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(54) **LIQUID CLEANING COMPOSITION**

FLÜSSIGREINIGUNGSZUSAMMENSETZUNG

COMPOSITION DE NETTOYAGE LIQUIDE

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Description**FIELD OF THE INVENTION**

[0001] This invention relates to a liquid cleaner composition. It particularly relates to a liquid cleaner composition comprising a copolymer which is effective as suspending active. The invention also relates to a method for preparing the liquid cleaner composition and use of the liquid cleaner composition.

BACKGROUND TO THE INVENTION

[0002] Aqueous liquid cleaning compositions typically comprise a variety of ingredients to provide an optimal cleaning experience to the user. Such ingredients include for example detergents, builders, sequestrants, disinfectants, oxidising or bleaching agents, agents providing secondary cleaning benefits, etcetera. The rheological properties of a cleaning composition are often instrumental both in providing optimal cleaning performance and in meeting consumer expectation of a cleaning composition. Rheology modifiers can therefore be used to provide a composition with the desired characteristics.

[0003] A particular challenge is provided when it is desired to incorporate particles or gases in a formulation. For many applications these should be suspended in the formulation without separating by precipitation, creaming or phase separation. Particles of very small dimensions may be kept in a dispersed state by means of colloidal stabilisation. Such stabilisation is much harder for larger particles or encapsulates or for instance air bubbles. However, it is often desirable to incorporate and stabilise particles of visible dimensions in a formulation, for instance to provide a visual cue to the consumer, or to enable abrasive cleaning. In these cases it would be impractical or very unattractive if such particles needed to be re-suspended, for instance by shaking, every time a consumer wants to use the composition. It is therefore an object of the present invention to provide cleaning compositions with rheological characteristics enabling suspension of particles or air bubbles.

[0004] Rheology modifiers are typically used as thickeners and/or structurants in a variety of consumer and industrial products, including cleaning compositions. They affect product performance, aesthetics, application and suspension, and delivery of active chemical agents. Rheology modifiers are generally classed in several categories dependent on the mechanism by which they function.

[0005] Hydrodynamic thickeners work by utilizing acid groups in their structure that form anionic charges when the pH is high enough (e.g. at neutral pH). These charges repel each other causing the polymer chains to expand and entangle. Thickening and suspending effects of the neutralized polymers are due to increased physical packing of the molecules. These materials are also known as "space filling" or "volume exclusion". Both viscosity and yield point increase with concentration. The alkali swellable emulsions (ASE) and carbomers fall within this category.

[0006] Associative thickeners operate by a twin mechanism. They utilize the aforementioned hydrodynamic thickening method. Secondly, they utilize the association of hydrophobic groups on the polymer backbone with other hydrophobic species. The latter can be other hydrophobic polymer groups, oils, particles and the like. Association creates hydrophobic regions distributed throughout the polymer chain network. This also renders the polymers effective as solubilising agents. The hydrophobically modified alkali swellable emulsions (HASE) fall into this category.

[0007] HASE/ASE polymers are produced by oil-in-water emulsion polymerization. Most consist of a lightly crosslinked backbone of ethyl acrylate and methacrylic acid.

[0008] US 4,529,773 (Witiak et al.) reports alkali-soluble emulsion polymers activated by neutralization to a pH above 6.5, and subsequently acidified in the presence of a surfactant. These are described as useful thickeners in acidified containing compositions. The polymers are best formed from a 3-component monomer system of methacrylic or acrylic acid, methacrylic or acrylic acid ester of a C8-C30 alkyl or hydrocarbyl monoether of polyethylene glycol, and a C1-C4 alkyl acrylate or methacrylate.

[0009] US 7,649,047 B2 and US 7,288,616, both to Tamareselvy et al., disclose multipurpose alkali-swellable and alkali-soluble associative polymers. They are formed from polymerizing a monomer mixture of at least one acidic vinyl monomer, at least one nonionic vinyl monomer, a first associative monomer having a first hydrophobic end group, a second associative monomer having a second hydrophobic end group, and a crosslinking or chain transfer agent. These patents describe the HASE type chemistry. A commercial product based on this chemistry is the Lubrizol Corp. supplied Aqua SF-1®.

[0010] WO 2010/026097 A1 (Graham et al.) describes rheology modifiers for use in home and personal care compositions. These modifiers are formed from four monomers. They include an amino-substituted vinyl monomer, a hydrophobic nonionic vinyl monomer (such as a C1-C30 alkyl ester of acrylic or methacrylic acid), an associative-like monomer (with a polyoxyalkylene unit end-capped with a hydrophobic group), and a further associative-like vinyl monomer.

[0011] EP 1 630 224 A1 (Rohm and Haas Company) discloses an aqueous composition having a pH of at least 10, and comprising from 0.1% to 5% of at least one crosslinked copolymer comprising from 2.5% to 65% (meth)acrylic acid

residues, from 10% to 80% C2-C4 alkyl (meth)acrylate residues, from 2% to 25% lipophilically modified (meth)acrylate residues and residues of a crosslinker that has no ester or amide functionality.

[0012] US 2007/0054832 A1 (Hocking et al.) discloses an aqueous hard surface cleaning composition comprising: a) a non-associative, acrylic copolymer alkali swellable emulsion (NACOPASE), b) a set of alkaline detergent builders comprising an alkaline builder, a condensed phosphate, and a sequestering agent, and c) a non-ionic surfactant.

[0013] Most rheology modifiers achieve structuring and suspension effects through thickening of the ligand formula. Very few suspend without significant thickening.

[0014] Many cleaning compositions need have good suspending properties but also require retaining of a relatively low viscosity. Such a relatively low viscosity is for instance necessary to enable dosing of the product e.g. by pouring, and especially by spraying. This is a particular challenge in applications aimed at consumers, which typically rely on trigger-operated spraying containers. Such sprayability may for instance be facilitated when a composition is shear-thinning. Shear thinning is a well-known rheological property of compositions, which indicates that the viscosity of a composition is reduced or even breaks down upon applying shear stress to the composition. Usually, a shear-thinning composition will return to its original higher viscosity after removal of the shear stress. This recovery of the viscosity may be a very slow process however, taking many minutes or even hours. This is problematic in typical spray-on cleaning applications, because such compositions should not run off a surface immediately after application. Ideally, a liquid cleaning composition provides good cling to a target surface immediately after spraying. It is generally believed that good cling is facilitated by quick recovery of a state of relatively high viscosity.

[0015] It is therefore an object of the present invention to provide a liquid cleaning composition capable of suspension. It is a more particular object of this invention to provide a cleaning composition capable of suspension which is sprayable, especially by means of a trigger-operated spraying head. It is another object to provide such a composition which also provides good cling to surfaces (in particular cleanable household surfaces) after spraying, preferably relatively quickly after spraying and whereby the surface preferably is a vertical surface.

It is another object to provide a liquid cleaning composition capable of suspending macroscopic particles, preferably in the size range of 1 μm to 2 mm, more preferably 10 μm to 1 mm, and even more preferably 100 to 500 μm , air bubbles, or other suspendables.

[0016] It is yet another object of the invention to provide a method for preparing a liquid cleaning composition, in particular one meeting the suspension, spray and cling characteristics expressed above.

SUMMARY OF THE INVENTION

[0017] We have now found that one or more of the above objectives are met by the liquid cleaning composition according to this invention. We found that a liquid cleaning composition having a pH of between 8 and 13 and comprising 1 to 10 %-wt of surfactants, and 0.4 to 1 %-wt of one or more rheology modifier copolymers as specified hereinbelow, exhibit excellent rheological properties, providing good suspension of particles or other suspendables when the composition is under conditions of no shear (*i.e.* at rest), the composition being very well sprayable, especially by means of a trigger-operated sprayer. Moreover, the composition also provides good cling to cleanable surfaces, notably vertical surfaces.

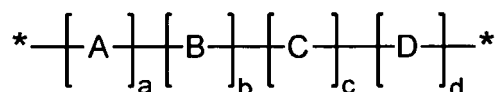
[0018] Therefore, according to a first aspect, the present invention relates to a liquid cleaner composition comprising

0.1 to 10 %-wt of one or more surfactants,
0.4 to 1 %-wt of one or more rheology modifier copolymers, and

water,

whereby the composition has a pH of between 8 and 13

and whereby the one or more rheology modifier copolymer are selected from the group of copolymers of the formula



wherein a, b, c, and d represent the percentage by weight that each repeating unit or derived monomer is contained within the copolymer,

whereby

a ranges from 0.5 to 25% by weight of the copolymer;

b ranges from 70 to 98% by weight of the copolymer;

c ranges from 0 to 15% by weight of the copolymer; and
d ranges from 0 to 5% by weight of the copolymer;

and whereby

A is a macromonomer comprising at at least one end a polymerisable group reactive during polymerisation with at least one of B, C, and D monomers, the polymerisable group at the at least one end of the macromonomer being attached to a chain formed of a homo- or co-polymer of C₁-C₁₀ alkyl acrylates, C₁-C₁₀ alkyl methacrylates, methacrylic acid, acrylic acid or combinations thereof, the macromonomer having a number average molecular weight ranging from 500 to 10,000; and

B is acrylic or methacrylic acid or a salt thereof;

C, when present, is a polyacidic vinyl monomer selected from the group consisting of maleic acid, fumaric acid, itaconic acid, citraconic acid, mesaconic acid, combinations thereof and anhydrides and salts thereof; and

D, when present, is a cross-linking monomer for introducing branching and controlling molecular weight, the cross linking monomer comprising polyfunctional units carrying multiple reactive functionalisation groups selected from the group consisting of vinyl, allylic and functional mixtures thereof,

and whereby the groups **A**, **B**, **C** and **D** are covalently bonded one to another in a random, a block, or a cross-linked copolymer format.

