolymère hydrosoluble comprenant au moins deux unités monomères insaturées aliphatiques différentes et ayant une capacité de dispersion du carbonate de calcium d'au moins 150 mg de $CaCO_3$/g de copolymère et
ii) un agent chélatant multidenté comprenant trois à six groupes complexants par molécule et formant des complexes hydrosolubles avec les ions Ca^{2+}, le rapport du copolymère à l'agent chélatant se situant entre plus de 1:1 et 3:1 (% en poids/% en poids sur la base de la composition totale) et la composition étant exempte de tous phosphates, silicates et composés cellulosiques.

2. Composition selon la revendication 1, comprenant 6 à 27,5 % en poids, de préférence 7,5 à 25 % en poids, et plus préférablement 9 à 20 % en poids du substitut du phosphate.

3. Composition selon la revendication 1 ou 2, la capacité de dispersion du carbonate de calcium du copolymère étant d'au moins 175 mg de $CaCO_3$/g de copolymère, de préférence d'au moins 200 mg de $CaCO_3$/g, plus préférablement d'au moins 250 mg de $CaCO_3$/g et se situant le plus préférablement entre 280 et 320 mg de $CaCO_3$/g.

4. Composition selon l'une quelconque des revendications 1 à 3, les au moins deux unités monomères insaturées aliphatiques différentes étant choisies dans le groupe constitué par l'acide acrylique, l'acide méthacrylique, l'acide maléique, l'anhydride maléique et l'acide fumarique, ou les sels de ceux-ci, une unité monomère insaturée aliphatique étant de préférence l'acide maléique ou les sels de celui-ci et la seconde unité monomère insaturée aliphatique étant de préférence l'acide acrylique ou les sels de celui-ci.

5. Composition selon l'une quelconque des revendications 1 à 4, l'agent chélatant étant un acide polycarboxylique ou un sel de celui-ci, de préférence choisi dans le groupe constitué par l'acide hydroxyéthylènediaminetriacétique (HEDTA), l'acide diéthylènetriaminepentaacétique (DTPA), l'acide méthylglycinediacétique (MGDA), l'acide glutamique-*N,N*-diacétique (GLDA), l'acide iminodisuccinique (IDSA), l'acide hydroxyiminodisuccinique (HIDS), l'acide éthylènediaminodisuccinique (EDDS), l'acide aspartique-*N,N*-diacétique (ASDA), les sels de ceux-ci, et les mélanges de ceux-ci.

6. Composition selon l'une quelconque des revendications 1 à 5, la composition étant exempte d'acide éthylènediaminetétraacétique (EDTA), d'acide nitrilotriacétique (NTA) et d'un quelconque composé contenant du silicium.

7. Composition selon la revendication 1, le tensioactif anionique étant choisi dans le groupe constitué par les alkylsulfates en C_8-C_{18}, les alkyléthersulfates en C_8-C_{18}, les alkylsulfonates en C_8-C_{18}, les α-oléfinesulfates en C_8-C_{18}, les acides gras sulfonés en C_8-C_{18}, les alkylbenzènesulfonates en C_8-C_{18}, les mono- et diesters sulfosucciniques en C_1-C_{12}, les alkylpolyglycoléthercarboxylates en C_8-C_{18}, les N-acyltaurides en C_8-C_{18}, les N-sarconisates en C_8-C_{18}, les alkyliséthionates en C_8-C_{18}, et les mélanges de ceux-ci.

8. Composition selon la revendication 1 ou 7, la source d'alcalinité étant choisie dans le groupe constitué par l'hydroxyde de sodium, l'hydroxyde de potassium, le carbonate de sodium, le carbonate de potassium, ou les mélanges de ceux-ci, et étant de préférence présente dans une quantité de 3 à 90 % en poids, plus préférablement dans une quantité de 5 à 50 % en poids, sur la base de la composition totale.

9. Composition selon l'une quelconque des revendications 1 à 8, la composition comprenant en outre des additifs choisis dans le groupe constitué par les agents modifiant le pH, les agents antimicrobiens, les agents modifiant la viscosité, les azurants optiques, les solvants organiques, les agents de blanchiment, les activateurs de blanchiment, les colorants, le parfum, les agents antimousse compatibles avec les membranes, les agents antirouille, les enzymes et les mélanges de ceux-ci.

10. Procédé de lavage de textiles utilisant une composition selon l'une quelconque des revendications 1 à 9.

11. Procédé selon la revendication 10, l'eau usée accumulée pendant tout le processus de lavage ou des parties de celui-ci étant purifiée lors d'un processus de filtration utilisant une ou plusieurs unités de filtration sur membrane, ledit processus de filtration comprenant de préférence une ou plusieurs étapes d'osmose inverse.

