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(54) Title: COMPOSITION

(57) Abstract: An internally structured aqueous detergent liquid composition comprising: (i) from 10.1 to 35.0% wt. a surfactant system comprising anionic surfactant, and (ii) at least 0.05 wt % of a cross-linked HASE polymer, and wherein the η_{sp}/c is at least 10 Pa.s, preferably no more than 1 000 Pa.s.



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COMPOSITION

Technical Field

- 5 This invention relates to aqueous detergent compositions including a rheology modifying polymer useful for home care applications, including laundry.

Background

- 10 A trend in detergent formulating is to reduce the amount of surfactant and to replace these petrochemical derived ingredients with highly weight efficient ingredients selected from cleaning and soil release polymers, sequestrants and enzyme cocktails. Typically some surfactant is retained in the composition and the work horse surfactant linear alkyl benzene sulphonate (LAS) is frequently a key part of the surfactant blend. The polymer
15 ethoxylated polyethylene imine may be used as one of the weight efficient ingredients. Suitable compositions are taught, for example, in WO09153184.

- It has been found that consumers prefer that the new type of concentrated liquid is thickened so that it conveys the impression of high contents when in the bottle. On the
20 other hand it is desirable that the pour viscosity is low enough that dosing can be done easily and accurately. A shear thinning composition is thus desired.

- Hydrophobically modified alkali swellable emulsion (HASE) copolymers are a type of synthetic associative rheology modifier. This rheology modifier typically contains a
25 backbone consisting of randomly distributed methacrylic acid (MAA) and ethylacrylate (EA) monomers, amongst other possible monomer components.

- Inserted into this backbone are a small proportion of hydrophobically modified groups, usually less than 3 mol%. The monomers to form these hydrophobic groups are
30 sometimes referred to as surfmers or associative monomers. Due to its structure, the copolymer, when dissolved in an alkaline aqueous liquid, induces a variety of interacting forces such as hydrophobic, hydrogen bonding, electrostatic, etc and this modifies the rheology of the liquid.

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HASE copolymers are usually synthesized via the emulsion polymerization technique. US 5 015 711 (Coatex) discloses a thickening terpolymer of the MAA/EA/surfmer type.

US 5 015 711 makes the following disclosure: "The first type of monomer, which is a carboxylic acid with an ethylenic unsaturation site, is a C₃-C₂₀, preferably C₃-C₁₂,

5 compound having an ethylenic bond and at least one carboxylic group or a carboxylic acid anhydride group. The carboxylated ethylenic monomer can be selected from among monoacids, such as acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid, cinnamic acid, diacids, such as itaconic acid, fumaric acid, maleic acid, and citraconic acid, carboxylic acid anhydrides, such as maleic anhydride and diacid hemiesters, such as the C₁₋₄ monoesters of maleic or itaconic acids. However, the carboxyl ethylene
10 monomer is preferably selected from the group consisting of acrylic acid, methacrylic acid and itaconic acid".

US 4 384 096 discloses a copolymer having 42% MAA, 6% IA, 42% EA and 10% surfmer
15 (where IA is itaconic acid). The surfmer used was nonylphenoxy poly(ethyleneoxy)₉ ethyl Methacrylate. US 4 384 096 contains a general disclosure relating to the use of Itaconic acid as follows: "Acrylic or methacrylic acid or a mixture thereof with itaconic or fumaric acid are preferred, but crotonic and aconitic acid and half esters of these and other polycarboxylic acids such as maleic acid with C₁ - C₄ alkanols are also suitable,
20 particularly if used in minor amount in combination with acrylic or methacrylic acid".

Crosslinked hydrophobically modified copolymers are exemplified in US2004 063855 (Rohm and Haas) and where such a polymer was used at 1.5 wt% with a specified clay and 22.3 wt% mixed surfactant. It is stated that the composition synergistically increases the low shear (e. g., suspending or stabilizing) viscosity significantly while having little
25 effect on the mid-shear (pouring) viscosity. We have found that these types of acrylates copolymers give an undesirably high pour viscosity if they are used at a high enough level to provide a suspending rheology. Alternative prior art copolymers do provide the shear thinning behaviour required for suspending but do not on their own provide the pour viscosity that is desired by consumers. This can lead to the need to use a second
30 rheology modifying material in conjunction with the acrylate copolymer. This is an unwanted complication.

WO 2013/045377 and WO 2014/082955 describe HASE rheology modifying copolymers. WO 2013/045377 describes copolymers in slightly acidic or neutral pH compositions

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which exhibit high viscosity at low shear. WO 2013/045377 further makes no mention of including viscosity reducing polymers.

5 WO 2014/082955 describes linear copolymers for use in isotropic, i.e. non-structured, alkaline compositions.

Low dosage compositions formulated this way are suitable for laundry applications. Both the removal of the surfactant and the use of cleaning polymers like ethoxylated polyethylene imine and polyester soil release polymers cause a drop in viscosity of the liquid. We have found that consumers desire that the pour viscosity of a concentrated liquid should be at least as high as a conventional dilute liquid and possibly even higher so that they have a reason to believe that the liquid contains the same cleaning power as a higher dosage detergent liquid with higher surfactant levels and possibly without such high levels of viscosity reducing polymer additives. However, it is also desirable for the liquid to behave as though it has an infinite viscosity when at rest, i.e. when in its container or package. Such products are more aesthetically pleasing and also have the advantage that they may be able to suspend particulate materials such as encapsulated actives, such as perfumes, as well as visual cues.

20 It is thus desirable that the liquid should have rheology that provides a yield stress) so that the compositions are more aesthetically pleasing and any particles remain stably suspended and dispersed and yet the composition may be poured from a bottle or dispensed by a suitable spray or pump mechanism.

25 It is an object of the present invention to provide detergent compositions with a copolymer that increases the pour viscosity while providing the required rheology for suspending, while counteracting the effect of inclusion of certain polymers that have the effect of reducing the pour viscosity of the composition. The copolymers may be utilised in compositions comprising linear alkyl benzene sulphonate anionic surfactant which is the workhorse surfactant found in most laundry and dish wash compositions.

30

Summary of the Invention

According to the present invention there is provided an internally structured aqueous detergent liquid composition comprising:

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- (i) from 10.1 to 35.0% wt. a surfactant system comprising anionic surfactant, and
- (ii) at least 0.05 wt % of a cross-linked HASE polymer,

and wherein the η_{10} is at least 10 Pa.s, preferably no more than 100 Pa.s.

10

We have surprisingly found that if the surfactant level is from 10.1% wt to 35% wt. that compositions can be formulated which have highly desirable rheological profiles.

Preferably, the composition has a pH of from 6.0 to 7.0.

15

By "internally structured" is meant that the structuring system is physically associated with the surfactant phase. This contrasts with an externally structured system where the structuring components do not form part of the surfactant phase of the formulation and instead forms a scaffold independently of the other components of the formulation.

20

Examples of externally structured components include clay, hydrogenated castor oil and citrus fibres.