[0019] According to a second aspect, the invention also provides a method for preparing a liquid cleaner composition according to the invention, comprising the steps of

- a. providing water, the one or more rheology modifier copolymers and optionally alkali;
- b. dissolving the copolymer in the water under alkaline conditions; and
- c. adding the surfactant to the composition comprising the dispersed copolymer.

[0020] It was found that preparing the composition by this method led to much quicker solubilisation of the rheology modifier copolymer, compared to methods in which the ingredients are combined in a different order.

[0021] According to a third aspect, the invention also provides use of a liquid cleaning composition according to the invention for cleaning a surface, wherein the composition is comprised in a container, and wherein the container further comprises a spray dispenser for dispensing the composition in the form of a spray.

DETAILED DESCRIPTION OF THE INVENTION

[0022] For the avoidance of doubt, any feature of one aspect of the present invention may be utilised in any other aspect of the invention. The word "comprising" is intended to mean "including" but not necessarily "consisting of" or "composed of." Thus, the term "comprising" is meant not to be limiting to any subsequently stated elements but rather to optionally also encompass non-specified elements of major or minor functional importance. In other words, the listed steps or options need not be exhaustive. Whenever the words "including" or "having" are used, these terms are meant to be equivalent to "comprising" as defined above. It is noted that the examples given in the description below are intended to clarify the invention and are not intended to limit the invention to those examples per se.

[0023] Except in the examples, or where otherwise explicitly indicated, all numbers in this description indicating amounts of material or conditions of reaction, physical properties of materials and/or use are to be understood as modified by the word "about". Unless specified otherwise, numerical ranges expressed in the format "from x to y" are understood to include x and y. When for a specific feature multiple preferred ranges are described in the format "from x to y", it is understood that all ranges combining the different endpoints are also contemplated.

[0024] The term "(meth)acrylic acid" refers to "methacrylic acid and/or acrylic acid". The same applies *mutatis mutandis* to "(meth)acrylate" and its derivatives.

[0025] Number average molecular weights of polymers or macromonomers as mentioned herein, may usually be determined by gel permeation chromatography or ¹H-NMR techniques.

Liquid cleaner composition

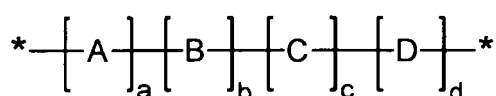
[0026] The liquid cleaner composition of the first aspect of this invention preferably is a surface cleaner composition, more preferably a hard surface cleaner composition. Typically, such hard surfaces are surfaces that commonly require

cleaning. Such surfaces may be found in many household or industrial environments, and may include for example kitchen and bathroom surfaces, table tops, floors, walls, windows, utensils, cutlery, and crockery. Such surfaces may be made from many different materials, including for instance plastics, wood, metal, ceramics, glass, concrete, marble, and painted surfaces.

[0027] It is particularly preferred that the composition is sprayable, and even more preferred that the composition is sprayable from a trigger spray bottle. By sprayable, it is meant that the composition is suitable to be dispensed in the form of a spray or a mist of fine droplets, for instance by expelling the composition through a suitable nozzle. Alternatively, the composition is suitable to be dispensed in the form of a foam.

Rheology modifier copolymer

[0028] The liquid cleaner composition comprises 0.4 to 1%-wt, preferably 0.5 to 0.8 %-wt of one or more rheology modifier copolymers, with respect to the weight of the composition. The copolymer is constructed from a macromonomer, an acrylic or methacrylic acid and optionally a polyacidic vinyl monomer and/or a cross-linking monomer. Thus, the one or more rheology modifier copolymers are selected from the group of copolymers of the formula:



wherein a, b, c, and d represent the percentage by weight that each repeating unit or derived monomer is contained within the copolymer.

[0029] The monomers **A** to **D** are described below. The above structure represents a copolymer formed from the monomers **A**, **B**, **C**, and **D** in any order of those monomers. Thus, the groups **A**, **B**, **C** and **D** are covalently bonded one to another in a random, a block, or a cross-linked copolymer format.

[0030] The rheology modifier copolymer provides the cleaner composition with excellent suspension properties, whilst preferably also proving good sprayability and cling to a surface to be cleaned.

Macromonomer A

[0031] **A** is a macromonomer comprising at at least one end a polymerisable group reactive during polymerisation with at least one of B, C, and D monomers. Preferably, **A** comprises such a polymerisable group at one of its ends. Alternatively, **A** may also comprise a polymerisable group at both ends, so that **A** is a telechelic macromonomer. The polymerisable group is a group capable of reacting with one or more of the monomers of **B**, **C**, and **D** to become incorporated into the rheology modifier copolymer. Thus, the polymerisable group will remain available for further vinyl reactivity with the other monomer constituents of the copolymers after formation of the macromonomer.

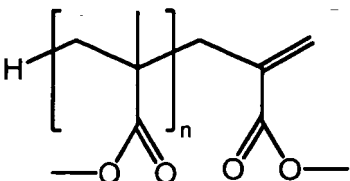
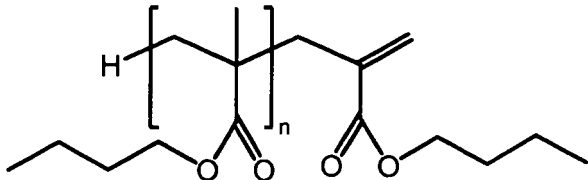
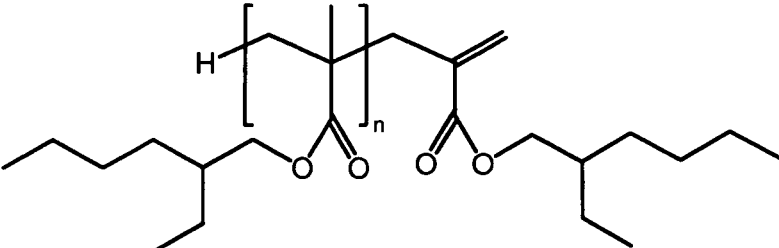
[0032] The polymerisable group at the at least one end of the macromonomer is attached to a chain formed of a homo- or co-polymer of C₁-C₁₀ alkyl acrylates, C₁-C₁₀ alkyl methacrylates, methacrylic acid, acrylic acid or combinations thereof. A suitable polymerisable end group may also be selected from C₁-C₁₀ alkyl acrylates, C₁-C₁₀ alkyl methacrylates, methacrylic acid, and acrylic acid.

[0033] The C₁-C₁₀ alkyl(meth)acrylates forming the above chain are preferably selected from one or more of methyl (meth)acrylate, butyl (meth)acrylate, and 2-ethyl-hexyl (meth)acrylate. Furthermore, it is preferred that the C₁-C₁₀ alkyl(meth)acrylates are C₁-C₁₀ alkylmethacrylates, because these alkylmethacrylates are more favourably prepared by catalytic chain transfer polymerisation. It is even more preferred that the C₁-C₁₀ alkylmethacrylates are selected from one or more of methylmethacrylate, butyl methacrylate, and 2-ethyl-hexyl methacrylate. Homo- or copolymers of these monomers have shown to be particularly efficacious.

[0034] Without wishing to be limited by theory, it is believed to be advantageous if the macromonomer **A** is relatively hydrophobic. Therefore, **A** preferably comprises from 70 to 100 %, more preferably from 80 to 100% and even more preferably from 90 to 100% of C₁-C₁₀ alkyl(meth)acrylates by weight with respect to the weight of **A**. Similarly, it is preferred that **A** comprises from 0 to 30 %, more preferably from 0 to 20 % and even more preferably from 0 to 10 % of (meth)acrylic acid by weight with respect to the weight of **A**.

[0035] The macromonomer has a number average molecular weight ranging from 500 to 10,000. Preferably, the number average molecular weight of **A** is between 500 and 2000, and more preferably between 700 and 1500. Table 1 shows the structures of three preferred macromonomers.

Table 1

Macromonomer	Structure
PMMA ⁽¹⁾	
PBMA ⁽²⁾	
PEHMA ⁽³⁾	
(1) polymethylmethacrylate macromonomer (2) poly-n-butylmethacrylate macromonomer (3) poly-(2-ethyl-hexyl)methacrylate macromonomer	

[0036] The value of *a* (indicating the amount of **A** in the copolymer) ranges from 0.5 to 25% by weight of the copolymer. Preferably, *a* ranges from 5 to 18 % by weight, more preferably from 8 to 17 % by weight of the copolymer.

[0037] The macromonomers can conveniently be prepared by catalytic chain transfer (CCT) polymerisation utilizing catalysts effective to achieve CCT. Preferred but not limiting catalysts include the cobalt porphyrins and the cobaloximes (e.g. a tetramethyl-cobaloxime boron fluoride and a tetraphenyl-cobaloxime boron fluoride). Macromonomers with relatively low molecular weights, such as the ones preferred for **A** can easily be produced with these catalysts unlike with most polymerisation techniques. Therefore, macromonomer **A** is preferably pre-formed by catalytic chain transfer polymerisation.