12. Utilisation d'une composition selon l'une quelconque des revendications 1 à 9 comme détergent dans les machines de blanchisserie du commerce et/ou les machines à laver domestiques, comme agent nettoyant et/ou lavant.

Fig. 1a

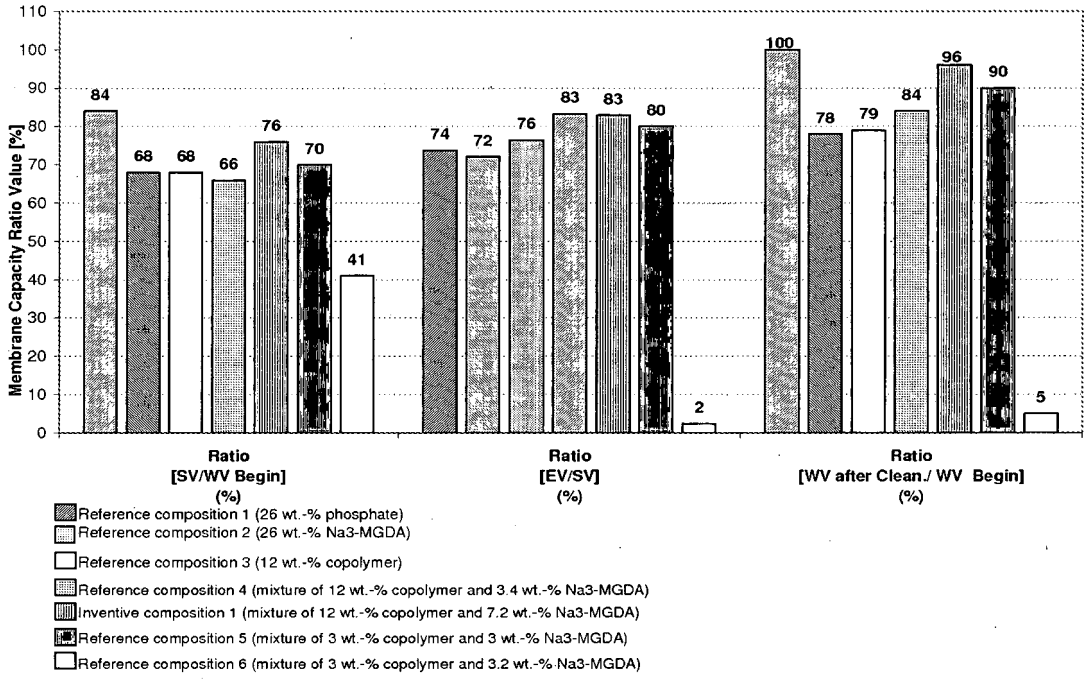

Membrane Capacity Ratio Value [%]
110
100
90
80
70
60
50
40
30
20
10
0
84
68
68
66
76
70
41
74
72
76
83
83
80
2
100
78
79
84
96
90
5
Ratio [SV/WV Begin] (%)
Ratio [EV/SV] (%)
Ratio [WV after Clean./ WV Begin] (%)
Reference composition 1 (26 wt.-% phosphate)
Reference composition 2 (26 wt.-% Na3-MGDA)
Reference composition 3 (12 wt.-% copolymer)
Reference composition 4 (mixture of 12 wt.-% copolymer and 3.4 wt.-% Na3-MGDA)
Inventive composition 1 (mixture of 12 wt.-% copolymer and 7.2 wt.-% Na3-MGDA)
Reference composition 5 (mixture of 3 wt.-% copolymer and 3 wt.-% Na3-MGDA)
Reference composition 6 (mixture of 3 wt.-% copolymer and 3.2 wt.-% Na3-MGDA)