Preferably, the composition comprises from 0 to 2% wt. external structurant, more preferably from 0 to 1% wt. More preferably, the composition is substantially free from external structurant.

25

A composition is said to be shear thinning when it has a low shear viscosity plateau of 10 Pa.s or more. A composition which has a low shear viscosity plateau of 10 Pa.s or more as defined by the η_{10} measurement enables particles such as encapsulated benefit agents to be suspended in the bulk for a consumer appropriate length of time.

30

The low shear viscosity plateau is measured by averaging the shear rate over the last 5 seconds of a 10s applied stress step where the applied stresses range from 0.01Pa to 1.0 Pa with the stress step varying logarithmically with 10 steps per decade. The viscosity at

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each stress is determined from the quotient of the shear stress and shear rate. The plateau viscosity is taken as that portion of the flow curve at low shear stresses where the variation in the viscosity is less than 20%. This plateau value is designated as 'eta10'.

The viscosity can be measured on a rheometer such as the TA Instruments DHR-2 with 4cm diameter 2 degree cone and plate.-All measurements at 25°C.

Preferably, the composition of the invention has an eta10 of no higher than 1000 Pa.s. Since viscosity is measured on a logarithmic scale the window defined by the range from 10 Pa.s to 1000 Pa.s is narrow.

Despite having an aesthetically pleasing appearance and high viscosity at low shear, the composition must also pour readily and in the manner of a premium product.

For the purposes of this invention a composition is considered optimally pourable if it has a viscosity between 200 and 1 500 mPa.s (preferably 200 and 1 000) at a shear rate of 21 s⁻¹.

The viscosity of the liquid at a shear rate of 21 s⁻¹ and 25°C is preferably at least 300 mPa.s, most preferably at least 400 mPa.s. This viscosity is also known as the 'pour viscosity' of the composition.

The compositions exhibit suitable pour viscosities while also having a useful rheology for suspending or spraying, despite the inclusion of polymers that have the effect of reducing the pour viscosity of the composition.

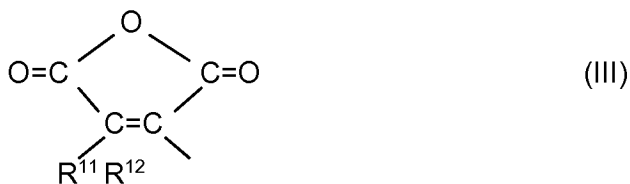
Preferably, the crosslinked polymer is formed by the addition polymerisation of:

(A) 0 to 5 wt% (more preferably 0.01 to 4.5%wt. of the polymer) of a first monomer consisting of an ethylenically unsaturated diacid of formula (II):



or an unsaturated cyclic anhydride precursor of such an ethylenically unsaturated diacid, the anhydride having formula (III):

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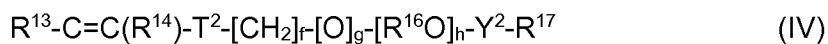


where R^{11} and R^{12} are individually selected from H, $\text{C}_1\text{-C}_3$ alkyl, phenyl, chlorine and bromine;

(B) 15 to 60 wt% of a second ethylenically unsaturated monoacidic monomer consisting of (meth)acrylic acid;

(C) 30 to 70 wt% of a third ethylenically unsaturated monomer consisting of $\text{C}_1\text{-C}_8$ alkyl ester of (meth)acrylic acid; and

(D) 1 to 25 wt% of a fourth ethylenically unsaturated monomer, consisting of surfmer of formula (IV):



wherein each R^{13} and R^{14} are each independently selected from H, methyl, -C(=O)OH , or -C(=O)OR^{15} ;

R^{15} is a $\text{C}_1\text{-C}_{30}$ alkyl;

T^2 is $\text{-CH}_2\text{C(=O)O-}$, -C(=O)O- , -O- , $\text{-CH}_2\text{O-}$, -NHC(=O)NH- , -C(=O)NH- , $\text{-Ar-(CG}_2\text{)}_z\text{-NHC(=O)O-}$, $\text{-Ar-(CG}_2\text{)}_z\text{-NHC(=O)NH-}$, or $\text{-CH}_2\text{CH}_2\text{NHC(=O)-}$;

Ar is divalent aryl;

G is H or methyl;

z is 0 or 1;

f is an integer in the range of 0 to 30; and g is 0 or 1; with the proviso that when f is 0, g is 0, and when f is in the range of 1 to 30; g is 1;

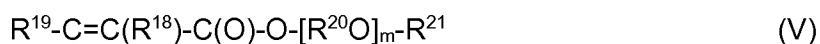
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(R¹⁶O)_h is polyoxyalkylene, which is a homopolymer, a random copolymer, or a block copolymer of C₂-C₄-oxyalkylene units, wherein R¹⁶ is C₂H₄, C₃H₆, C₄H₈, or a mixture thereof, and h is an integer in the range of 5 to 250; Y² is -R¹⁶O-, -R¹⁶H-, -C(=O)-, -C(=O)NH-, =R¹⁶NHC(=O)NH-, or -C(=O)NHC(=O)-; and R¹⁷ is substituted or unsubstituted alkyl selected from the group consisting of C₈-C₄₀ linear alkyl, C₈-C₄₀ branched alkyl, C₈-C₄₀ carbocyclic alkyl, C₂-C₄₀ alkyl-substituted, phenyl, aryl-substituted C₂-C₄₀ alkyl, and C₈-C₈₀ complex ester; wherein the R₁₇ alkyl group optionally comprises one or more substituents selected from the group consisting of hydroxy, alkoxy, and halogen.

and

(E) 0.005 to 5 wt% of a cross linking agent, 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, allyl and functional mixtures thereof.

Preferably monomer (Surfmer) D has the formula (V)



where:

R¹⁸ and R¹⁹ are each independently selected from H, and C₁₋₃ alkyl;

R²⁰ is C₂-C₄ and mixtures thereof, preferably C₂;

m, the average number of alkoxy units R²⁰O, is from 6 to 40;

R²¹ is alkyl or alkylaryl where the alkyl part is linear or branched; and the total number of carbons is from 8 to 40.

The liquid detergent composition may optionally include at least 0.01 wt% suspended particles. Additionally or alternatively, the liquid detergent composition may optionally include at least 2 wt% of a viscosity reducing polymer.

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In this specification the term (meth)acrylic acid includes both acrylic acid and methacrylic acid and the term (meth)acrylate includes both acrylate and methacrylate.

When used, the suspended particles may comprise microcapsules and a preferred type of microcapsules is perfume encapsulates. Alternatively or additionally the suspended
5 particles may comprise visual cues. The visual cues may be beads or may comprise lamellar particles formed from sheets of polymer film.

Noteworthy viscosity reducing polymers are ethoxylated polyethylene imine and/or polyester soil release polymer. Preferably the composition comprises at least 3 wt% of
10 ethoxylated polyethylene imine.

