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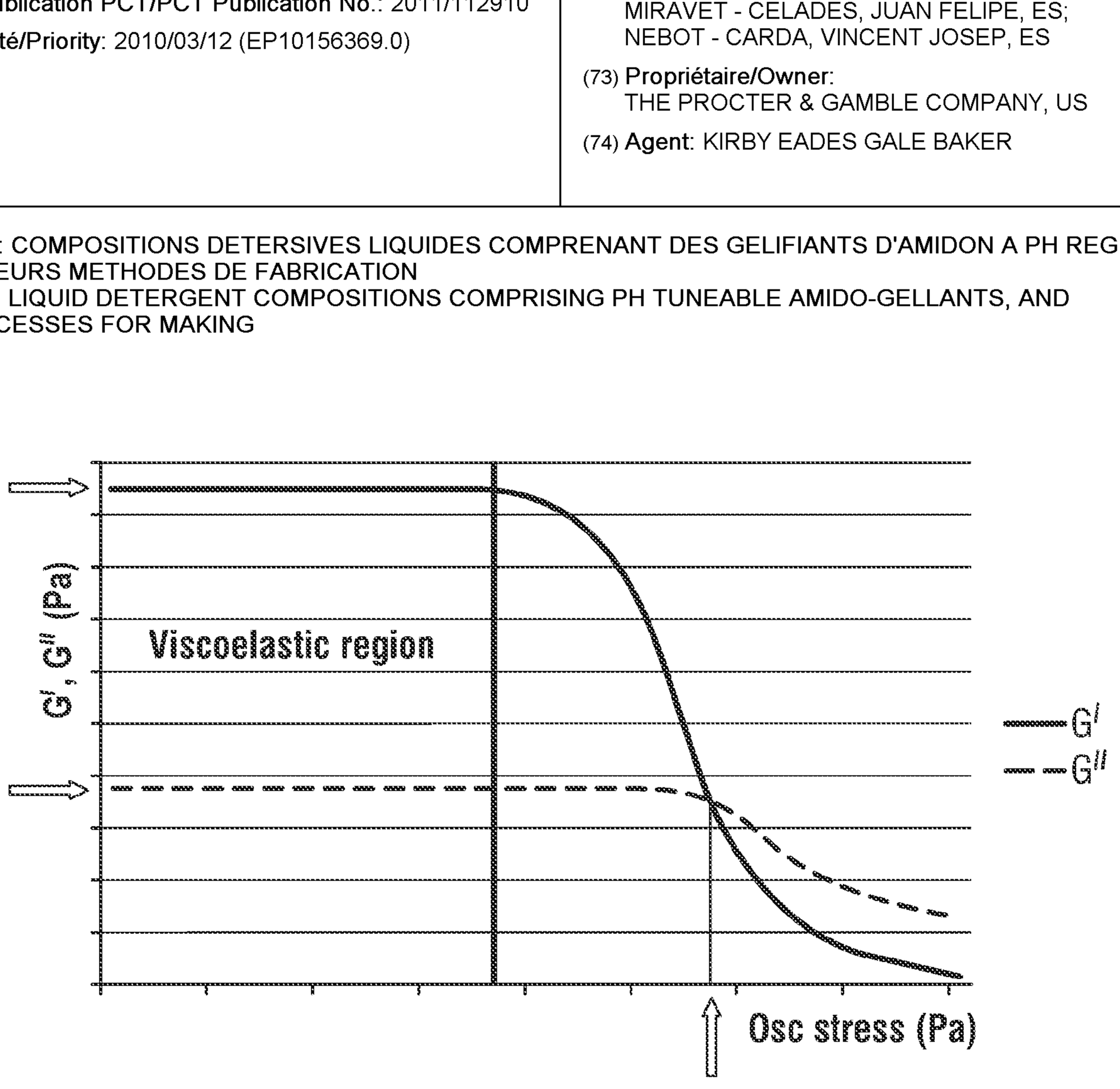
(54) Title: LIQUID DETERGENT COMPOSITIONS COMPRISING PH TUNEABLE AMIDO-GELLANTS, AND PROCESSES FOR MAKING



(57) Abrégé/Abstract:
The invention is directed to a fluid detergent composition comprising a pH tuneable amido gellant and a surfactant, and a method for structuring said composition.

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(54) **Title**: LIQUID DETERGENT COMPOSITIONS COMPRISING PH TUNEABLE AMIDO-GELLANTS, AND PROCESSES FOR MAKING