Fig. 1b

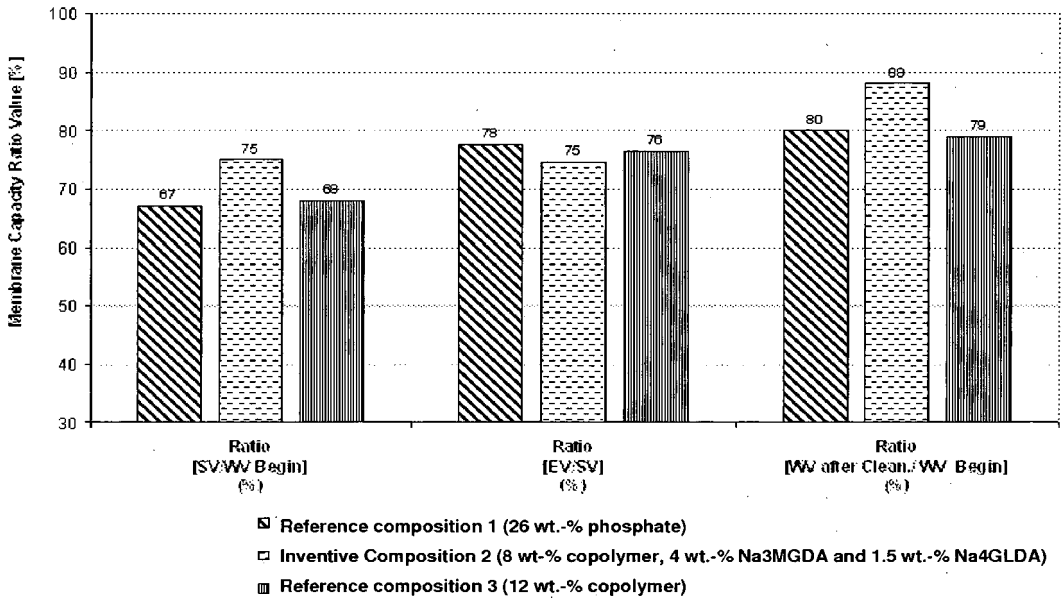

Membrane Capacity Ratio Value [%]
100
90
80
70
60
50
40
30
67
75
69
78
75
76
80
89
79
Ratio [SV:WV Begin] (%)
Ratio [EV:SV] (%)
Ratio [WV after Clean./WV Begin] (%)
Reference composition 1 (26 wt.-% phosphate)
Inventive Composition 2 (8 wt-% copolymer, 4 wt.-% Na3MGDA and 1.5 wt.-% Na4GLDA)
Reference composition 3 (12 wt.-% copolymer)

Fig. 2

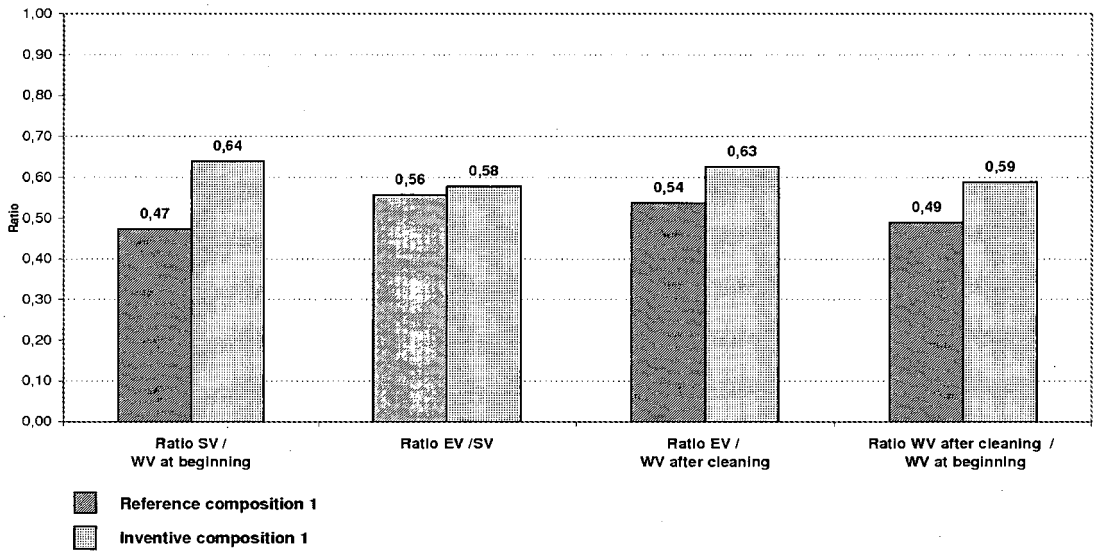
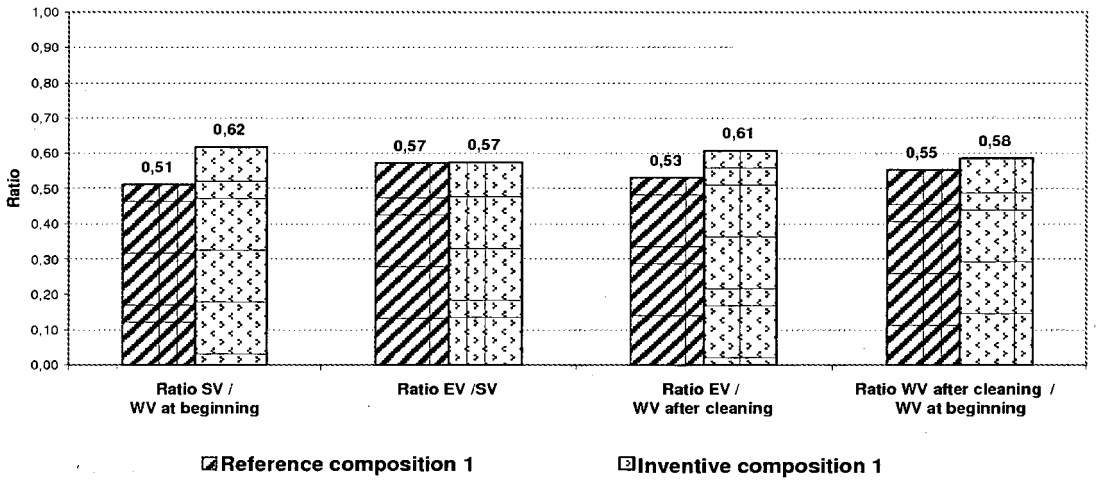