[0038] In copolymers of the present invention, cobalt ions may remain residually present in amounts from 1 to 100 ppm, more likely from 1 to 30 ppm, and even more likely from 3 to 10 ppm by weight. Residual cobalt in the macromonomer units may range for 1 to 100 pph by weight.

Monomer **B**

[0039] Monomer **B** is acrylic or methacrylic acid or a salt thereof. Preferably, **B** is acrylic acid or a salt thereof. In certain embodiments, the acid groups of the monomer may already be neutralised, forming salts. Typical salt counterions to the acid groups are sodium, potassium, ammonium and triethanolammonium cations.

[0040] The value of *b* (indicating the amount of **B**) ranges from 70 to 98% by weight of the copolymer. Preferably, *b* ranges from 78 to 93 % by weight, more preferably from 81 to 87 % by weight of the copolymer.

Monomer **C**

[0041] Monomer **C** is an optional monomer. **C**, when present, is a polyacidic vinyl monomer selected from the group consisting of maleic acid, fumaric acid, itaconic acid, citraconic acid, mesaconic acid, combinations thereof and anhydrides and salts thereof. It is preferred that **C** is selected from maleic acid, maleic anhydride and mixtures thereof.

[0042] Salts include the mono- and disalts of the polyacidic vinyl monomers. In one embodiment, maleic acid can be generated from maleic anhydride as starting material and hydrolysing this to the diacid in the subsequent emulsion

polymerisation of the rheology modifier copolymer.

[0043] The value of c ranges from 0 to 15% by weight of the copolymer. Preferably, c ranges from 0 to 5 % by weight, more preferably c ranges from 2 to 4 % by weight of the copolymer.

5 Monomer D

[0044] Monomer **D** is an optional monomer. **D**, when present, is a cross-linking monomer for introducing branching and controlling molecular weight, the cross linking monomer comprising polyfunctional units carrying multiple reactive functionalisation groups selected from the group consisting of vinyl, allylic and functional mixtures thereof.

10 **[0045]** These cross-linking monomers will be polyunsaturated. Illustrative, non-limiting examples are divinyl benzene, divinyl naphthalene, trivinyl benzene, triallyl pentaerythritol, diallyl pentaerythritol, diallyl sucrose, octaallyl sucrose, trimethylol propane diallyl ether, 1,6-hexanediol di(meth)acrylate, tetramethylene tri(meth)acrylate, trimethylol propane tri(meth)acrylate, polyethoxylated glycol di(meth)acrylate, alkylene bisacrylamides, bisphenol A, polyethoxylated dimethacrylate, trimethylol propane polyethoxylated trimethacrylate and similar materials. Preferred for the present invention are bisphenol A polyethoxylated glycol diacrylate, trimethylol propane triacrylate and pentaerythritol allyl ether. It is more preferred that wherein **D** is pentaerythritol allyl ether.

15 **[0046]** The value of d ranges from 0 to 5% by weight of the copolymer. Preferably, d ranges from 0 to 2 % by weight, more preferably from 0.5 to 1.5 % by weight, and even more preferably from 0.7 to 1.0 % by weight of the copolymer.

20 Preferred copolymers

[0047] The rheology modifier copolymer is preferably selected from the group of copolymers wherein

- 25 • A is a poly-*n*-butyl methacrylate macromonomer having a number average molecular weight of between 500 and 2000, and a is in the range of between 5 %-wt and 20 %-wt;
- B is acrylic acid;
- C is maleic anhydride and c is in the range of between 2 and 4 %-wt; and
- D is pentaerythritol allyl ether and d is in the range between 0.75 and 1%-wt;

30 or the group of copolymers wherein

- A is a poly-methyl methacrylate macromonomer having a number average molecular weight of between 500 and 2000, and a is in the range of between 5 %-wt and 20 %-wt;
- B is acrylic acid;
- 35 • C is maleic anhydride and c is in the range of between 0 and 4 %-wt;
- D is pentaerythritol allyl ether and d is in the range between 0.75 and 1%-wt;

and wherein the specified percentages are by weight of the copolymer.

[0048] The rheology modifier copolymer is more preferably selected from one or more copolymers wherein

- 40 • A is a poly-*n*-butyl methacrylate macromonomer having a number average molecular weight of between 500 and 2000, and a is in the range of between 8 %-wt and 12 %-wt;
- B is acrylic acid;
- C is maleic anhydride and c is in the range of between 2 and 3 %-wt;
- 45 • D is pentaerythritol allyl ether and d is in the range between 0.75 and 1%-wt.

[0049] The number average molecular weight of the one or more rheology modifier copolymers according to the present invention is preferably 50 000 or more. For non-cross-linked copolymers, the number average molecular weight typically is in the range of from $5 \cdot 10^4$ to $5 \cdot 10^5 \text{ g} \cdot \text{mol}^{-1}$. For cross-polymers, the number average molecular weight typically is in the range of from $5 \cdot 10^5$ to $5 \cdot 10^6 \text{ g} \cdot \text{mol}^{-1}$.

50 **[0050]** The rheology modifier copolymer of the present invention can conveniently be synthesised by methods well-known in the art, such as, for instance precipitation polymerisation.

Surfactants

55 **[0051]** Surfactants can for instance advantageously contribute to the cleaning efficacy or the formulation stability of the liquid cleaner composition according to the present invention. Therefore, the liquid cleaner composition comprises 0.1 to 10 %-wt, preferably from 1 to 9, more preferably from 2 to 7 %-wt, and even more preferably from 4 to 6 %-wt of

one or more surfactants.

[0052] Any type of surfactant, i.e. anionic, cationic, nonionic, zwitterionic or amphoteric can be used. The one or more surfactants are generally chosen from anionic and non-ionic detergent actives. The cleaning composition may further comprise cationic, and zwitterionic or amphoteric surfactants.

[0053] Suitable synthetic (non-soap) anionic surfactants are water-soluble salts of organic sulphuric acid mono-esters and sulphonic acids which have in the molecular structure a branched or straight chain alkyl group containing from 6 to 22 carbon atoms in the alkyl part.

[0054] Examples of such anionic surfactants are water soluble salts of:

- (primary) long chain (e.g. 6-22 C-atoms) alcohol sulphates (hereinafter referred to as PAS), especially those obtained by sulphating the fatty alcohols produced by reducing the glycerides of tallow or coconut oil;
- alkyl benzene sulphonates, such as those in which the alkyl group contains from 6 to 20 carbon atoms;
- secondary alkanesulphonates;

and mixtures thereof.

[0055] Also suitable are the salts of:

- alkylglyceryl ether sulphates, especially of the ethers of fatty alcohols derived from tallow and coconut oil;
- fatty acid monoglyceride sulphates;
- sulphates of ethoxylated aliphatic alcohols containing 1-12 ethyleneoxy groups;
- alkylphenol ethyleneoxy-ether sulphates with from 1 to 8 ethyleneoxy units per molecule and in which the alkyl groups contain from 4 to 14 carbon atoms;
- the reaction product of fatty acids esterified with isethionic acid and neutralised with alkali,

and mixtures thereof.

[0056] The preferred water-soluble synthetic anionic surfactants are the alkali metal (such as sodium and potassium) and alkaline earth metal (such as calcium and magnesium) salts of alkyl-benzenesulphonates and mixtures with olefin-sulphonates and alkyl sulphates, and the fatty acid mono-glyceride sulphates.

[0057] The most preferred anionic surfactants are alkyl-aromatic sulphonates such as alkylbenzenesulphonates containing from 6 to 20 carbon atoms in the alkyl group in a straight or branched chain, particular examples of which are sodium salts of alkylbenzenesulphonates or of alkyl-toluene-, -xylene- or -phenolsulphonates, alkylnaphthalene-sulphonates, ammonium diaminonaphthalene-sulphonate, and sodium dinonyl-naphthalene-sulphonate.

[0058] If synthetic anionic surfactant is to be employed the amount present in the cleaning compositions of the invention will generally be from 0.1 to 10 %-wt, preferably from 1 to 9, more preferably from 2 to 7 %-wt, and even more preferably from 4 to 6 %-wt.

[0059] A suitable class of nonionic surfactants can be broadly described as compounds produced by the condensation of simple alkylene oxides, which are hydrophilic in nature, with an aliphatic or alkyl-aromatic hydrophobic compound having a reactive hydrogen atom. The length of the hydrophilic or polyoxyalkylene chain which is attached to any particular hydrophobic group can be readily adjusted to yield a compound having the desired balance between hydrophilic and hydrophobic elements.

[0060] This enables the choice of nonionic surfactants with the right HLB. Particular examples include:

- the condensation products of aliphatic alcohols having from 8 to 22 carbon atoms in either straight or branched chain configuration with ethylene oxide, such as a coconut alcohol/ethylene oxide condensates having from 2 to 15 moles of ethylene oxide per mole of coconut alcohol;
- condensates of alkylphenols having C6-C15 alkyl groups with 5 to 25 moles of ethylene oxide per mole of alkylphenol;
- condensates of the reaction product of ethylene-diamine and propylene oxide with ethylene oxide, the condensates containing from 40 to 80% of ethyleneoxy groups by weight and having a molecular weight of from 5,000 to 11,000.