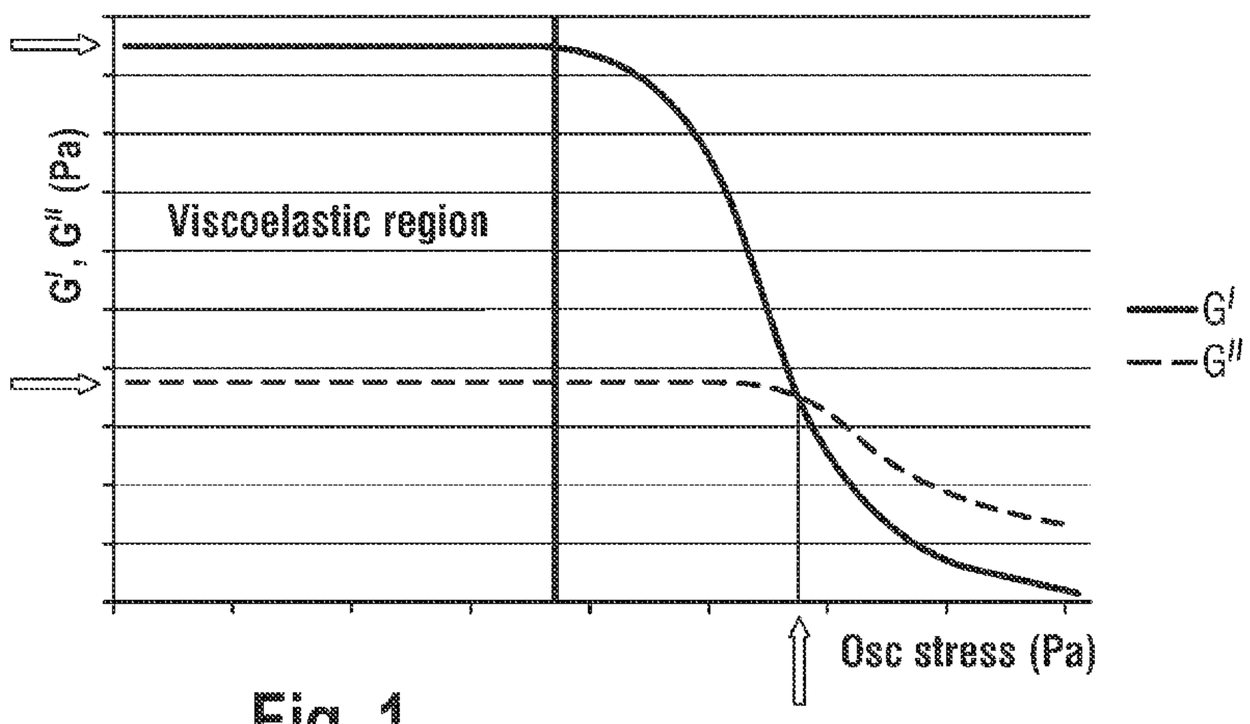

Fig. 1

(57) **Abstract**: The invention is directed to a fluid detergent composition comprising a pH tuneable amido gellant and a surfactant, and a method for structuring said composition.

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LIQUID DETERGENT COMPOSITIONS COMPRISING PH TUNEABLE AMIDO-GELLANTS, AND PROCESSES FOR MAKING

FIELD OF THE INVENTION

The present invention relates to fluid detergent compositions comprising a structurant that is compatible with a broad range of detergent compositions and does not affect product clarity, and a process for making them.

BACKGROUND OF THE INVENTION

Today's consumers desire high performance liquid detergent compositions having sufficient structuring to give a rich impression and stabilize performance ingredients. External structurants for providing rheological benefits to fluid detergent compositions include those derived from castor oil, fatty acids, fatty esters, or fatty soap water-insoluble waxes. However, the required performance ingredients often complicate the addition of external structurants known in the art and may even be incompatible with them. For instance, many external structurants are degraded by performance ingredients, such as enzymes, including protease and lipase (lipase hydrolyses ester bonds present in castor oil derivatives), which are desirable for improved low temperature cleaning. They are also often incompatible with low pH and peroxide bleaches. In addition, external structurants generally require the use of structurant premixes incorporating large amounts of water. Such structurant premixes are unsuitable for compact detergents and for unit-dose applications.

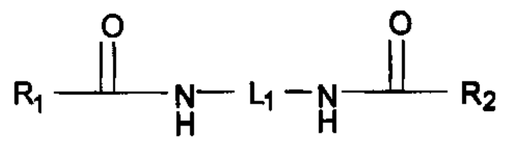
Amido-gellants provide a solution for structuring fluid detergent compositions while also being compatible with a broad range of optional detergent ingredients, such as bleaches and/or enzymes. They also provide an aesthetically pleasing pour profile without negatively impacting the composition clarity. They can be formulated into structurant premixes that are entirely water-free. However, most amido-gellants require premixes that have to be heated to as high as 100°C to reduce the viscosity to a level where they can be easily mixed with a detergent composition. Since ingredients such as enzymes and perfumes start to degrade at temperatures as low as 50°C, they must be added after the amido-gellant, and after a cooling step.

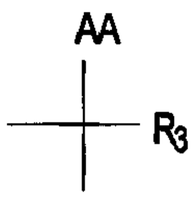
As such, a need remains for a structurant for fluid detergent compositions, that is compatible with a broad range of ingredients (including heat-sensitive ingredients such as

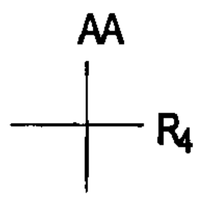
enzymes), while also being easy to incorporate into the composition without requiring excessive heating.