In some embodiments cross linked polymer is formed by addition polymerisation in the presence of: 0.1 to 5 wt% of monomer A; 15 to 60 wt% of monomer B; 30 to 70 wt% of
15 monomer C; 1 to 25 wt% of monomer D and 0.005 to 5 wt.% of cross-linking agent E.

The cross-linked polymer preferably has a molecular weight Mw of at least 500 000, more preferably 1 million Daltons.

It is preferred to use maleic anhydride as the first monomer (A) in the copolymerisation of
20 the copolymer.

In some embodiments 1 wt.% or less, 0.6 wt.% or less, 0.5 wt.% or less of the first monomer (A) is present in the copolymerisation. In further embodiments, first monomer (A) is present in the copolymerisation in an amount in the range of 0.1 to 1 wt.%, in the
25 range 0.25 to 0.75 wt.%, or in the range of 0.4 to 0.6 wt.%.

The cross linked HASE polymers are crosslinked alkali swellable hydrophobically modified acrylic copolymers, C-HASE. These polymers require alkaline conditions to swell and so should be added to the composition such that they are exposed to
30 appropriate alkaline conditions at some stage during the manufacture of the detergent liquid. It is not essential that the finished liquid composition is alkaline.

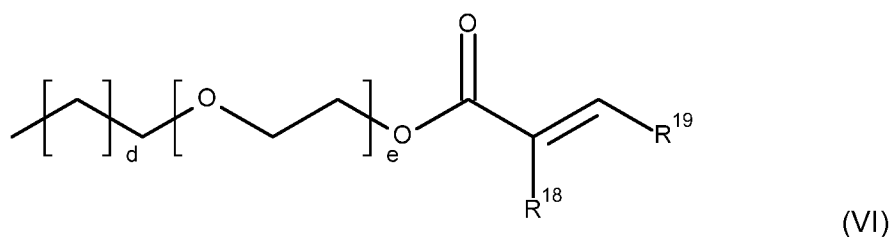
Typically the total surfactant will be a mixture of nonionic and anionic surfactant. Preferably, the anionic surfactant is predominately, and more preferably essentially, a

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non-soap anionic surfactant. In particularly preferred embodiments of the invention the anion of the anionic surfactant is selected from the group consisting of linear alkyl benzene sulphonate (LAS), primary alkyl sulphate (PAS), alkyl ether sulphate (AES) and mixtures thereof. In some embodiments zwitterionic surfactants are used as part of the surfactant mixture. Zwitterionics, in particular betaines, improve particulate soil detergency in the compositions of the invention. Preferably the surfactant system comprises linear alkyl benzene sulphonate, nonionic surfactant and alkali metal alkyl sulphate. More preferably, in such a surfactant system comprising linear alkyl benzene sulphonate, nonionic surfactant and alkali metal alkyl sulphate the alkali metal alkyl sulphate comprises from 20 to 50%, more preferably from 30 to 40% by weight of the surfactant.

Advantageously the detergent composition comprises an effective amount of at least one enzyme selected from the group comprising, pectate lyase, protease, amylase, cellulase, lipase, mannanase. More advantageously it comprises at least 2 of this group of enzymes even more advantageously at least 3 and most advantageously at least 4 of the enzymes from this group.

The fourth monomer D is more preferably a surfmer of formula (VI):



in which each R^{18} and R^{19} are independently selected from H, C_1 to C_3 alkyl, preferably R^{18} is a methyl group and R^{19} is H;

d ranges from 6 to 40 and e ranges from 6 to 40, preferably d ranges from 10 to 30 and e ranges 15 to 35 most preferably d ranges from 12 to 22 and e ranges from 20 to 30. It is preferable that e is greater or equal to d.

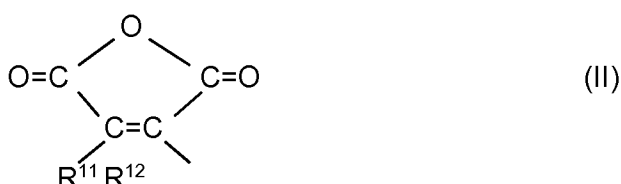
Preferably the amount of monomer D in copolymer is in the range of 2 to 15 wt.%, more preferably 3 to 12 wt.% and more preferably 5 to 10 wt. %.

Detailed Description of the Invention

5 The cross linked HASE polymers described herein are crosslinked addition polymers formed by copolymerisation and crosslinking in the presence of three or four different ethylenically unsaturated monomers and a cross-linker. Throughout this specification the monomer ratios are wt% and are based on the amounts of the monomers used. The monomers will lose their unsaturation as they are polymerised and may become salts
 10 when neutralised or swollen. Monomer nomenclature and ratios are all made with reference to the unsaturated, and where appropriate un-neutralised, starting monomer materials.

First Monomer A

15 The copolymer may be formed in the presence of a monomer A which may ring open to form a diacidic unit in the polymer. Diacidic unit means that carboxylate groups are attached to adjacent carbon atoms in the carbon backbone of the copolymer. Conveniently this unit is formed from a cyclic ethylenically unsaturated anhydride
 20 monomer of formula (II). It is preferred that monomer A is such an anhydride.



25 where R¹¹ and R¹² are individually selected from H, C₁-C₃ alkyl, phenyl, chlorine and bromine. Use of a cyclic anhydride monomer with ethylenic unsaturation gives a cis diacid if the ring opens. Such a diacid has both carboxylate groups arranged on the
 30 same side of the polymer – but on different carbon atoms.

Preferably R¹¹ is hydrogen and R¹² is selected from the group comprising hydrogen, methyl, bromine and phenyl. More preferably R¹¹ is hydrogen and R¹² is selected from

hydrogen and methyl. Most preferably R^{11} and R^{12} are hydrogen so that the anhydride is maleic anhydride. This is the precursor for maleic acid. It is thought that because maleic acid produces carboxylate groups on adjacent carbon atoms in the polymer backbone this increases the localised charge density and causes the difference in performance compared with copolymers not containing this diacid. Itaconic acid which is outside the scope of this invention provides a polymer element where one carbon carries two carboxylate groups and the other carries none. Fumaric acid is the trans isomer of maleic acid it cannot be formed from maleic anhydride monomer by hydrolysis during the emulsion polymerization.

Amounts of Monomer A present in the copolymerisation may range from 0.1 to 5 wt%, preferably from 0.2 to 4 wt%, and more preferably from 0.3 to 1 wt%, and optimally from 0.4 to 0.6 wt% of the total copolymer.

Second Monomer B

The second monomer B is a monoacidic vinyl monomer. Suitable monomers are acrylic acid, methacrylic acid, and combinations thereof.

In the compositions, the acid groups may be neutralized to form salts. Typical salt counterions to the acid groups are sodium, potassium, ammonium and triethanolammonium cations.

Amounts of the monoacidic vinyl monomer in the copolymerisation may range from 15 to 60 wt%, preferably from 20 to 55 wt%, more preferably from 25 to 50 wt% of the total monomers.