[0061] Other classes of nonionic surfactants are:

- tertiary amine oxides of structure $R^1R^2R^3N-O$, where R^1 is an alkyl group of 8 to 20 carbon atoms and R^2 and R^3 are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, e.g. dimethyldodecylamine oxide;
- tertiary phosphine oxides of structure $R^1R^2R^3P-O$, where R^1 is an alkyl group of 8 to 20 carbon atoms and R^2 and R^3 are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, for instance dimethyl-dodecylphosphine oxide;
- dialkyl sulfoxides of structure $R^1R^2S=O$, where R^1 is an alkyl group of from 10 to 18 carbon atoms and R^2 is methyl or ethyl, for instance methyl-tetradecyl sulfoxide;
- fatty acid alkylolamides, such as the ethanol amides;

- alkylene oxide condensates of fatty acid alkylolamides;
- alkyl mercaptans;
- alkyl polyglucosides (APG), for example C₈-C₁₆ alkyl polyglycoside, including those from the Glucopon® range, e.g. Glucopon® 425.

[0062] It is preferred that the liquid cleaner composition according to the present invention comprises non-ionic surfactants. It is even more preferred that at least 50 %, still more preferably at least 75 %-wt and still more preferably at least 90% by weight of the surfactants are non-ionic surfactants. Even more preferably, the one or more surfactants are non-ionic surfactants. Thus, it is preferred that the liquid cleaner composition comprises from 0.1 to 10 %-wt, preferably from 1 to 9, more preferably from 2 to 7 %-wt, and even more preferably from 4 to 6 %-wt of one or more non-ionic surfactants.

[0063] It is preferred that the non-ionic surfactants are selected from ethoxylated alkyl alcohols and alkyl polyglucosides. More preferably the surfactants are ethoxylated alkyl alcohols and even more preferably ethoxylated C₈-C₁₂ alkyl alcohols, whereby yet more preferably the average degree of ethoxylation is between 5 and 8. An example of particularly effective (and therefore preferred) surfactants are ethoxylated C₉-C₁₁ alkyl alcohols with an average degree of ethoxylation of 8, including for instance the commercially surfactant Neodol 91-8.

[0064] It is also possible optionally to include amphoteric, cationic or zwitterionic surfactants in said compositions.

[0065] Suitable amphoteric surfactants are derivatives of aliphatic secondary and tertiary amines containing an alkyl group of 8 to 20 carbon atoms and an aliphatic group substituted by an anionic water-solubilising group, for instance sodium 3-dodecylamino-propionate, sodium 3-dodecylaminopropane-sulphonate and sodium *N*-2-hydroxy-dodecyl-*N*-methyltaurate.

[0066] Examples of suitable cationic surfactants can be found among quaternary ammonium salts having one or two alkyl or aralkyl groups of from 8 to 20 carbon atoms and two or three small aliphatic (e.g. methyl) groups, for instance cetyltrimethylammonium chloride.

[0067] A specific group of surfactants are the tertiary amines obtained by condensation of ethylene and/or propylene oxide with long chain aliphatic amines. The compounds behave like nonionic surfactants in alkaline medium and like cationic surfactants in acid medium.

[0068] Examples of suitable zwitterionic surfactants can be found among derivatives of aliphatic quaternary ammonium, sulphonium and phosphonium compounds having an aliphatic group of from 8 to 18 carbon atoms and an aliphatic group substituted by an anionic water-solubilising group, for instance betaine and betaine derivatives such as alkyl betaine, in particular C₁₂-C₁₆ alkyl betaine, 3-(*N,N*-dimethyl-*N*-hexadecyl-ammonium)-propane-1-sulphonate betaine, 3-(dodecyl-methyl-sulphonium)-propane-1-sulphonate betaine, 3-(cetylmethyl-phosphonium)-propane-1-sulphonate betaine and *N,N*-dimethyl-*N*-dodecyl-glycine. Other well-known betaines are the alkylamidopropyl betaines e.g. those wherein the alkylamido group is derived from coconut oil fatty acids.

[0069] In general, further examples of surfactants may be chosen from the surfactants described in well-known textbooks like "Surface Active Agents" Vol. 1, by Schwartz & Perry, Interscience 1949, Vol. 2 by Schwartz, Perry & Berch, Interscience 1958, and/or the current edition of "McCutcheon's Emulsifiers and Detergents" published by Manufacturing Confectioners Company or in "Tenside-Taschenbuch", H. Stache, 2nd Edn., Carl Hauser Verlag, 1981; "Handbook of Industrial Surfactants" (4th Edn.) by Michael Ash and Irene Ash; Synapse Information Resources, 2008.

Water and pH

[0070] The liquid cleaner composition of the present invention comprises water. Preferably, the composition comprises at least 70 %-wt, more preferably between 76 and 98 wt-%, even more preferably between 84 and 93 %-wt of water.

[0071] The composition has a pH of between 8 and 13, more preferably between 10 and 12 and even more preferably between 10 and 11. The pH of the composition can suitably be adapted to fall within the required or preferred range by means of a pH modifier. Such pH modifiers are well-known in the art. The composition preferably comprises a pH modifier selected from ethanolamine, potassium hydroxide, sodium hydroxide and mixtures thereof.

Suspendables

[0072] The liquid cleaner composition of the present invention is particularly efficacious at providing suspension to materials dispersed in the liquid. Therefore, in the context of this invention, a suspendable is an entity that is capable of being suspended by the liquid cleaner composition. Typically, a suspendable would cream or sediment in a Newtonian liquid of equivalent density, since a Newtonian liquid is incapable of suspension. Typically, a suspendable is in a different phase than the liquid, so it may be gaseous or solid. A suspendable typically is immiscible and/or insoluble in the liquid cleaner composition (at least at a timescale corresponding to the shelf life of the composition). The following are non-limiting examples of suspendables.

[0073] The suspendables may for instance act as visual cues, providing a sense of cleaning activity to the user of the cleaner liquid. Examples of visual cues suitable to be suspended include mica platelets, mica/silica particles (e.g. Timeron MP1001 ex Merck), or wax beads.

[0074] Alternatively, abrasives may be used as suspendables, including for example calcite (e.g. OmyaCarb 30AV, ex Omya), or silica particles or olive stone fragments.

[0075] In yet another alternative, the suspendables may be encapsulates, containing encapsulated substances, including for example fragrance, insecticide, antibacterial agents or enzymes.

[0076] The suspendables need not be solid. Thus, gas bubbles, including e.g. air, or nitrogen can also be efficiently suspended.

The size of the suspendables preferably is in the size range of 1 μm to 2 mm, more preferably of 10 μm to 1 mm, and even more preferably of 100 to 500 μm . Nevertheless, it is noted that when the suspendable consists of air bubbles, the size may be larger than 2 mm. In case the liquid cleaner composition is intended to be suitable for spraying, suitable suspendables are preferably smaller than 500 μm . Suspendable abrasive particles preferably have a volume average median diameter $d(0.5)$ of 100 μm or below, more preferably of between 20 and 70 μm .

Polymeric amines

[0077] Surprisingly, we found that the presence of certain polymeric amines strongly enhances the suspension effect of the liquid cleaner composition according to the invention. This effect is for example evidenced by a marked increase in the yield stress of the composition upon addition of even a small amount of the polymeric amines. Thus, addition of such polymeric amines can either provide stronger suspension, for instance to suspend particles under more challenging conditions or, alternatively, the amount of other active ingredients - in particular of the rheology modifier copolymer - can be reduced whilst still obtaining sufficient suspension. We also found that the liquid cleaner composition retains its other benefits including sprayability and cling in the presence of the polymeric amines

[0078] Therefore, the liquid cleaner composition according to the present invention preferably comprises a polymeric amine ingredient, wherein the polymeric amine ingredient includes a (co-)polymer selected from the group consisting of poly(ethylene imine)s, alkoxylated poly(ethylene imine)s, alkylated poly(ethylene imine)s, poly(vinyl amine)s, alkoxylated poly(vinyl amine)s, alkylated poly(vinyl amine)s.

[0079] Preferably, the polymeric amine is selected from the group consisting of poly(ethylene imine)s, alkoxylated poly(ethylene imine)s, alkylated poly(ethylene imines) and mixtures thereof. Even more preferably, the polymeric amine is selected from poly(ethylene imine)s, alkoxylated poly(ethylene imine)s and mixtures thereof.

[0080] The concentration of the polymeric amine in the cleaning composition of the invention is preferably in the range of from 0.01 to 5.0% by weight, more preferably 0.01 to 2.0% by weight, most preferably 0.05 to 1.0% by weight.

[0081] Furthermore, the polymeric amine preferably has a number average molecular weight of from 500 to $1 \cdot 10^7$, more preferably from 500 to $2 \cdot 10^6$, still more preferably from 1000 to $2 \cdot 10^6$.

[0082] It is particularly preferred that the liquid cleaner composition according to the invention comprises between 0.01 and 1 %-wt, more preferably between 0.05 and 0.5 %-wt, even more preferably between 0.1 and 0.4 %-wt and still more preferably between 0.2 and 0.3 %-wt of one or more polymeric amines selected from the group consisting of polyethylenimines and hydroxyethylated polyethylenimines. Suitable examples of polyethylenimines and hydroxyethylated polyethylenimines include branched polyethylene imines (e.g. Lupasol® PS) and ethoxylated branched polyethylene imine (e.g. Lupasol® SC 61 B).