SUMMARY OF THE INVENTION

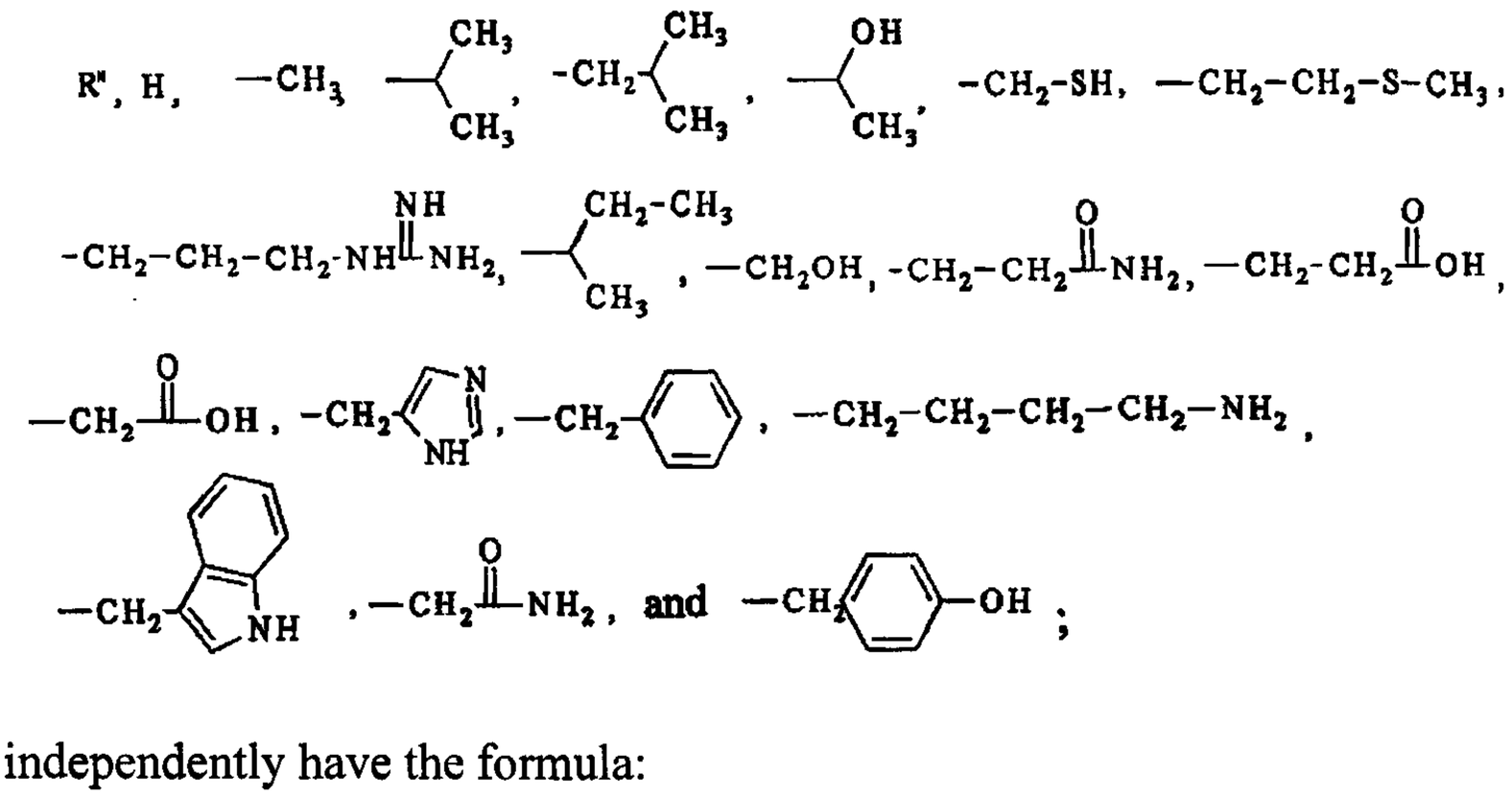
Certain exemplary embodiments provide a fluid detergent composition comprising: a) from 1% to 70% by weight of a surfactant selected from the group: anionic, nonionic surfactants and mixtures thereof; and b) from 0.01 wt% to 10 wt% of a pH tuneable amido-gellant as an external structuring system having a formula



wherein: at least one of L_1, R_1 or R_2 comprises a pH-sensitive group; L_1 is a backbone moiety having molecular weight from 14 to 500 g/mol; R_1 is R_3 or 

, R_2 is R_4 or 

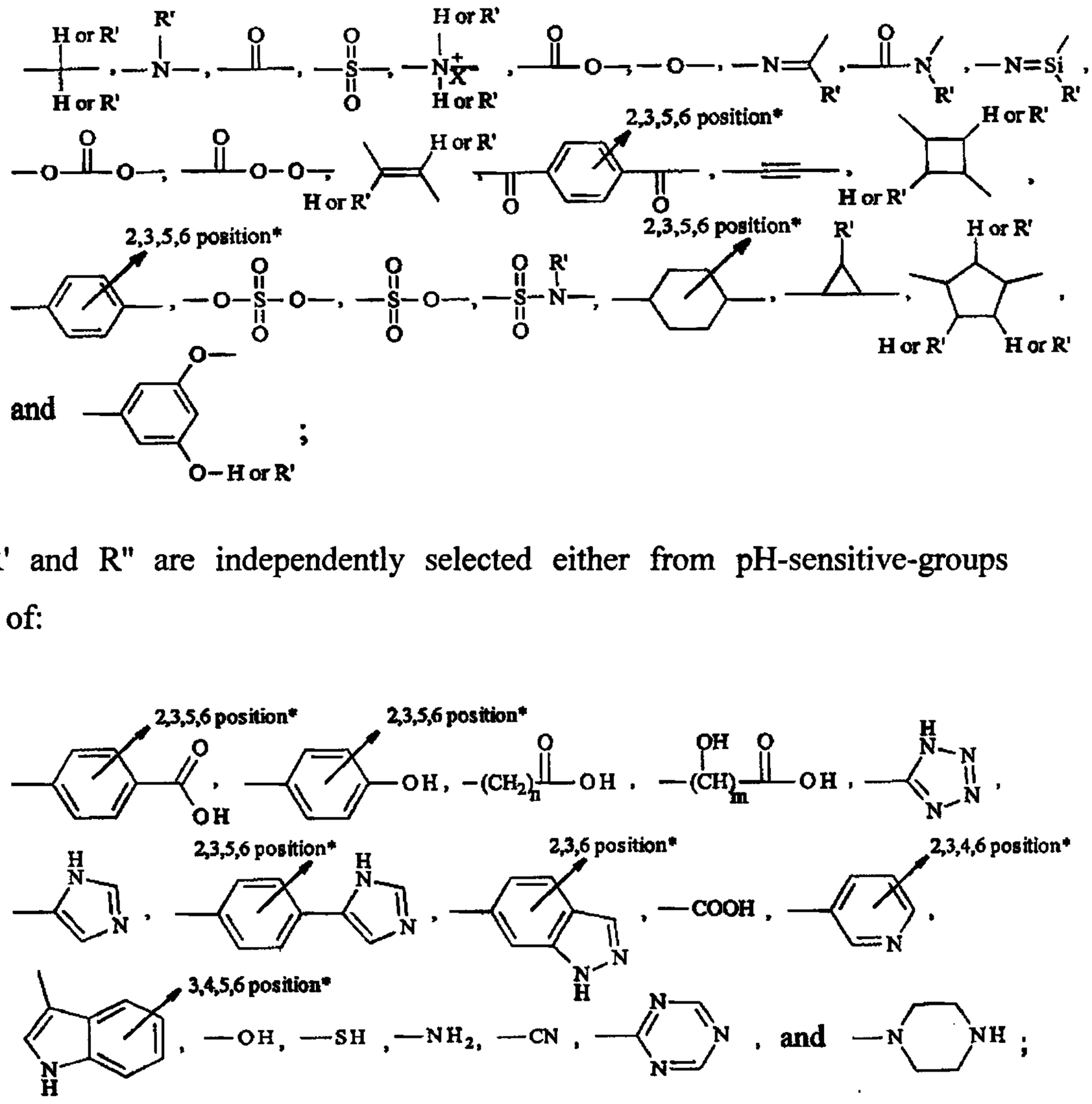
, wherein each AA is independently selected from the group consisting of:



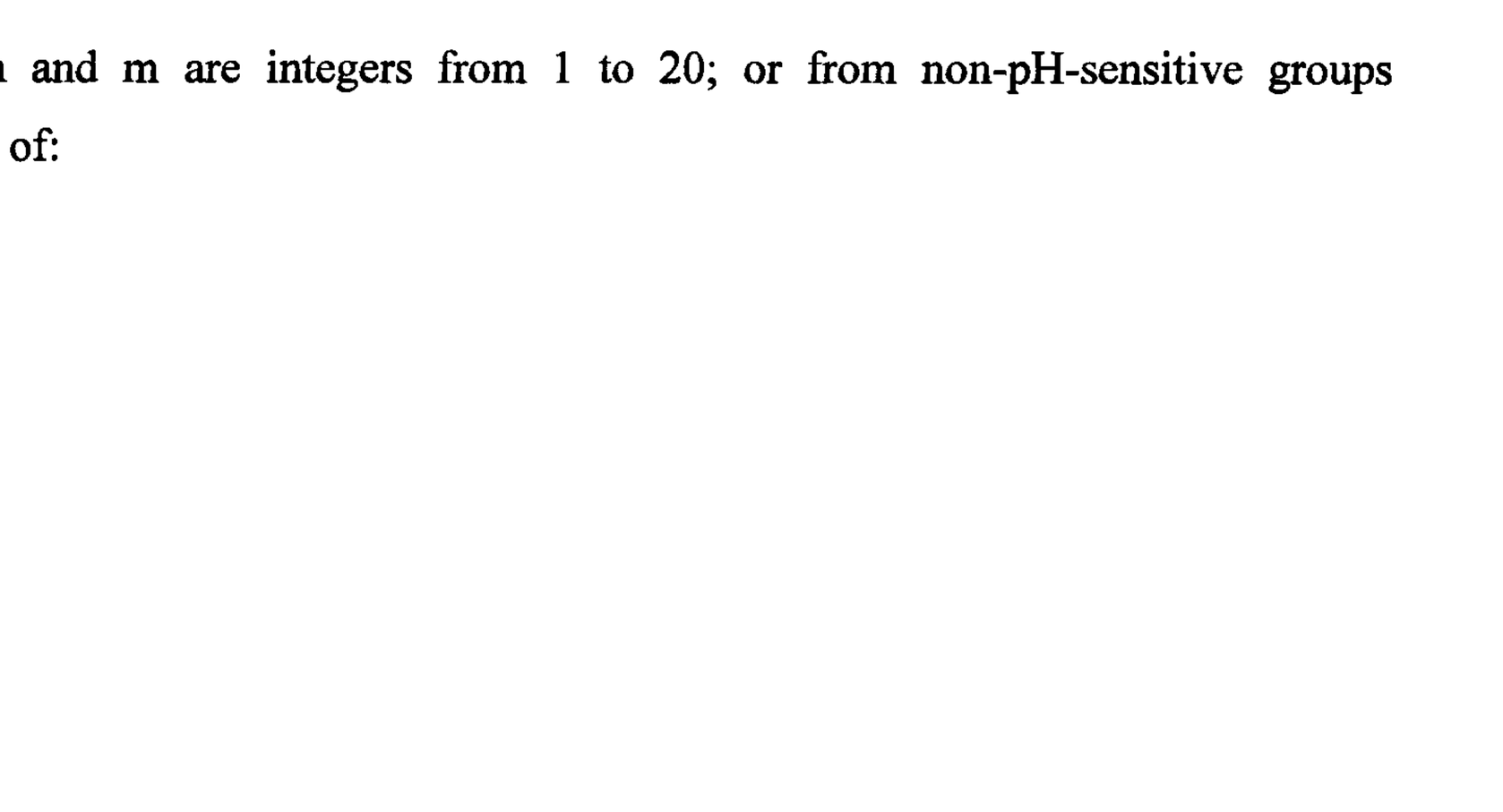
R_3 and R_4 independently have the formula:

$$(L')_o\text{-}(L'')_q\text{-}R,$$

wherein: (o + q) is from 1 to 10; L' and L" are independently selected from:

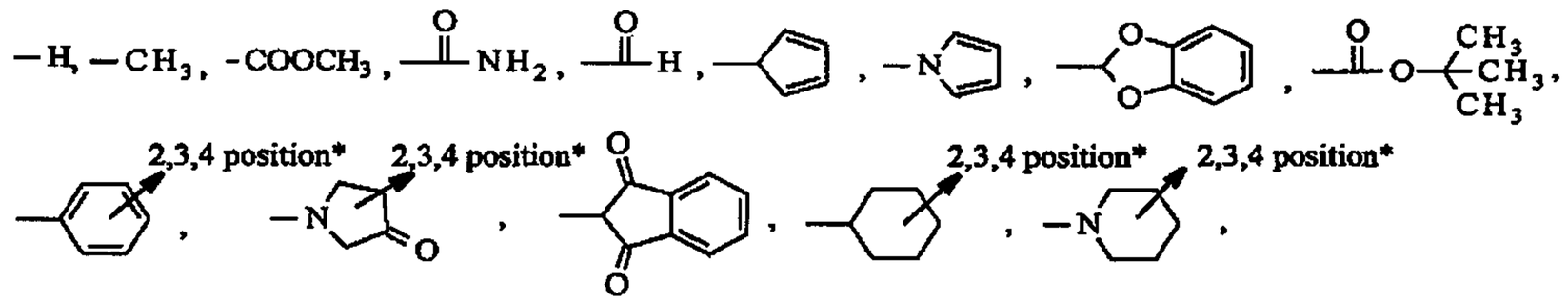


and R, R' and R" are independently selected either from pH-sensitive-groups consisting of:



wherein n and m are integers from 1 to 20; or from non-pH-sensitive groups consisting of:

2b



such that at least one of R, R' and R" comprises a pH-sensitive group; wherein the pH tuneable amido-gellant has a pKa of from 1 to 30.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 details G' and G" within the linear viscoelastic region and the oscillation stress at the point where G' and G" cross over as a measure for gel strength.

Figure 2 details G' and G" cross over as a measure of restructuring kinetics.

DETAILED DESCRIPTION OF THE INVENTION

Fluid detergent compositions as described herein include but are not limited to consumer products such as: shampoos; skin cleaners and exfolients; shaving liquids, foams and gels; products for treating fabrics, hard surfaces and any other surfaces in the area of fabric and home care, including: dishwashing, laundry cleaning, laundry and rinse additives, hard surface cleaning including floor and toilet bowl cleaners; products relating to oral care including toothpastes and gels and whiteners. A particularly preferred embodiment of the invention is a "fluid laundry detergent composition". As used herein, "fluid laundry detergent composition" refers to any laundry treatment composition comprising a fluid capable of wetting and cleaning fabric e.g., clothing, in a domestic washing machine.

The fluid detergent composition can include solids or gases in suitably subdivided form, but the overall composition excludes product forms which are non-

fluid overall, such as tablets or granules. The fluid detergent compositions preferably have densities in the range from of 0.9 to 1.3 grams per cubic centimeter, more preferably from 1.00 to 1.10 grams per cubic centimeter, excluding any solid additives but including any bubbles, if present.

The fluid detergent compositions of the invention may be opaque, semi-transparent or even clear. When clarity of the fluid detergent composition is desired, the fluid detergent composition has a turbidity of from 5 NTU to less than 3000 NTU, preferably less than 1000 NTU, more preferably less than 500 NTU and most preferably less than 100 NTU.

All percentages, ratios and proportions used herein are by weight percent of the composition, unless otherwise specified. All average values are calculated "by weight" of the composition or components thereof, unless otherwise expressly indicated.

Anionic and nonionic surfactants:

Detergent compositions of the present invention comprise from 1% to 70%, preferably from 5% to 60% by weight, more preferably from 10% to 50%, and most preferably from 15% to 45% by weight of a surfactant selected from the group consisting of: anionic, nonionic surfactants and mixtures thereof. The preferred ratio of anionic to nonionic surfactant is from 100:0 (i.e. no nonionic surfactant) to 5:95, more preferably from 99:1 to 1:4, most preferably 5:1 to 1.5:1.

1. Anionic surfactants:

The fluid detergent compositions of the present invention preferably comprises from 1 to 50%, preferably from 5 to 40%, more preferably from 10 to 30% by weight of one or more anionic surfactants. Preferred anionic surfactant are selected from the group consisting of: C11-C18 alkyl benzene sulfonates, C10-C20 branched-chain and random alkyl sulfates, C10-C18 alkyl ethoxy sulfates, mid-chain branched alkyl sulfates, mid-chain branched alkyl alkoxy sulfates, C10-C18 alkyl alkoxy carboxylates comprising 1-5 ethoxy units, modified alkylbenzene sulfonate, C12-C20 methyl ester sulfonate, C10-C18 alpha-olefin sulfonate, C6-C20 sulfosuccinates, and mixtures thereof. However, by nature, every anionic surfactant known in the art of detergent compositions may be used, such as those disclosed in "Surfactant Science Series", Vol. 7, edited by W. M. Linfield, Marcel Dekker. However, the compositions of the present invention comprise preferably at least one sulphonic acid surfactant, such as a linear alkyl benzene sulphonic acid, or the water-soluble salt forms.

Anionic sulfonate or sulfonic acid surfactants suitable for use herein include the acid and salt forms of linear or branched C5-C20, more preferably C10-C16, most preferably C11-C13 alkylbenzene sulfonates, C5-C20 alkyl ester sulfonates, C6-C22 primary or secondary alkane sulfonates, C5-C20 sulfonated polycarboxylic acids, and mixtures thereof. The aforementioned surfactants can vary widely in their 2-phenyl isomer content.

Anionic sulphate salts suitable for use in compositions of the invention include: primary and secondary alkyl sulphates, having a linear or branched alkyl or alkenyl moiety having from 9 to 22 carbon atoms, more preferably from 12 to18 carbon atoms; beta-branched alkyl sulphate surfactants; and mixtures thereof.

Mid-chain branched alkyl sulphates or sulfonates are also suitable anionic surfactants for use in the compositions of the invention. Preferred are the C5-C22, preferably C10-C20 mid-chain branched alkyl primary sulphates. When mixtures are used, a suitable average total number of carbon atoms for the alkyl moieties is preferably within the range of from 14.5 to 17.5. Preferred mono-methyl-branched primary alkyl sulphates are selected from the group consisting of the 3-methyl to 13-methyl pentadecanol sulphates, the corresponding hexadecanol sulphates, and mixtures thereof. Dimethyl derivatives or other biodegradable alkyl sulphates having light branching can similarly be used.