Third Monomer C

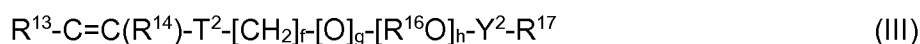
The third monomer, C, includes one or more C_1 - C_8 esters of acrylic or methacrylic acid. Illustrative ester monomers are ethylacrylate, methylacrylate, ethylmethacrylate, methylmethacrylate, butylacrylate, butylmethacrylate and mixtures thereof. Ethyl acrylate is preferred.

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The amount of acrylate ester monomers in the copolymerisation may range from 30 to 70 wt%, preferably from 25 to 60 wt%, and more preferably from 40 to 65 wt% of the total monomers.

5 Fourth Monomer D

The fourth ethylenically unsaturated monomer, consists of a surfmer of formula (III):



10

wherein

R^{13} and R^{14} are each independently selected from H, methyl, $-C(=O)OH$, or $-C(=O)OR^{15}$; and R^{15} is a C_1 - C_{30} alkyl;

T^2 is $-CH_2C(=O)O-$, $-C(=O)O-$, $-O-$, $-CH_2O-$, $-NHC(=O)NH-$, $-C(=O)NH-$,

15 $-Ar-(CG_2)_z-NHC(=O)O-$, $-Ar-(CG_2)_z-NHC(=O)NH-$, or $-CH_2CH_2NHC(=O)-$;

Ar is divalent aryl;

G is H or methyl;

z is 0 or 1;

f is an integer in the range of 0 to 30; and g is 0 or 1; with the proviso that when f is 0, g is

20 0, and when f is in the range of 1 to 30; g is 1;

$(R^{16}O)_n$ is polyoxyalkylene, which is a homopolymer, a random copolymer, or a block copolymer of C_2 - C_4 -oxyalkylene units, wherein R^{16} is C_2H_4 , C_3H_6 , C_4H_8 , or a mixture thereof, and n is an integer in the range of 5 to 250; Y^2 is $-R^{16}O-$, $-R^{16}H-$, $-C(=O)-$, -

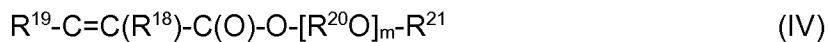
25 $C(=O)NH-$, $=R^{16}NHC(=O)NH-$, or $-C(=O)NHC(=O)-$; and

R^{17} is substituted or unsubstituted alkyl selected from the group consisting of C_8 - C_{40} linear alkyl, C_8 - C_{40} branched alkyl, C_8 - C_{40} carbocyclic alkyl, C_2 - C_{40} alkyl-substituted, phenyl, aryl-substituted C_2 - C_{40} alkyl, and C_8 - C_{80} complex ester; wherein the R^{17} group optionally

30 comprises one or more substituents selected from the group consisting of hydroxy, alkoxy, and halogen.

Preferably Surfmer D has the formula (IV):

- 13 -



where:

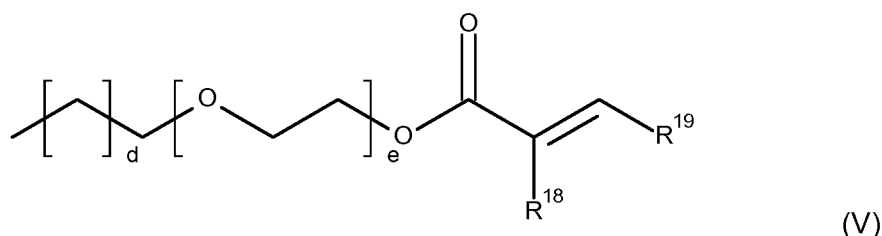
R^{18} and R^{19} are each independently selected from H, and C_{1-3} alkyl;

5 R^{20} is C_2-C_4 and mixtures thereof, preferably C_2 ;

m , the average number of alkoxy units $R^{20}O$, is from 6 to 40;

R^{21} is alkyl or alkylaryl where the alkyl part is linear or branched; and the total number of carbons is from 8 to 40.

10 The fourth monomer D is more preferably a surfmer of formula (V).



in which each R^{18} and R^{19} are independently selected from H, C_1 to C_3 alkyl.

15

Preferably R^{18} is a methyl group and R^{19} is H.

d ranges from 6 to 40 and e ranges from 6 to 40, preferably d ranges from 10 to 30 and e ranges 15 to 35 most preferably d ranges from 12 to 22 and e ranges from 20 to 30. It is

20 preferable that d is greater or equal to e .

The amount of surfmer D in the copolymer may range from 1 to 25 wt%, preferably from 3 to 20 wt%, and more preferably from 2 to a 12 wt% of the total copolymer.

25 Cross Linking Agent E

A crosslinking agent, such as a monomer having two or more ethylenic unsaturated groups, is included with the copolymer components during polymerization. Illustrative examples are divinyl benzene, divinyl naphthalene, trivinyl benzene, triallyl

30 pentaerythritol, diallyl pentaerythritol, diallyl sucrose, octaallyl sucrose, trimethylol

- 14 -

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, trimethylolpropane polyethoxylated trimethacrylate, ethylene glycol dimethacrylate and butylene glycol dimethacrylate, diallyl phthalate, allyl methacrylate, diacrylobutylene and similar materials. Preferred for the present invention is bisphenol A polyethoxylated glycol diacrylate, diallyl pentaerythritol and trimethylolpropane triacrylate.

Amounts of the cross linking agent used in the copolymerisation may range from 0.005 to 5 wt%, preferably from 0.05 to 3 wt%, more preferably from 1 to 2 wt%, optimally from 0.2 to 1 wt% of the total monomers.

The molecular weight of the copolymer is typically over 1 million.

The copolymer may be prepared in the presence of a chain transfer agent when a crosslinking agent is used. Examples of suitable chain transfer agents are carbon tetrachloride, bromoform, bromotrichloromethane, and compounds having a mercapto group, e.g., long chain alkyl mercaptans and thioesters such as dodecyl-, octyl-, tetradecyl- or hexadecyl-mercaptans or butyl-, isooctyl- or dodecyl-thioglycolates. When used, the amount of chain transfer agent is typically from 0.01 % to 5%, preferably from 0.1 % to 1%, based on weight of the copolymer components. If the crosslinking agent is used in conjunction with a chain transfer agent, which are conflicting operations for polymerization purposes, not only is exceptional efficiency observed but also very high compatibility with hydrophilic surfactants.

Amount of cross linked HASE polymer

Total amount of cross-linked HASE polymer when present in the composition is from 0.05 to 3 wt% of the total composition; more preferably from 0.08 to 2 wt%, even 0.1 to 1 wt%.

The polymer may be used with other rheology modifiers or thickeners to make up the rheology modified system but it is preferred that the cross-linked HASE polymer is the

only internally or externally structuring component. Preferred thickeners are thickening polymers and thickening clays.