Optional other ingredients

[0083] The cleaning composition of the present invention may include abrasives. In a preferred embodiment - in particular when the composition comprises polymeric amines as specified above - the composition of the present invention does not contain an abrasive. The composition may contain other ingredients which aid in its cleaning performance.

[0084] For example, the composition may contain detergent builders and mixtures of builders in an amount of up to 25%; in particular when the composition contains one or more anionic surfactants. If present, the builder preferably will form at least 0.1 % of the cleaning composition. Suitable inorganic and organic builders are well known to those skilled in the art.

[0085] A further optional ingredient of the composition of the invention is a suds regulating material, which can be employed in compositions which have a tendency to produce excessive suds in use. Examples thereof are fatty acids or their salts (soap), isoparaffins, silicone oils and combinations thereof.

[0086] Soaps are salts of fatty acids and include alkali metal soaps such as the sodium, potassium and ammonium salts of fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 10 to about 20 carbon atoms. Particularly useful are the sodium and potassium and mono-, di- and triethanolamine salts of the mixtures of fatty acids derived from palm oil, coconut oil and ground nut oil. When employed, the amount of fatty acid or soap can form

at least 0.005%, preferably 0.1 % to 2% by weight of the composition.

[0087] In certain embodiments it is preferred that the composition comprises one or more additional organic solvents. It is preferred that the organic solvent is water-immiscible. It is more preferred that the organic solvent is suitable to serve as a co-surfactant. It is even more preferred that the liquid cleaner composition of the invention comprises from

0.01 to 0.5 %-wt of a water-immiscible organic solvent, preferably dipropylene glycol monobutyl ether.

[0088] Compositions may also contain, in addition to the ingredients already mentioned, various other optional ingredients such as colorants, whiteners, optical brighteners, soil suspending agents, detergent enzymes, compatible bleaching agents (particularly peroxide compounds and active chlorine releasing compounds), solvents, co-solvents, gel-control agents, further freeze-thaw stabilisers, bactericides, preservatives (for example 1,2-benzisothiazolin-3-one), hydrotropes and perfumes.

[0089] In certain preferred embodiments, the liquid cleaner composition favourably includes one or more next-time cleaning benefit agents. A "next time cleaning benefit" refers to an improved ease of removal of soil after re-soiling of a hard surface cleaned using a composition comprising a next-time cleaning benefit agent. This improved ease may for example be indicated by an increased amount of soil being removed from a metal surface using a certain fixed cleaning effort (e.g. the same no. of wiping actions using the same force per wiping action). Suitable next-time cleaning benefit agents include for example the polymeric amines as specified above, tannic acid (or related compounds such as gallic acid and/or propyl gallate) or malonic acid.

Liquid dispensers and use

[0090] The liquid cleaning composition of the invention may be stored in and dispensed by any suitable means, but spray applicators are particularly preferred. Pump dispensers (whether spray or non-spray pumps) and pouring applicators (bottles etc) are also possible. Thus, the invention also provides the use of a liquid cleaning composition according to the invention for cleaning a surface, wherein the composition is comprised in a container, and wherein the container further comprises a spray dispenser for dispensing the composition in the form of a spray. The spray dispenser is preferably a trigger spray dispenser but may be any mechanical means for ejecting the liquid in spray or aerosol form. The surface preferably is a hard surface, more preferably a vertical hard surface. This use of the composition of the invention optimally exploits the advantageous suspension, sprayability and cling properties of the composition.

Method of preparation

[0091] According to a second aspect of the invention, we found that the liquid cleaner composition of the invention can advantageously be prepared by a method, comprising the steps of

- a. providing water, the one or more rheology modifier copolymers and optionally alkali;
- b. dissolving the copolymer in the water under alkaline conditions; and
- c. adding the surfactant to the composition comprising the dispersed copolymer.

[0092] The optional alkali serves to provide suitable alkaline conditions, if these are not already inherently provided by the copolymer. Thus, the aqueous solution in which the copolymer is dissolved preferably has a pH of above 8, more preferably above 10 and even more preferably above 12. Suitable alkali materials are the pH modifiers as specified above.

[0093] In step b, the copolymer need not be dissolved in all the water that is comprised in the final composition. It is particularly advantageous to first prepare a relatively concentrated solution of the copolymer. Such a concentrated solution preferably is in the form of a gel and preferably comprises 1 to 20 %-wt, more preferably 5 to 15 %-wt and even more preferably 8 to 12 %-wt of the copolymer. Subsequently, this concentrated solution may conveniently be combined with an aqueous solution comprising the surfactant under step c.

[0094] Additional ingredients of the composition are preferably added after step b, more preferably during or after step c.

EXAMPLES

EXAMPLE 1 Synthesis of copolymers

Typical macromonomer synthesis

[0095] Macromonomers were synthesised by a catalytic chain transfer polymerisation reaction. Azo-isobutyronitrile (0.70g) (AIBN) was dissolved in 2-ethylhexyl methacrylate (150mL) and butanone (150mL) in a 2-arm round bottomed flask fitted with a condenser. The solution was purged with nitrogen for 45 minutes before addition of Cobaloxime Boron Fluoride (COBF) (10.3mg). The solution was purged with nitrogen for a further 5 minutes and the reaction mixture heated

to 75°C for 24 hours. Samples were taken periodically for conversion and molecular weight analysis using ¹H NMR analysis. The resulting macromonomers were purified by removal of solvent and excess monomer *in vacuo*. Butanone (150mL) was added to the viscous oil and removed again *in vacuo*. This cycle was repeated three times to reduce residual monomer content.

[0096] Macromonomers of methylmethacrylate and *n*-butylmethacrylate were prepared in a similar fashion.

Copolymer synthesis

[0097] The copolymers according to the present invention were prepared by precipitation polymerisation. Stock solutions of acrylic acid (250mL, 50 w. %), maleic anhydride (250mL, 15 wt. %), macromonomer (250mL, 5 wt%), pentaerythritol allyl ether (250mL, 1wt%), AIBN (250mL, 0.25wt%), and potassium carbonate were made up with ethyl acetate/cyclohexane (54/46v/v%) in Schott Duran 200mL flasks. Each flask was purged with nitrogen for 30 minutes before being added to a Chemspeed Swing Platform. Each reaction flask was manually purged with argon before the Chemspeed Swing Platform was sealed and purged with nitrogen for 30 minutes. The robot was then initialized to add aliquots of each stock solution to the reaction flasks. The reaction flasks were then heated in an H&P heating block at 83°C for 3 hours. The resulting white precipitates were dried by decanting off the solvent and removing any residual monomer and solvent *in vacuo* spelling to a fine powder using a food blender. Table 2 lists the compositions of the reaction mixtures used to prepare the copolymers CP1, CP2, and CP3 with the compositions as specified in Table 3.

Table 2 - Macromer preparation

Sample ⁽¹⁾	CP1	CP2	CP3
Ethyl Acetate	55.08	55.08	55.08
Cyclohexane	46.98	46.98	46.98
Acrylic Acid	15.093	14.472	15.552
Maleic Anhydride	0.45	0.45	0
PBMA 950 ⁽²⁾	1.8	2.7	0
PMMA 1400 ⁽³⁾	0	0	1.8
pentaerythritol allyl ether	0.1548	0.1548	0.1548
AIBN	0.0594	0.0594	0.0594
Potassium Carbonate	0.495	0.495	0.495
(1) all quantities in grams (2) PBMA 950 = poly- <i>n</i> -butyl methacrylate macromonomer with number average molecular weight Mn is about 900 Da. (3) PMMA 1400 = polymethylmethacrylate macromonomer (Mn is about 1400 Da)			

Table 3 - Macromers

Example	A		B	C	D
	PBMA 950 macromer wt-%	PMMA 1500 macromer wt-%	Acrylic Acid wt-%	Maleic Anhydride wt-%	Pentaerythritol allyl ether wt-%
CP1	10.3	-	86.2	2.6	0.9
CP2	15.2	-	81.4	2.5	0.9
CP3	-	10.3	88.8	0	0.9

EXAMPLE 2 - Liquid cleaner compositions

[0098] Liquid cleaner compositions were formulated as specified in Table 4. The process involved initial swelling of the copolymer in alkali solution before addition of remaining materials in any order. The swelling of the copolymer involved firstly mixing with water on a 1:9 weight ratio to form a rough gel, followed by addition of the copolymer gel to a mixture

of NaOH and water with stirring.