Other suitable anionic surfactants for use herein include fatty methyl ester sulphonates and/or alkyl ethyoxy sulphates (AES) and/or alkyl polyalkoxylated carboxylates (AEC). Mixtures of anionic surfactants can be used, for example mixtures of alkylbenzenesulphonates and AES.

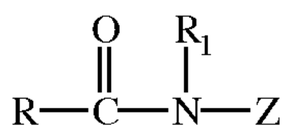
The anionic surfactants are typically present in the form of their salts with alkanolamines or alkali metals such as sodium and potassium. Preferably, the anionic surfactants are neutralized with alkanolamines such as monoethanolamine or triethanolamine, and are fully soluble in the liquid phase.

2. Nonionic surfactants:

The fluid detergent compositions of the present invention preferably comprise up to 30%, preferably from 1 to 15%, more preferably from 2 to 10% by weight of one or more nonionic surfactants. Suitable nonionic surfactants include, but are not limited to C12-C18 alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates, C6-C12 alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propoxy), block alkylene oxide condensate of C6-C12 alkyl phenols, alkylene oxide condensates of C8-C22 alkanols and ethylene oxide/propylene oxide block polymers (Pluronic®-BASF Corp.), as well as semi polar nonionics (e.g., amine oxides and phosphine oxides). An extensive disclosure of suitable nonionic surfactants can be found in U.S. Pat. 3,929,678.

Alkylpolysaccharides such as disclosed in U.S. Pat. 4,565,647 are also useful nonionic surfactants for compositions of the invention. Also suitable are alkyl polyglucoside surfactants.

In some embodiments, suitable nonionic surfactants include those of the formula $R_1(OC_2H_4)_nOH$, wherein R_1 is a C10-C16 alkyl group or a C8-C12 alkyl phenyl group, and n is from 3 to about 80. In some embodiments, the nonionic surfactants may be condensation products of C12-C15 alcohols with from 5 to 20 moles of ethylene oxide per mole of alcohol, e.g., C12-C13 alcohol condensed with about 6.5 moles of ethylene oxide per mole of alcohol. Additional suitable nonionic surfactants include polyhydroxy fatty acid amides of the formula:



wherein R is a C9-C17 alkyl or alkenyl, R_1 is a methyl group and Z is glycidyl derived from a reduced sugar or alkoxylated derivative thereof. Examples are N-methyl N-1-deoxyglucityl cocoamide and N-methyl N-1-deoxyglucityl oleamide.

External Structurant:

The external structurant preferably imparts a shear thinning viscosity profile to the fluid detergent composition, independently from, or extrinsic from, any structuring effect of the detersive surfactants of the composition. Preferred external structurants include those which provide a pouring viscosity from 50 cps to 20,000 cps, more preferably from 200 cps to 10,000 cps, most preferably from 500 cps to 7,000 cps. The fluid detergent composition preferably has a resting viscosity of at least 1,500 cps, preferably at least 10,000 cps, more preferably at least 50,000 cps. This resting (low stress) viscosity represents the viscosity of the fluid detergent composition under gentle shaking in the package and during transportation. Alternatively, the fluid detergent composition may be a thixotropic gel. Such compositions may have a resting viscosity of from 10,000 cps to 500,000 cps, preferably from 100,000 cps to 400,000 cps, more preferably from 200,000 to 300,000. The preferred shear-thinning characteristics of the fluid detergent is defined as a ratio of low stress viscosity to pouring viscosity of at least 2, preferably at least 10, more preferably at least 100, up to 2000.

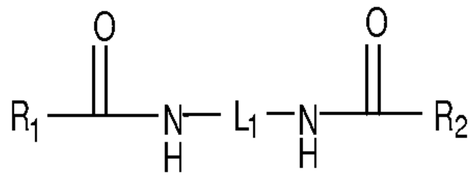
The pouring viscosity is measured at a shear rate of 20 sec^{-1}, which is a shear rate that the fluid detergent composition is typically exposed to during pouring. The resting (low stress) viscosity is determined under a constant stress of 0.1 Pa during a viscosity creep experiment over a 5 minute interval. Rheology measurements over the 5 minute interval are made after the composition has has rested at zero shear rate for at least 10 minutes, between loading the sample in the rheometer and running the test. The data over the last 3 minutes are used to fit a straight

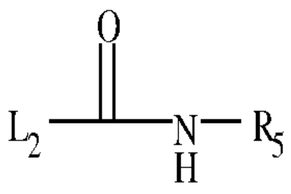
line, and from the slope of this line, the low stress viscosity is calculated. The viscosity is measured at 21°C using a TA AR 2000 (or AR G2) rheometer with a 40 mm stainless steel plate having a gap of 500 microns.

1. pH tuneable amido gellant

The pH tuneable amido gellant provides the fluid detergent composition with a viscosity profile that is dependent on the pH of the composition. The pH tuneable amido gellants comprise at least one pH sensitive group. When a pH tuneable amido gellant is added to a polar protic solvent such as water, it is believed that the nonionic species form the viscosity building network while the ionic species are soluble and do not form a viscosity building network. By increasing or decreasing the pH (depending on the selection of the pH-sensitive groups) the amido gellant is either protonated or deprotonated. Thus, by changing the pH of the solution, the solubility, and hence the viscosity building behaviour, of the amido gellant can be controlled. By careful selection of the pH-sensitive groups, the pKa of the amido gellant can be tailored. Hence, the choice of the pH-sensitive groups can be used to select the pH at which the amido gellant builds viscosity.