The polymer in aqueous dispersion or in the dry form, may be blended into an aqueous system to be thickened followed, in the case of a pH-responsive thickener, by a suitable addition of acidic or basic material if required. In the case of pH-responsive thickeners, the pH of the system to be thickened is at, or is adjusted to, at least 5, preferably at least 6, more preferably at least 7; preferably the pH is adjusted to no more than 13. The neutralizing agent is preferably a base such as an amine base or an alkali metal or ammonium hydroxide, most preferably sodium hydroxide, ammonium hydroxide or triethanolamine (TEA). Alternatively, the polymer may first be neutralized in aqueous dispersion and then blended. The surfactant preferably is blended into the aqueous composition separately from the copolymer prior to neutralization. A commercially available X-linked HASE polymer is Acusol Millennium (ex. Dow).

Suspended particles

The composition has a shear thinning rheology that makes it suitable for suspending particles. Thus preferred compositions comprise suspended particles. These particles are preferably solid; that is to say they are neither liquid nor gas. However, within the term solid we include particles with either rigid or deformable solid shells which may then contain fluids. For example the solid particles may be microcapsules such as perfume encapsulates, or care additives or other benefit agents in encapsulated form. The particles may be enzymes or other cleaning actives that are insoluble or are encapsulated to prevent or reduce interaction with other composition ingredients. The particles may take the form of insoluble ingredients such as silicones, quaternary ammonium materials, insoluble polymers, insoluble optical brighteners and other known benefit agents as described, for example, in EP1328616. The amount of suspended particles may be from 0.001 to up to 10 or even 20 wt%. One type of solid particle to be suspended is a visual cue, for example the type of flat film cue described in EP13119706. The cue may itself contain a segregated component of the detergent composition. Because the cue must be water-soluble, yet insoluble in the composition, it is conveniently made from a modified polyvinyl alcohol that is insoluble in the presence of the mixed surfactant system. In that case, the detergent composition preferably comprises at least 5 wt% anionic surfactant.

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The suspended particles can be any type. This includes perfume encapsulates, care encapsulates and/ or visual cues or suspended solid opacifier such as mica or other suspended pearlescent materials and mixtures of these materials. The closer the match of the density of the suspended particles to that of the liquid. Typically, up to 5 wt% of suspended particles may be suspended stably; however, amounts up to 20 wt% are possible.

The benefit agents that may be delivered via suspended particles include any compatible benefit agent which can provide a benefit to a substrate which is treated with a preferably surfactant-containing composition can be used. Advantages of the particles of the invention in the presence of surfactant are a good retention of the benefit agent on storage of a formulation and controllable release of the benefit agent during and after product usage.

Preferred benefit agents are fragrances, pro-fragrance, clays, enzymes, antifoams, fluorescers, bleaching agents and precursors thereof (including photo-bleach), dyes and/or pigments, conditioning agents (for example cationic surfactants including water-insoluble quaternary ammonium materials, fatty alcohols and/or silicones), lubricants (e.g. sugar polyesters), colour and photo-protective agents (including sunscreens), antioxidants, ceramides, reducing agents, sequestrants, colour care additives (including dye fixing agents), unsaturated oil, emollients, moisturisers, insect repellents and/or pheromones, drape modifiers (e.g. polymer latex particles such as PVAc) and anti-microbial and microbe control agents. Mixtures of two or more of these may be employed. Particular benefit agents are described in further detail below.

Benefits include, for laundry applications, benefits of softening, conditioning, lubricating, crease reducing, ease of ironing, moisturising, colour preserving and/or anti-pilling, quick drying, UV protecting, shape retaining, soil releasing, texturising, insect repelling, fungicidal, dyeing and/or fluorescent benefit to the fabric. A highly preferred benefit is the delivery of fragrance (whether free and/or encapsulated), or pro-fragrance or other volatile benefit agent.

Preferred sunscreens are vitamin B3 compounds. Suitable vitamin B3 compounds are selected from niacin, niacinamide, nicotinyl alcohol, or derivatives or salts thereof.

Preferred anti-oxidants include vitamin E, retinol, antioxidants based on hydroxytoluene such as Irganox™ or commercially available antioxidants such as the Trollox™ series.

5 Perfume is one example of a volatile benefit agent. Typical volatile benefit agents have a molecular weight of from 50 to 500. Where pro-fragrances are used the molecular weight will generally be higher.

Useful components of the perfume include materials of both natural and synthetic origin. They include single compounds and mixtures. Specific examples of such components
10 may be found in the current literature, e.g., in Fenaroli's Handbook of Flavour Ingredients, 1975, CRC Press; Synthetic Food Adjuncts, 1947 by M. B. Jacobs, edited by Van Nostrand; or Perfume and Flavour Chemicals by S. Arctander 1969, Montclair, N.J. (USA). These substances are well known to the person skilled in the art of perfuming, flavouring, and/or aromatizing consumer products, i.e., of imparting an odour and/or a
15 flavour or taste to a consumer product traditionally perfumed or flavoured, or of modifying the odour and/or taste of said consumer product.

By perfume in this context is not only meant a fully formulated product fragrance, but also selected components of that fragrance, particularly those which are prone to loss, such as
20 the so-called 'top notes'. The perfume component could also be in the form of a pro-fragrance. WO 2002/038120 (P&G), for example, relates to photo-labile pro-fragrance conjugates which upon exposure to electromagnetic radiation are capable of releasing a fragrant species.

25 Top notes are defined by Poucher (Journal of the Society of Cosmetic Chemists 6(2):80 [1955]). Examples of well known top-notes include citrus oils, linalool, linalyl acetate, lavender, dihydromyrcenol, rose oxide and cis-3-hexanol. Top notes typically comprise 15 to 25 wt% of a perfume composition and in those embodiments of the invention which contain an increased level of top-notes it is envisaged that at least 20 wt% would be
30 present within the encapsulate.

Typical perfume components which it is advantageous to encapsulate include those with a relatively low boiling point, preferably those with a boiling point of less than 300, preferably 100 to 250 Celsius.

It is also advantageous to encapsulate perfume components which have a low LogP (i.e. those which will be partitioned into water), preferably with a LogP of less than 3.0.

Another group of perfumes with which the present invention can be applied are the so-called 'aromatherapy' materials. These include many components also used in perfumery, including components of essential oils such as Clary Sage, Eucalyptus, Geranium, Lavender, Mace Extract, Neroli, Nutmeg, Spearmint, Sweet Violet Leaf and Valerian. By means of the present invention these materials can be transferred to textile articles that will be worn or otherwise come into contact with the human body (such as handkerchiefs and bed-linen).