Table 4 - Liquid cleaner compositions

Example	2:1	2:2	2:3	2:4	2:5	2:6 ⁽ⁱ⁾	2:7 ⁽ⁱ⁾	2:8 ⁽ⁱ⁾	2:9	2:10	2:11 ⁽ⁱ⁾	2:12 ⁽ⁱ⁾
NaOH	1.00	1.00	1.00	1.00	1.00	0.25	1.00	1.00	1.00	1.00	1.00	1.00
Citric acid	1.00	1.00		1.10	1.00	0.70	1.20	1.00	1.10	1.00	1.20	1.20
CP1 ^(a)	0.60	--	--	0.60	0.60	0.60	--	0.60	0.60	0.60	--	--
CP2 ^(a)	--	0.80	0.80	--	--	--	--	--	--	--	--	--
CP3 ^(a)	--	--	0.60	--	--	--	--	--	--	--	--	--
Aculyn 28 ^(b)	--	--	--	--	--	--	0.60	--	--	--	--	--
Neodol 91-8 ^(c)	5.00	5.00	5.00	--	--	5.00	5.00	20.00	5.00	5.00	5.00	5.00
Neodol 91-5 ^(d)	--	--	--	5.00	--	--	--	--	--	--	--	--
Glucopon 425 ^(e)	--	--	--	--	5.00	--	--	--	--	--	--	--
Dowanol DPnB ^(f)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Lupasol PS ^(g)	--	--	--	--	--	--	--	--	0.25	--	0.25	--
Lupasol SC 61B ^(h)	--	--	--	--	--	--	--	--	--	0.25	--	0.25
Water	to 100%											
pH	10.5		10.6	10.4	10.8	4.7	10.7	10.7	10.8	10.4	10.3	10.5
(a) Rheology modifier copolymers from Example 2 (b) Non-cross-linked HASE acrylate/beheneh-25 methacrylate copolymer rheology modifier polymer ex Dow Chemicals. (c) C ₉ -C ₁₁ alcohol ethoxylate, (8EO), ex Shell (d) C ₉ -C ₁₁ alcohol ethoxylate, (5EO), ex Shell (e) Alkyl polyglycoside, C ₈ -C ₁₆ , ex BASF. (f) Dipropylene glycol n-butyl ether, Dow Chemicals. (g) Branched polyethylene imine, Mn = 750 kDa (light scattering), BASF. (h) Ethoxylated branched polyethylene imine, Mn = 110kDa (calculated), BASF. (i) Comparative example												

EXAMPLE 3 - Performance of the compositions

[0099] The performance of the cleaner compositions according to the invention is assessed on the basis of their suspending capability, their sprayability and their cling to a surface. The results of the tests were interpreted as explained in Table 5.

Suspension test

[0100] An amount of 100 mg of red bentonite particles with a relative density of 1.5 and a volume-average median particle diameter of 500 μm was placed in a 10 mL glass vial. The test liquid (5 grams) was added after which the vial was sealed and shaken to disperse the particles throughout the liquid. The vial was stored at 20°C for 24 hours prior to visual inspection.

Yield stress test

[0101] The yield stress of the cleaning liquids was determined and used as a measure of the suspending capability of the liquids. Thus, the stress required to overcome the elastic state the liquids exist in at very low or zero shear and to allow strain (net flow) of the liquid is measured. The maximum value of G', the elastic or storage modulus, was measured by oscillatory rheological measurement using an Anton Paar ASC rheometer, fitted with a smooth 'cup and bob' geometry (CC27), run in oscillation mode at 25°C. The bob was oscillated at 1 Hz with increasing strain (rotational

amplitude) from 0.01 to 100% of full rotation. G' was measured at 60 strain values across the 4 decades, spaced logarithmically, with 10s per measurement. The Elastic Stress is then calculated ($ES = G' \times \text{strain}$) and the maximum value for this is equivalent to the Yield Stress as reported below.

Sprayability test

[0102] The cleaning liquids were sprayed using a Cif trigger spray device. If the liquids were sprayable, the volume average mean diameter $D[4,3]$ of the droplets of the spray was determined using a Spraytec spray particle analyser (ex Malvern).

Cling test

[0103] The extent to which a cleaning liquid clings to a typical household surface after spraying was determined. For every measurement, a glass tiles of 150×150 mm was cleaned using calcite and rinsed with demineralised water and dried (with absorbent tissue). After weighing the tile, between 2 and 3 grams of the cleaner composition was sprayed onto the horizontal tile from a conventional Cif spraying device at a distance of 30 cm. Subsequently, the tile was weighed again to obtain the initial product weight. The tile was then held vertically for 10 seconds, was returned to a horizontal orientation and reweighed to obtain the weight of the composition remaining on the tile. The cling value is reported as the average percentage by weight of the sprayed composition that remained on the tile in three repeated tests.

[0104] For compositions according to the invention, there was no difference in visual appearance of the material after applying the material to a horizontal surface and rotating it to vertical compared to applying the material to a vertical surface. This indicates that good cling occurs very rapidly after application.

Table 5 - Interpretation of test results

	Good	Acceptable	Unacceptable
Suspension Test	No sedimentation of bentonite particles observed.	Bentonite particles separated into lower 99 to 90% of test liquid.	Bentonite particles separated into less than 90% of test liquid.
Yield Stress	Yield Stress >1.0 Pa	Yield Stress >0.6 Pa	Yield Stress <0.6 Pa
Spray Test	Droplet size $D[4,3]$ between 190 and $240 \mu\text{m}$; no observation of non-nebulised liquid in spray-cone.	Droplet size $D[4,3]$ < $500 \mu\text{m}$; and observation of majority of liquid in spray-cone nebulised.	Droplet size $D[4,3]$ > $500 \mu\text{m}$; and/or observation of majority of liquid in cone non-nebulised.
Cling Test	>90% product remaining after test	80-90% product remaining after test	<80% product remaining after test

Table 6 - Summary of results

Example	Bentonite suspension	Yield Stress (Pa)	Cling (%@10s)	Spray $D[4,3]$ (μm)	pH
2:01	Good	1.687	92.96	360	10.5
2:02	Good	1.42	96.99	335 ^(a)	10.3
2:03	Good	0.681	91.62	370	10.6
2:04	Good	1.793	95.91	426	10.4
2:05	Good	2.118	94.02	393	10.8
2:6^(b)	No	0.487	66.82	372	4.7
2:7^(b)	No	0.007	57.32	453	10.7
2:8^(b)	No	0.295	82.25	423	10.7
2:09	Good	5.417	89.58	352	10.8
2:10	not tested	2.62	95.47	not tested	10.4

(continued)

Example	Bentonite suspension	Yield Stress (Pa)	Cling (%@10s)	Spray D[4,3] (μm)	pH
2:11 ^(b)	not tested	<0.1	25.79	not tested	10.3
2:12 ^(b)	not tested	<0.1	25.32	not tested	10.5
(a) measured with formulation containing 0.6%-wt of CP2					
(b) comparative example					

Results

[0105] The liquid cleaner compositions according to the invention all provided good general cleaning efficacy. The results of table 6 show that liquid cleaning compositions according to the invention also provide the desired characteristics of good suspension, sprayability and cling.

[0106] A comparison of Ex. (2:1), (2:2) and (2:3) shows the efficacy of three different copolymers according to the invention. A comparison of Ex. (2:1), (2:4), and (2:5) shows the efficacy in the presence of different surfactants. Ex. (2:6), (2:7) and (2:8) are comparative examples showing that suspension and cling of a composition are not acceptable when the pH is outside the specified range (2:6), when a commercial rheology modifier is used (2:7), or when the surfactant is present at a level outside the specified range (2:8).

[0107] A comparison of Ex. (2:1), (2:9), and (2:10) shows that there is a significant enhancement of the yield stress of the composition, when PEI or EPEI is present, whilst the cling also remains good and the spray stays acceptable. This enhancement of yield stress enables the reduction of the level of copolymer of the invention, whilst keeping the desirable suspension and cling characteristics. This is a surprising result in view of the absence of any thickening or suspension effect in the absence of the copolymer: comparative examples (2:11) and (2:12) show that compositions with just PEI or EPEI have a yield stress which is too low to be determined and a very poor cling.

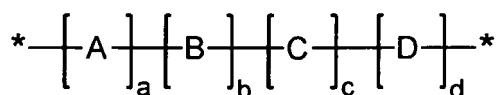
Claims

1. A liquid cleaner composition comprising

0.1 to 10 %-wt of one or more surfactants,

0.4 to 1 %-wt of one or more rheology modifier copolymers, and water,

whereby the composition has a pH of between 8 and 13 and whereby the one or more rheology modifier copolymer are selected from the group of copolymers of the formula



wherein a, b, c, and d represent the percentage by weight that each repeating unit or derived monomer is contained within the copolymer,
whereby

a ranges from 0.5 to 25% by weight of the copolymer;

b ranges from 70 to 98% by weight of the copolymer;

c ranges from 0 to 15% by weight of the copolymer; and

d ranges from 0 to 5% by weight of the copolymer;

and whereby

A is a macromonomer comprising at at least one end a polymerisable group reactive during polymerisation with at least one of B, C, and D monomers, the polymerisable group at the at least one end of the macromonomer being attached to a chain formed of a homo- or co-polymer of C₁-C₁₀ alkyl acrylates, C₁-C₁₀ alkyl methacrylates, methacrylic acid, acrylic acid or combinations thereof, the macromonomer having a number average molecular

weight ranging from 500 to 10,000; and

B is acrylic or methacrylic acid or a salt thereof;

C, when present, is a polyacidic vinyl monomer selected from the group consisting of maleic acid, fumaric acid, itaconic acid, citraconic acid, mesaconic acid, combinations thereof and anhydrides and salts thereof; and

D, when present, is a cross-linking monomer for introducing branching and controlling molecular weight, the cross linking monomer comprising polyfunctional units carrying multiple reactive functionalisation groups selected from the group consisting of vinyl, allylic and functional mixtures thereof,

and whereby the groups **A**, **B**, **C** and **D** are covalently bonded one to another in a random, a block, or a cross-linked copolymer format.

2. A liquid cleaner composition according to claim 1, wherein the number average molecular weight of **A** is between 500 and 2000.