1,00
0,90
0,80
0,70
0,60
0,50
0,40
0,30
0,20
0,10
0,00
Ratio
0,47
0,64
0,56
0,58
0,54
0,63
0,49
0,59
Ratio SV / WV at beginning
Ratio EV /SV
Ratio EV / WV after cleaning
Ratio WV after cleaning / WV at beginning
Reference composition 1
Inventive composition 1

Fig. 3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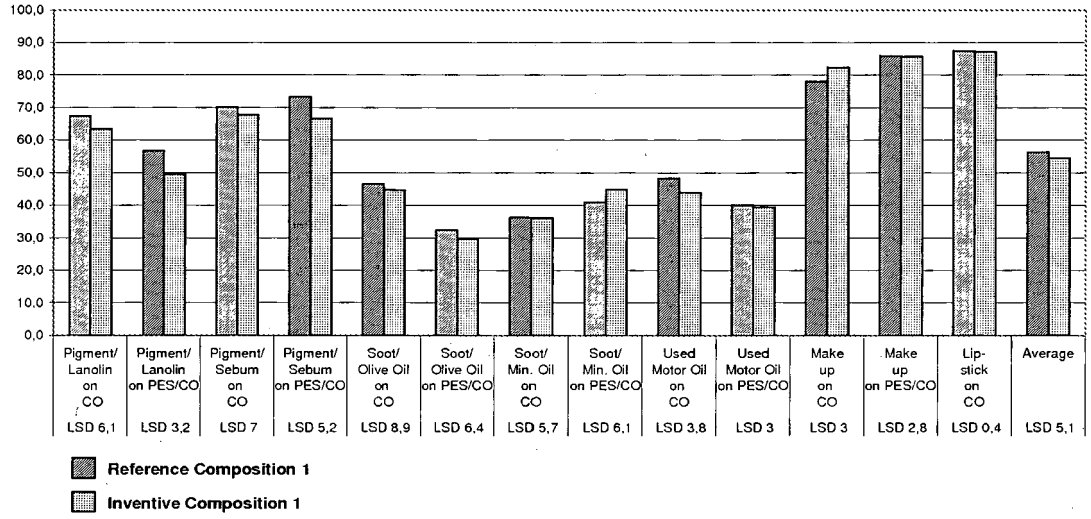
0,20
0,10
0,00
Ratio
0,51
0,62
0,57
0,57
0,53
0,61
0,55
0,58
Ratio SV / WV at beginning
Ratio EV /SV
Ratio EV / WV after cleaning
Ratio WV after cleaning / WV at beginning
Reference composition 1
Inventive composition 1

Fig. 4


100,0
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20,0
10,0
0,0
Pigment/ Lanolin on CO
LSD 6,1
Pigment/ Lanolin on PES/CO
LSD 3,2
Pigment/ Sebum on CO
LSD 7
Pigment/ Sebum on PES/CO
LSD 5,2
Soot/ Olive Oil on CO
LSD 8,9
Soot/ Olive Oil on PES/CO
LSD 6,4
Soot/ Min. Oil on CO
LSD 5,7
Soot/ Min. Oil on PES/CO
LSD 6,1
Used Motor Oil on CO
LSD 3,8
Used Motor Oil on PES/CO
LSD 3
Make up on CO
LSD 3
Make up on PES/CO
LSD 2,8
Lip-stick on CO
LSD 0,4
Average
LSD 5,1
Reference Composition 1
Inventive Composition 1

REFERENCES CITED IN THE DESCRIPTION

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