The volatile benefit agents also include insect repellent materials (where insect should be read broadly to include other pests which are arthropods but not strictly hexapods – for example ticks). Many of these materials overlap with the class of perfume components and some are odourless to humans or have a non-perfume odour. Commonly used repellents include: DEET (N,N-diethyl-m-toluamide), essential oil of the lemon eucalyptus (*Corymbia citriodora*) and its active compound p-menthane-3,8-diol (PMD), Icaridin, also known as Picaridin, D-Limonene, Bayrepel, and KBR 3023, Nepetalactone, also known as "catnip oil", Citronella oil, Permethrin, Neem oil and Bog Myrtle. Known insect repellents derived from natural sources include: *Achillea alpina*, alpha-terpinene, Basil oil (*Ocimum basilicum*), *Callicarpa americana* (Beautyberry), Camphor, Carvacrol, Castor oil (*Ricinus communis*), Catnip oil (*Nepeta* species), Cedar oil (*Cedrus atlantica*), Celery extract (*Apium graveolens*), Cinnamon (*Cinnamomum Zeylanicum*, leaf oil), Citronella oil (*Cymbopogon fleusus*), Clove oil (*Eugenic caryophyllata*), Eucalyptus oil (70%+ eucalyptol, also known as cineol), Fennel oil (*Foeniculum vulgare*), Garlic Oil (*Allium sativum*), Geranium oil (also known as *Pelargonium graveolens*), Lavender oil (*Lavandula officinalis*), Lemon eucalyptus (*Corymbia citriodora*) essential oil and its active ingredient p-menthane-3,8-diol (PMD), Lemongrass oil (*Cymbopogon flexuosus*), Marigolds (*Tagetes* species), Marjoram (*Tetranychus urticae* and *Eutetranychus orientalis*), Neem oil (*Azadirachta indica*), Oleic acid, Peppermint (*Mentha x piperita*), Pennyroyal (*Mentha pulegium*), Pyrethrum (from *Chrysanthemum* species, particularly *C. cinerariifolium* and *C. coccineum*), Rosemary oil (*Rosmarinus officinalis*), Spanish Flag Lantana camara (*Helopeltis theivora*), *Solanum villosum* berry juice, Tea tree oil (*Melaleuca alternifolia*) and Thyme (*Thymus* species) and mixtures thereof.

The benefit agent may be encapsulated alone or co-encapsulated with carrier materials, further deposition aids and/or fixatives. Preferred materials to be co-encapsulated in carrier particles with the benefit agent include waxes, paraffins, stabilizers and fixatives.

- 5 Silicas, amorphous silicates, crystalline nonlayer silicates, layer silicates, calcium carbonates, calcium/sodium carbonate double salts, sodium carbonates, sodalites, alkali metal phosphates, pectin, carboxyalkylcelluloses, gums, resins, gelatin, gum arabic, porous starches, modified starches, carboxyalkyl starches, cyclodextrins, maltodextrins, synthetic polymers such as polyvinyl pyrrolidone (PVP), polyvinyl alcohol (PVA), cellulose
- 10 ethers, polystyrene, polyacrylates, polymethacrylates, polyolefins, aminoplast polymers, crosslinkers and mixtures thereof can all provide a basis for benefit agent delivery particles. Polymer particles are however preferred, especially polymer particles which comprise an aminoplast polymer.
- 15 Suspension is achieved through providing a yield stress. The yield stress needs to be larger than the stress imposed on the network by the microcapsules or cues otherwise the network is disrupted and the particles can sink or float depending on whether or not they are denser than the base liquid. Perfume microcapsules are almost neutrally buoyant and small, so the required yield stress is low. Air bubbles are bigger and have
- 20 the biggest density difference and so require a high yield stress (>0.5 Pa, depending on bubble size). If the yield stress is not too high the air bubbles can escape by floating and disengaging from the surface.
- Microcapsules preferably comprise a solid shell. Microcapsules carrying an anionic
- 25 charge should be well dispersed to avoid agglomeration issues. Microcapsules with a cationic charge may also be used. The microcapsule may have a melamine formaldehyde shell. Other suitable shell material may be selected from (poly)urea, (poly)urethane, starch/ polysaccharide, xyloglucan and aminoplasts.
- 30 Delivery aids may be present at the surface of the particle (microcapsule). These can advantageously be selected from non-ionic materials, preferably cellulose derivatives and polyesters, so give better substantivity to a plurality of substrates. Particularly preferred polysaccharide additional deposition aids include dextran, hydroxy-propyl methyl cellulose, hydroxy-ethyl methyl cellulose, hydroxy-propyl guar, hydroxy-ethyl ethyl

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cellulose, methyl cellulose, locust bean gum, xyloglucan, guar gum. Particularly preferred polyester additional deposition aids include polymers having one or more nonionic hydrophilic components comprising oxyethylene, polyoxyethylene, oxypropylene or polyoxypropylene segments, and, one or more hydrophobic components comprising terephthalate segments.

The average particle diameter of the microcapsules lies in the range from 1 to 100 micrometer and at least 90 wt% of the microcapsules preferably has a diameter in this range. More preferably, 90 wt% of the microcapsules have a diameter in the range 2 to 50 micrometers, even more preferably 5 to 50 micrometers. Most preferred are microcapsules with diameters less than 30 micrometers. It is advantageous to have a very narrow particle size distribution, for instance 90 wt% of microcapsules in the range 8 to 11 microns. Microcapsules in the range 2 to 5 microns cannot be dispersed so effectively due to the high surface area of the smaller particles.

Preferably the composition comprises at least 0.01 wt% of microcapsules, preferably with an anionic charge. Such microcapsules may deliver a variety of benefit agents by deposition onto substrates such as laundry fabric. To obtain maximum benefit they should be well dispersed through the liquid detergent composition and the vast majority of the microcapsules must not be significantly agglomerated. Any microcapsules that become agglomerated during manufacture of the liquid remain so in the container and will thus be dispensed unevenly during use of the composition. This is highly undesirable. The contents of the microcapsules are normally liquid. For example, fragrances, oils, fabric softening additives and fabric care additives are possible contents. Preferred microcapsules are particles termed core-in-shell microcapsules. As used herein, the term core-in-shell microcapsules refers to encapsulates whereby a shell which is substantially or totally water-insoluble at 40°C surrounds a core which comprises or consists of a benefit agent (which is either liquid or dispersed in a liquid carrier).

Suitable microcapsules are those described in US-A-5 066 419 which have a friable coating, preferably an aminoplast polymer. Preferably, the coating is the reaction product of an amine selected from urea and melamine, or mixtures thereof, and an aldehyde selected from formaldehyde, acetaldehyde, glutaraldehyde or mixtures thereof. Preferably, the coating is from 1 to 30 wt% of the particles.

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Core-in-shell microcapsules of other kinds are also suitable for use in the present invention. Ways of making such other microcapsules of benefit agents such as perfume include precipitation and deposition of polymers at the interface such as in coacervates, as disclosed in GB-A-751 600, US-A-3 341 466 and EP-A-385 534, as well as other
5 polymerisation routes such as interfacial condensation, as described in US-A-3 577 515, US-A-2003/0125222, US-A-6 020 066 and WO-A-03/101606. Microcapsules having polyurea walls are disclosed in US-A-6 797 670 and US-A-6 586 107. Other patent applications specifically relating to use of melamine-formaldehyde core-in-shell microcapsules in aqueous liquids are WO-A-98/28396, WO02/074430, EP-A-1 244 768,
10 US-A-2004/0071746 and US-A-2004/0142868.

Perfume encapsulates are a preferred type of microcapsule suitable for use in the present invention.