The fluid detergent composition comprises from 0.01 wt% to 10 wt%, preferably from 0.05 wt% to 5 wt%, more preferably from 0.1 wt% to 2 wt%, most preferably from 0.4 wt% to 1 wt%, of a pH tuneable amido-gellant as an external structuring system. In an alternative embodiment, the fluid detergent composition comprises from 0.1 wt% to 0.5 wt% of the pH tuneable amido-gallant. The pH tuneable amido-gellant has a formula selected from the group consisting of:

[I]  wherein R_1 and R_2 are aminofunctional end-groups; L_1 is a backbone moiety having molecular weight from 14 to 500 g/mol; and at least one of L_1, R_1 or R_2 comprises a pH-sensitive group.

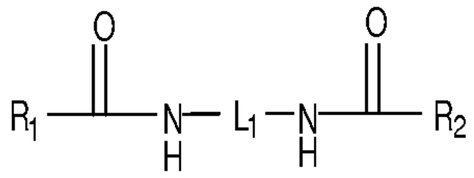
[II]  wherein R_5 is an aminofunctional moiety; L_2 is a backbone moiety having molecular weight from 14 to 500 g/mol; and at least one of L_2 or R_5 comprises a pH-sensitive group;

and mixtures thereof;

wherein the pH tuneable amido-gellant has a pKa of from 1 to 30, preferably a pKa of from 1.5 to 14.

The pH tuneable amido gellant comprises at least one amido functional group, and further comprises at least one pH-sensitive group. Preferably, the pH tuneable amido gellant has a molecular weight from 150 to 1500 g/mol, more preferably from 300 g/mol to 900 g/mol, most preferably from 400 g/mol to 700 g/mol.

In one embodiment, the pH tuneable amido gellant has the following structure [I]:

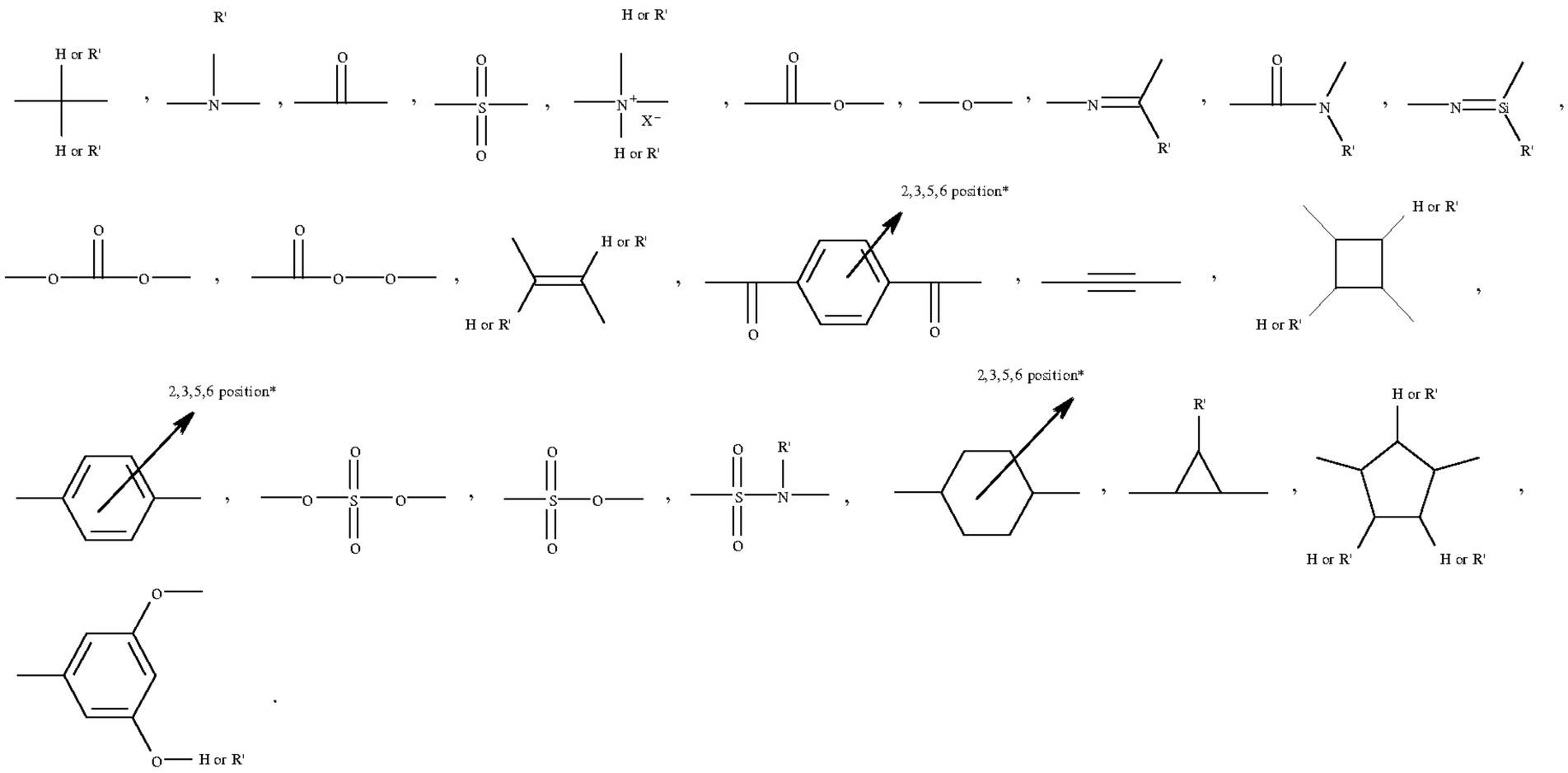


wherein R_1 and R_2 are aminofunctional end-groups; L_1 is a backbone moiety having molecular weight from 14 to 500 g/mol; and at least one of L_1, R_1 or R_2 comprises a pH-sensitive group.