3. A liquid cleaner composition according to claim 1 or 2, wherein c ranges from 2 to 4 % by weight.

4. A liquid cleaner composition according to any one of claims 1 to 3, wherein d ranges from 0.5 to 1.5 % by weight,

5. A liquid cleaner composition according to any one of claims 1 to 4, wherein A comprises from 70 to 100 % of C₁-C₁₀ alkyl(meth)acrylates by weight with respect to the weight of A.

6. A liquid cleaner composition according to any one of claims 1 to 5, wherein the C₁-C₁₀ alkyl(meth)acrylates are selected from one or more of methyl (meth)acrylate, butyl (meth)acrylate, and 2-ethyl-hexyl (meth)acrylate.

7. A liquid cleaner composition according to any one of claims 1 to 6 wherein **B** is a acrylic acid or a salt thereof.

8. A liquid cleaner composition according to any one of claims 1 to 7 wherein **C** is selected from maleic acid, maleic anhydride and mixtures thereof.

9. A liquid cleaner composition according to any one of claims 1 to 8 wherein **D** is pentaerythritol allyl ether.

10. A liquid cleaner composition according to any one of claims 1 to 9 wherein the rheology modifier copolymer is selected from the group of copolymers wherein

- A is a poly-n-butyl methacrylate macromonomer having a number average molecular weight of between 500 and 2000, and a is in the range of between 5 %-wt and 20 %-wt;
- B is acrylic acid;
- C is maleic anhydride and c is in the range of between 2 and 4 %-wt; and
- D is pentaerythritol allyl ether and d is in the range between 0.75 and 1%-wt;

or the group of copolymers wherein

- A is a poly-methyl methacrylate macromonomer having a number average molecular weight of between 500 and 2000, and a is in the range of between 5 %-wt and 20 %-wt;
- B is acrylic acid;
- C is maleic anhydride and c is in the range of between 0 and 4 %-wt;
- D is pentaerythritol allyl ether and d is in the range between 0.75 and 1%-wt;

and wherein the specified percentages are by weight of the copolymer.

11. A liquid cleaner composition according to claim 10 wherein the rheology modifier copolymer is selected from one or more copolymers wherein

- A is a poly-n-butyl methacrylate macromonomer having a number average molecular weight of between 500 and 2000, and a is in the range of between 8 %-wt and 12 %-wt;
- B is acrylic acid;
- C is maleic anhydride and c is in the range of between 2 and 3 %-wt;
- D is pentaerythritol allyl ether and d is in the range between 0.75 and 1%-wt.

12. A liquid cleaner composition according to any one of claims 1 to 11 wherein the one or more surfactants are non-ionic surfactants, more preferably ethoxylated C₈-C₁₂ alcohols, whereby even more preferably the average degree of ethoxylation is between 5 and 8.

13. A liquid cleaner composition according to any one of claims 1 to 12 wherein the composition comprises between 0.01 and 1 %-wt of one or more polymeric amines selected from the group consisting of polyethylenimines and hydroxyethylated polyethylenimines.

14. Method for preparing a liquid cleaner composition according to any one of claims 1 to 13, comprising the steps of

- a. providing water, the one or more rheology modifier copolymers and optionally alkali;
- b. dissolving the copolymer in the water under alkaline conditions; and
- c. adding the surfactant to the composition comprising the dispersed copolymer.

15. Use of a liquid cleaning composition according to any one of claims 1 to 13 for cleaning a surface, wherein the composition is comprised in a container, and wherein the container further comprises a spray dispenser for dispensing the composition in the form of a spray.

Patentansprüche

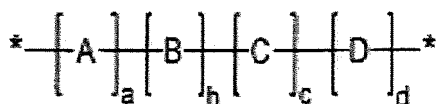
1. Flüssige Reinigungszusammensetzung, umfassend

0,1 bis 10 Gew.-% eines oder mehrerer Tenside,

0,4 bis 1 Gew.-% eines oder mehrerer Rheologie-modifizierender Copolymere und Wasser,

wobei die Zusammensetzung einen pH zwischen 8 und 13 aufweist und

wobei das eine oder die mehreren Rheologie-modifizierenden Copolymeren aus der Gruppe von Copolymeren der Formel



ausgewählt sind,

worin a, b, c und d Gewichtsprozent darstellen, mit dem jede(s) Wiederholungseinheit oder abgeleitete Monomer innerhalb des Copolymers enthalten ist,

wobei

a zwischen 0,5 und 25 Gewichts-% des Copolymers liegt,

b zwischen 70 und 98 Gewichts-% des Copolymers liegt,

c zwischen 0 und 15 Gewichts-% des Copolymers liegt und

d zwischen 0 und 5 Gewichts-% des Copolymers liegt,

und wobei

A ein Makromonomer darstellt, das an mindestens einem Ende eine polymerisierbare Gruppe enthält, die während der Polymerisation mit mindestens einem der B-, C- und D-Monomeren reaktiv ist, wobei die polymerisierbare Gruppe an dem mindestens einen Ende des Makromonomers mit einer Kette verknüpft ist, die von einem Homo- oder Co-Polymer von C₁-C₁₀-Alkylacrylaten, C₁-C₁₀-Alkylmethacrylaten, Methacrylsäure, Acrylsäure oder Kombinationen davon gebildet ist, wobei das Makromonomer ein zahlenmittleres Molekulargewicht von 500 bis 10.000 aufweist, und

B eine Acryl- oder Methacrylsäure oder ein Salz davon ist,

C, wenn es vorliegt, ein mehrbasiges Vinylmonomer ist, das aus der aus Maleinsäure, Fumarsäure, Itaconsäure, Citraconsäure, Mesaconsäure, Kombinationen davon und Anhydriden und Salzen davon bestehenden Gruppe ausgewählt ist, und

D, wenn es vorliegt, ein vernetzendes Monomer zum Einführen von Verzweigung und zum Steuern des Mole-

kulargewichts darstellt, wobei das vernetzende Monomer polyfunktionelle Einheiten umfasst, die mehrfach reaktive Funktionalisierungsgruppen tragen, die aus der aus Vinylverbindungen, allylischen Verbindungen und funktionellen Mischungen davon bestehenden Gruppe ausgewählt sind,

wobei die Gruppen **A**, **B**, **C** und **D** in einem statistischen, Block- oder vernetzten Copolymer-Format eine mit der anderen kovalent gebunden sind.

2. Flüssige Reinigungszusammensetzung nach Anspruch 1, wobei das zahlengemittelte Molekulargewicht **A** zwischen 500 und 2000 liegt.

3. Flüssige Reinigungszusammensetzung nach Anspruch 1 oder 2, wobei c zwischen 2 und 4 Gewichts-% liegt.

4. Flüssige Reinigungszusammensetzung nach irgendeinem der Ansprüche 1 bis 3, wobei d zwischen 0,5 und 1,5 Gewichts-% liegt.

5. Flüssige Reinigungszusammensetzung nach irgendeinem der Ansprüche 1 bis 4, wobei A 70 bis 100% C₁-C₁₀-Alkyl(meth)acrylate, in Gewicht, im Hinblick auf das Gewicht von A, umfasst.

6. Flüssige Reinigungszusammensetzung nach irgendeinem der Ansprüche 1 bis 5, wobei die C₁-C₁₀-Alkyl(meth)acrylate unter einem oder mehreren von Methyl(meth)acrylat, Butyl(meth)acrylat und 2-Ethylhexyl(meth)acrylat ausgewählt sind.

7. Flüssige Reinigungszusammensetzung nach irgendeinem der Ansprüche 1 bis 6, wobei **B** Acrylsäure oder ein Salz davon ist.

8. Flüssige Reinigungszusammensetzung nach irgendeinem der Ansprüche 1 bis 7, wobei **C** unter Maleinsäure, Maleinsäureanhydrid und Mischungen davon ausgewählt ist.

9. Flüssige Reinigungszusammensetzung nach irgendeinem der Ansprüche 1 bis 8, wobei **D** Pentaerythritallylether ist.

10. Flüssige Reinigungszusammensetzung nach irgendeinem der Ansprüche 1 bis 9, wobei das Rheologie-modifizierende Copolymer unter der Gruppe von Copolymeren ausgewählt ist, worin

- A ein Poly-n-butylmethacrylat-Makromonomer mit einem zahlengemittelten Molekulargewicht zwischen 500 und 2000 ist und a zwischen 5 Gew.-% und 20 Gew.-% liegt,
- B Acrylsäure ist,
- C Maleinsäureanhydrid ist und c in dem Bereich zwischen 2 und 4 Gew.-% liegt und
- D Pentaerythritallylether ist und d in dem Bereich zwischen 0,75 und 1 Gew.-% liegt;

oder der Gruppe von Copolymeren, worin

- A ein Poly-methylmethacrylat-Makromonomer mit einem zahlengemittelten Molekulargewicht zwischen 500 und 2000 ist und a in dem Bereich zwischen 5 Gew.-% und 20 Gew.-% liegt,
- B Acrylsäure ist,
- C Maleinsäureanhydrid ist und c in dem Bereich zwischen 0 und 4 Gew.-% liegt,
- D Pentaerythritallylether ist und d in dem Bereich zwischen 0,75 und 1 Gew.-% liegt,

und worin sich die angegebenen Prozente auf das Gewicht des Copolymers beziehen.