15 A preferred class of core-in-shell perfume microcapsule comprises those disclosed in WO 2006/066654 A1. These comprise a core having from about 5% to about 50 wt% of perfume dispersed in from about 95% to about 50 wt% of a carrier material. This carrier material preferably is a non-polymeric solid fatty alcohol or fatty ester carrier material, or mixtures thereof. Preferably, the esters or alcohols have a molecular weight of from
20 about 100 to about 500 and a melting point from about 37°C to about 80°C, and are substantially water-insoluble. The core comprising the perfume and the carrier material are coated in a substantially water-insoluble coating on their outer surfaces. Similar microcapsules are disclosed in US 5,154,842 and these are also suitable.

25 The microcapsules may attach to suitable substrates, e.g. to provide persistent fragrance that is desirably released after the cleaning process is complete.

Optional ingredients

30 The formulation may comprise, by way of example: clays; enzymes, particularly: lipase, cellulase, protease, mannanase, amylase and pectate lyase; cleaning polymers, including ethoxylated polyethylene imines (EPEI) and polyester soil release polymers; chelating agents or sequestrants, including HEDP (1-Hydroxyethylidene -1,1,-diphosphonic acid) which is available, for example, as Dequest® 2010 from Thermphos; detergency builders;

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hydrotropes; neutralising and pH adjusting agents; optical brighteners; antioxidants and other preservatives, including Proxel®; other active ingredients, processing aids, dyes or pigments, carriers, fragrances, suds suppressors or suds boosters, chelating agents, clay soil removal/ anti-redeposition agents, fabric softeners, dye transfer inhibition agents, and
5 transition metal catalyst in a composition substantially devoid of peroxygen species.

These and further possible ingredients for inclusion are further described in WO2009/153184.

10 Packaging

The compositions may be packaged in any form of container. Their shear thinning properties means that they may be dispensed from a squeeze bottle, from a pump dispenser, from a trigger spray dispenser or by being simply poured from a bottle. The
15 most advantageous form of packing is the type where the product is poured from a bottle, possibly into a measuring cup. The controlled high pour viscosity of the compositions as claimed makes the compositions ideally suited to this mode of dispensing. Typically a plastic bottle with a detachable closure/pouring spout. The bottle may be rigid or deformable. A deformable bottle allows the bottle to be squeezed to aid dispensing. If
20 clear bottles are used they may be formed from PET. Polyethylene or clarified polypropylene may be used. Preferably the container is clear enough that the liquid, with any visual cues therein, is visible from the outside. The bottle may be provided with one or more labels, or with a shrink wrap sleeve which is desirably at least partially transparent, for example 50% of the area of the sleeve is transparent. The adhesive
25 used for any transparent label should not adversely affect the transparency.

EXAMPLES

Formulation composition:

Ingredient	Wt% inclusion (as 100%)
LAS	4
SLES	12
CAPB	3
NaCl	0.5
Buffer	0.218
TEA	0.667
Citric Acid	0.178
EPEI	0.75
Soil Release Polymer	0.1
Perfume	0.34
Preservative	0.02
X-linked HASE Polymer	1.25

5

The remaining is water. pH: 6.208

CLAIMS

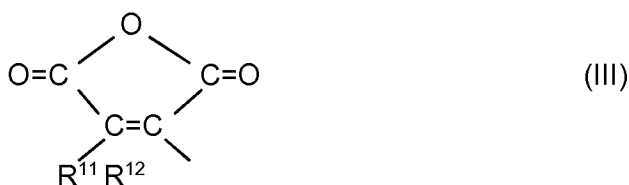
1. An internally structured aqueous detergent liquid composition comprising:
- (i) from 10.1 to 35.0% wt. a surfactant system comprising anionic surfactant, and
- (ii) at least 0.05 wt % of a cross-linked HASE polymer,
- and wherein the η_{10} is at least 10 Pa.s, preferably no more than 1 000 Pa.s.

2. A composition according to claim 1 wherein the HASE polymer is a copolymer formed by addition polymerisation in the presence of:

- (A) 0 to 5 wt% of a first monomer consisting of an ethylenically unsaturated diacid of formula (II):



or an unsaturated cyclic anhydride precursor of such an ethylenically unsaturated diacid, the anhydride having formula (III)



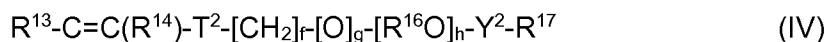
where R^{11} and R^{12} are individually selected from H, $\text{C}_1\text{-C}_3$ alkyl, phenyl, chlorine and bromine;

- (B) 15 to 60 wt% of a second ethylenically unsaturated monoacidic monomer consisting of (meth)acrylic acid;

- (C) 30 to 70 wt% of a third ethylenically unsaturated monomer consisting of $\text{C}_1\text{-C}_8$ alkyl ester of (meth)acrylic acid; and

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(D) 1 to 25 wt% of a fourth ethylenically unsaturated monomer, consisting of surfmer of formula (IV):



5

wherein each R^{13} and R^{14} are each independently selected from H, methyl, -C(=O)OH, or -C(=O)OR¹⁵;

R^{15} is a C₁-C₃₀ alkyl;

T^2 is -CH₂C(=O)O-, -C(=O)O-, -O-, -CH₂O-, -NHC(=O)NH-, -C(=O)NH-,

10

-Ar-(CG₂)_z-NHC(=O)O-, -Ar-(CG₂)_z-NHC(=O)NH-, or -CH₂CH₂NHC(=O)-;

Ar is divalent aryl;

G is H or methyl;

z is 0 or 1;

f is an integer in the range of 0 to 30; and g is 0 or 1; with the proviso that

15

when f is 0, g is 0, and when f is in the range of 1 to 30; g is 1;

($R^{16}O$)_h is polyoxyalkylene, which is a homopolymer, a random copolymer, or a block copolymer of C₂-C₄-oxyalkylene units, wherein R^{16} is C₂H₄, C₃H₆, C₄H₈, or a mixture thereof, and h is an integer in the range of 5 to 250; Y^2 is - $R^{16}O$ -,

20

- $R^{16}H$ -, -C(=O)-, -C(=O)NH-, = $R^{16}NHC(=O)NH$ -, or -C(=O)NHC(=O)-; and

R^{17} is substituted or unsubstituted alkyl selected from the group consisting of C₈-C₄₀ linear alkyl, C₈-C₄₀ branched alkyl, C₈-C₄₀ carbocyclic alkyl, C₂-C₄₀ alkyl-substituted, phenyl, aryl-substituted C₂-C₄₀ alkyl, and C₈-C₈₀ complex ester; wherein the R^{17} alkyl group optionally comprises one or more

25

substituents selected from the group consisting of hydroxy, alkoxy, and halogen.