11. Flüssige Reinigungszusammensetzung nach Anspruch 10, wobei das Rheologie-modifizierende Copolymer unter einem oder mehreren Copolymeren ausgewählt ist, worin

- A ein Poly-n-butylmethacrylat-Makromonomer mit einem zahlengemittelten Molekulargewicht zwischen 500 und 2000 ist und a in dem Bereich zwischen 8 Gew.-% und 12 Gew.-% liegt,
- B Acrylsäure ist,
- C Maleinsäureanhydrid ist und c in dem Bereich zwischen 2 und 3 Gew.-% liegt,
- D Pentaerythritallylether ist und d in dem Bereich zwischen 0,75 und 1 Gew.-% liegt.

12. Flüssige Reinigungszusammensetzung nach irgendeinem der Ansprüche 1 bis 11, worin das eine oder die mehreren Tenside nicht-ionische Tenside sind, bevorzugter ethoxylierte C₈-C₁₂-Alkohole, wobei sogar bevorzugter der Durchschnittsgrad der Ethoxylierung zwischen 5 und 8 liegt.

13. Flüssige Reinigungszusammensetzung nach irgendeinem der Ansprüche 1 bis 12, wobei die Zusammensetzung 0,01 bis 1 Gew.-% eines oder mehrerer polymerer Amine umfasst, die aus der aus Polyethylenimininen und hydroxyethylierten Polyethylenimininen bestehenden Gruppe ausgewählt sind.

14. Verfahren zur Herstellung einer flüssigen Reinigungszusammensetzung nach irgendeinem der Ansprüche 1 bis 13, umfassend die Schritte

a. Bereitstellen von Wasser, der ein oder mehreren Rheologie-modifizierenden Copolymeren und gegebenenfalls Alkali,

b. Auflösen des Copolymers in Wasser unter alkalischen Bedingungen und

c. Zugabe des Tensids zu der Zusammensetzung, die das dispergierte Copolymer enthält.

15. Verwendung einer flüssigen Reinigungszusammensetzung nach irgendeinem der Ansprüche 1 bis 13 zur Reinigung einer Oberfläche, wobei die Zusammensetzung von einem Behälter umfasst ist und worin der Behälter des Weiteren einen Sprühverteiler zur Abgabe der Zusammensetzung in Form eines Sprays umfasst.

Revendications

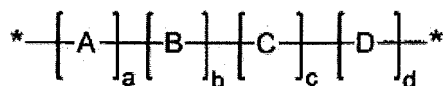
1. Composition de nettoyant liquide comprenant

0,1 à 10 % en masse d'un ou plusieurs tensioactifs,

0,4 à 1 % en masse d'un ou plusieurs copolymères d'agents de modification de la rhéologie, et de l'eau,

la composition présente par là un pH de 8 à 13

et les un ou plusieurs copolymères d'agents de modification de la rhéologie sont par là choisis dans le groupe de copolymères linéaires de la formule



où a, b, c, et d représentent le pourcentage en masse pour lequel chaque unité répétitive ou monomère dérivé est contenu dans le copolymère, sur quoi

a est de 0,5 à 25 % en masse du copolymère;

b est de 70 à 98 % en masse du copolymère;

c est de 0 à 15 % en masse du copolymère; et

d est de 0 à 5 % en masse du copolymère;

et sur quoi

A est un macromonomère comprenant à au moins une extrémité un groupe polymérisable réactif pendant la polymérisation avec au moins un des monomères B, C, et D, le groupe polymérisable à la au moins une extrémité du macromonomère étant fixé à une chaîne formée d'un homo- ou co-polymère d'acrylates d'alkyle en C₁-C₁₀, de méthacrylates d'alkyle en C₁-C₁₀, d'acide méthacrylique, d'acide acrylique ou de combinaisons de ceux-ci, le macromonomère ayant une masse moléculaire moyenne en nombre de 500 à 10 000; et

B est l'acide acrylique ou méthacrylique ou un sel de ceux-ci;

C, lorsqu'il est présent, est un monomère vinylique polyacide choisi dans le groupe constitué d'acide maléique, d'acide fumarique, d'acide itaconique, d'acide citraconique, d'acide mésaconique, de combinaisons de ceux-ci et d'anhydrides et de sels de ceux-ci; et

D, lorsqu'il est présent, est un monomère de réticulation pour introduire une ramification et contrôler la masse moléculaire, le monomère de réticulation comprenant des unités polyfonctionnelles supportant des groupes de fonctionnalisation réactifs multiples choisis dans le groupe constitué d'un groupe vinylique, allylique et de mé-

lances fonctionnels de ceux-ci,

et sur quoi les groupes A, B, C et D sont liés de manière covalente les uns aux autres dans un format de copolymère statistique, séquencé ou réticulé.

2. Composition de nettoyant liquide selon la revendication 1, dans laquelle la masse moléculaire moyenne en nombre de A est de 500 à 2000.

3. Composition de nettoyant liquide selon la revendication 1 ou 2, dans laquelle c est de 2 à 4 % en masse.

4. Composition de nettoyant liquide selon l'une quelconque des revendications 1 à 3, dans laquelle d est de 0,5 à 1,5 % en masse.

5. Composition de nettoyant liquide selon l'une quelconque des revendications 1 à 4, dans laquelle A comprend de 70 à 100 % de (méth)-acrylates d'alkyle en C_1 - C_{10} en masse par rapport à la masse de A.

6. Composition de nettoyant liquide selon l'une quelconque des revendications 1 à 5, dans laquelle les (méth)acrylates d'alkyle en C_1 - C_{10} sont choisis parmi un ou plusieurs de (méth)acrylate de méthyle, (méth)acrylate de butyle, et (méth)acrylate de 2-éthyl-hexyle.

7. Composition de nettoyant liquide selon l'une quelconque des revendications 1 à 6, dans laquelle B est un acide acrylique ou un sel de celui-ci.

8. Composition de nettoyant liquide selon l'une quelconque des revendications 1 à 7, dans laquelle C est choisi parmi l'acide maléique, l'anhydride maléique et des mélanges de ceux-ci.

9. Composition de nettoyant liquide selon l'une quelconque des revendications 1 à 8, dans laquelle D est l'allyléther de pentaérythritol.

10. Composition de nettoyant liquide selon l'une quelconque des revendications 1 à 9, dans laquelle le copolymère d'agent de modification de la rhéologie est choisi dans le groupe de copolymères où

- A est un macromonomère de poly(méthacrylate de n-butyle) présentant une masse moléculaire moyenne en nombre de 500 à 2 000, et a se trouve dans l'intervalle de 5% en masse à 20 % en masse;
- B est l'acide acrylique;
- C est l'anhydride maléique et c se trouve dans l'intervalle de 2 à 4 % en masse; et
- D est l'allyléther de pentaérythritol et d se trouve dans l'intervalle de 0,75 à 1 % en masse;

ou le groupe de copolymères où

- A est un macromonomère de poly(méthacrylate de méthyle) présentant une masse moléculaire moyenne en nombre de 500 à 2 000, et a se trouve dans l'intervalle de 5 % en masse à 20 % en masse;
- B est l'acide acrylique;
- C est l'anhydride maléique et c se trouve dans l'intervalle de 0 à 4 % en masse;
- D est l'allyléther de pentaérythritol et d se trouve dans l'intervalle de 0,75 à 1 % en masse;

et dans laquelle les pourcentages spécifiés sont en masse du copolymère.

11. Composition de nettoyant liquide selon la revendication 10, dans laquelle le copolymère d'agent de modification de la rhéologie est choisi parmi un ou plusieurs copolymères où

- A est un macromonomère de poly(méthacrylate n-butyle) présentant une masse moléculaire moyenne en nombre de 500 à 2 000, et a se trouve dans l'intervalle de 8 % en masse à 12 % en masse;
- B est l'acide acrylique;
- C est l'anhydride maléique et c se trouve dans l'intervalle de 2 à 3 % en masse;
- D est l'allyléther de pentaérythritol et d se trouve dans l'intervalle de 0,75 à 1 % en masse.

12. Composition de nettoyant liquide selon l'une quelconque des revendications 1 à 11, dans laquelle les un ou plusieurs

tensioactifs sont des tensioactifs non ioniques, encore mieux des alcools en C₈-C₁₂ éthoxylés, sur quoi le degré moyen d'éthoxylation est bien mieux encore de 5 à 8.

5 **13.** Composition de nettoyant liquide selon quelconque des revendications 1 à 12, dans laquelle la composition comprend de 0,01 à 1 % en masse d'une ou plusieurs amines polymères choisies dans le groupe constitué de polyéthylèneimines et de polyéthylèneimines hydroxyéthylées.

10 **14.** Procédé de préparation d'une composition de nettoyant liquide selon l'une quelconque des revendications 1 à 13, comprenant les étapes

- a. de fourniture d'eau, des un ou plusieurs copolymères d'agents de modification de la rhéologie et éventuellement d'un alcali;
- b. de dissolution du copolymère dans l'eau dans des conditions alcalines; et
- c. d'addition du tensioactif à la composition comprenant le copolymère dispersé.

15 **15.** Utilisation d'une composition de nettoyant liquide selon l'une quelconque des revendications 1 à 13 pour le nettoyage d'une surface, dans laquelle la composition est comprise dans un récipient, et dans laquelle le récipient comprend de plus un distributeur de pulvérisation pour distribuer la composition dans la forme d'une pulvérisation.

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REFERENCES CITED IN THE DESCRIPTION

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