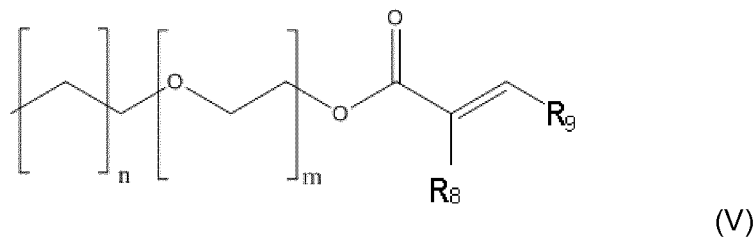
and

30

(E) 0.005 to 5 wt% of a cross linking agent, 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, allyl and functional mixtures thereof.

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3. A composition according to any preceding claim in which the Surfmers D in copolymer has the formula (V):



5

in which each R_8 and R_9 are independently selected from H, C_1 to C_3 alkyl;
 n ranges from 6 to 40 and m ranges from 6 to 40.

4. A composition according to any preceding claim in which the amount of monomer D
 10 in the cross-linked HASE polymer is in the range of 2 to 15 wt.%.
5. A composition according to any preceding claim wherein the composition includes 2
 15 wt.% or more of a viscosity reducing polymer comprising ethoxylated polyethylene
 imine and/or polyester soil release polymer.
6. A composition according to any preceding claim in which the surfactant system
 comprises up to 25 wt% total surfactant.
7. A composition according to any preceding claim which comprises alkyl benzene
 20 sulphonate anionic surfactant.
8. A composition according to any preceding claim wherein the cross-linked polymer is
 present at up to 2.0% wt. and preferably up to 1.0% wt. of the composition.
9. A composition according to any preceding claim which is a fabric cleaning
 25 composition.
10. A method for cleaning fabrics by applying a composition according to any preceding
 30 claim in a wash liquor to fabrics.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/060078

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D3/37
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2015/299620 A1 (JARVIS ADAM PETER [GB] ET AL) 22 October 2015 (2015-10-22)	1-10
Y	claims 2, 3; tables 1, 3; compounds Copolymer 2, composition C paragraphs [0129] - [0133], [0142] - [0164], [0175]	1,2,4-10
X	----- WO 2016/120034 A1 (UNILEVER PLC [GB]; UNILEVER NV [NL]; CONOPCO INC DBA UNILEVER [US]) 4 August 2016 (2016-08-04) example 2; compound Copolymer 2 page 5, line 28 - line 29 page 7, line 3 - page 8, line 7 page 11, line 10 - page 12, line 8 page 26, line 22 - line 27 page 27, line 9 - page 29, line 12 ----- -/--	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

7 September 2018

Date of mailing of the international search report

17/09/2018

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2018/060078

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2013/040870 A1 (ARISANDY CHRISTOFER [DE] ET AL) 14 February 2013 (2013-02-14) example 5; table 1; compound Formulation type A paragraphs [0137] - [0141], [0155] - [0164] -----	1-10
Y	WO 2007/090759 A1 (CIBA SPECIALTY CHEM HOLDING INC) 16 August 2007 (2007-08-16) examples 1, 11, E, G, H; table 1 page 28, line 9 - line 30 page 40, line 1 - line 16 -----	1,2,4-10
A	US 5 062 995 A (WU SHANG-REN [US] ET AL) 5 November 1991 (1991-11-05) example 1 column 6, line 61 - column 9, line 15 -----	1,2,4-10

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2018/060078

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 3-10(completely); 1, 2(partially)

An aqueous detergent liquid composition comprising the technical features of claims 1-10, with the composition comprising 10.1 to 35.0 % wt. of a surfactant system comprising anionic surfactant; and at least 0.05 wt.% of a polymer formed from the polymerisation of monomers (A)-(D) and cross linking agent (E), with 0 to 5 wt.% monomer (A) being an ethylenically unsaturated diacid of formula (II) $\text{H00C-CR11=CR12-C00H}$ or anhydride monomer of formula (III); 15-60% wt. monomer (B) being a C1-C8 alkyl ester of (meth)acrylic acid; 30-70 % wt. of monomer (C) being a third ethylenically unsaturated monomer consisting of C1-C8 alkyl ester of (meth)acrylic acid; and 1-25 % wt. monomer (D) consisting of a surfmer being an ester of formula $\text{R13-C=CR14-T2-[CH2]f-[O]g-[R160]h-Y2-R17}$, with T2 being $-\text{CH2C(=O)O}-$ or $-\text{C(=O)O}-$, and 0.005-5 wt.% of the cross-linker (E) comprising polyfunctional units (R groups and sub-indices as defined in claim 1).

2. claims: 4-10(completely); 1, 2(partially)

An aqueous detergent liquid composition comprising the technical features of claims 1-2 and 4-10, with the composition comprising 10.1 to 35.0 % wt. of a surfactant system comprising anionic surfactant; and at least 0.05 wt.% of a polymer formed from the polymerisation of monomers (A)-(D) and cross linking agent (E), with 0 to 5 wt.% monomer (A) being an ethylenically unsaturated diacid of formula (II) $\text{H00C-CR11=CR12-C00H}$ or anhydride monomer of formula (III); 15-60% wt. monomer (B) being a C1-C8 alkyl ester of (meth)acrylic acid; 30-70 % wt. of monomer (C) being a third ethylenically unsaturated monomer consisting of C1-C8 alkyl ester of (meth)acrylic acid; and 1-25 % wt. monomer (D) consisting of a surfmer being an ester of formula $\text{R13-C=CR14-T2-[CH2]f-[O]g-[R160]h-Y2-R17}$, with T2 being $-\text{O}-$ or $-\text{CH2O}-$, and 0.005-5 wt.% of the cross-linker (E) comprising polyfunctional units (R groups and sub-indices as defined in claim 1).

3. claims: 4-10(completely); 1, 2(partially)

An aqueous detergent liquid composition comprising the technical features of claims 1-4 and 7-15, with the composition comprising 10.1 to 35.0 % wt. of a surfactant system comprising anionic surfactant; and at least 0.05 wt.% of a polymer formed from the polymerisation of monomers (A)-(D) and cross linking agent (E), with 0 to 5 wt.% monomer (A) being an ethylenically unsaturated diacid of formula (II) $\text{H00C-CR11=CR12-C00H}$ or anhydride monomer of

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formula (III); 15-60% wt. monomer (B) being a C1-C8 alkyl ester of (meth)acrylic acid; 30-70 % wt. of monomer (C) being a third ethylenically unsaturated monomer consisting of C1-C8 alkyl ester of (meth)acrylic acid; and 1-25 % wt. monomer (D) consisting of a surfmer being an ester of formula $R_{13}-C=CR_{14}-T_2-[CH_2]_f-[O]_g-[R_{160}]_h-Y_2-R_{17}$, with T_2 being $-NHC(=O)NH-$, $-C(=O)NH-$, $-Ar-(CE_2)_x-NHC(=O)O-$, $-Ar-(CE_2)_x-NHC(=O)-NH-$, or $-CH_2CH_2NHC(=O)-$, and 0.005-5 wt.% of the cross-linker (E) comprising polyfunctional units (R groups and sub-indices as defined in claim 1).

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