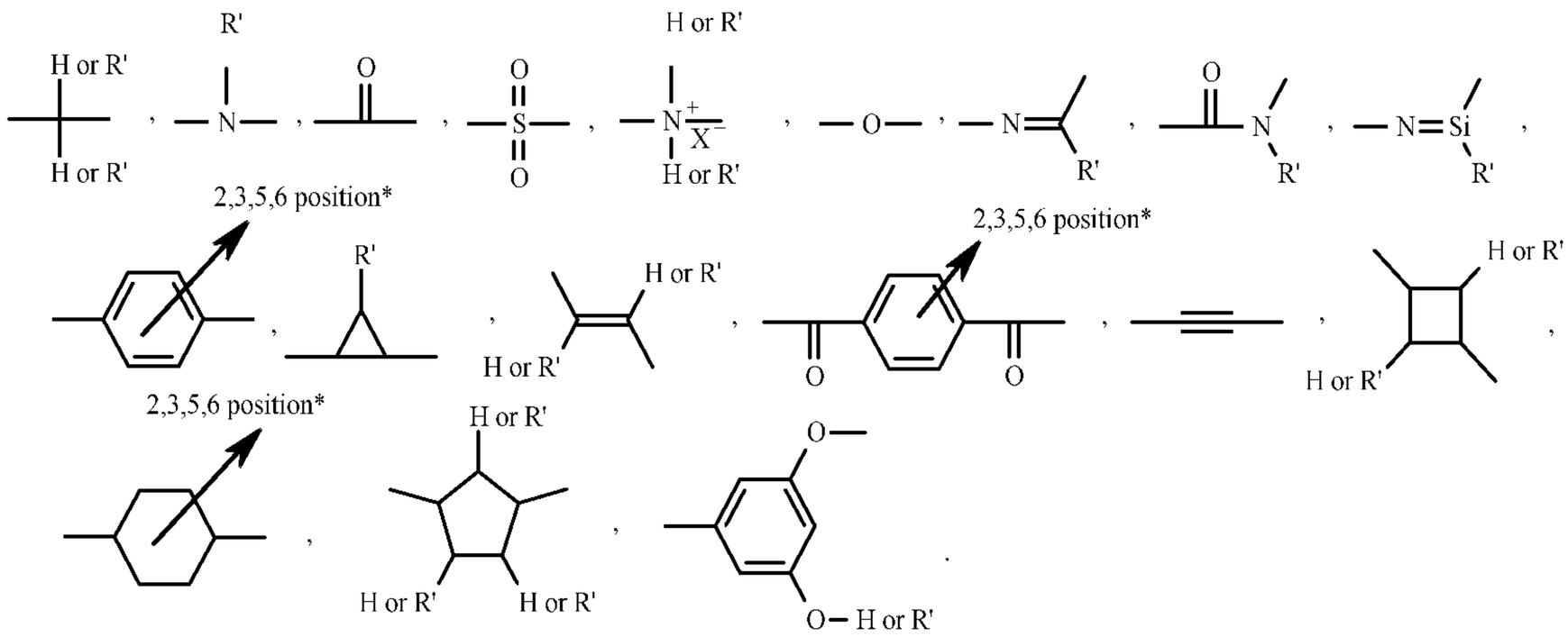
L_1 preferably has the formula:

[III] $L_1 = A_a\text{-}B_b\text{-}C_c\text{-}D_d$,

wherein: (a+b+c+d) is from 1 to 20; and A, B, C and D are independently selected from the linking groups consisting of:



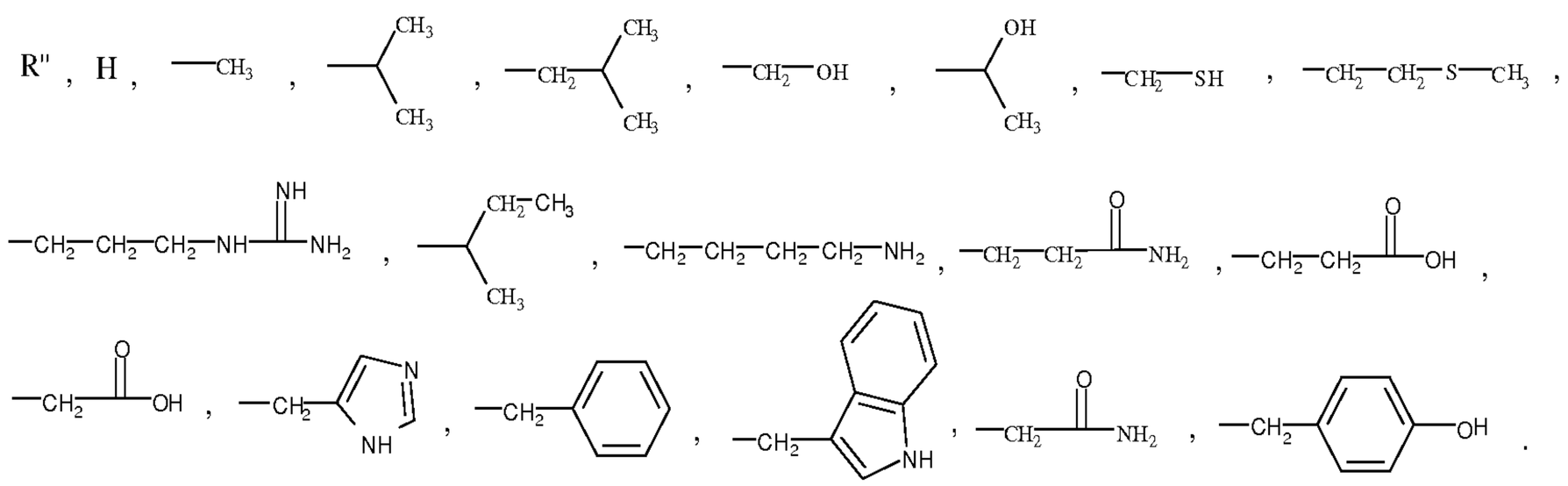
Preferably, A, B, C and D are independently selected from the linking groups consisting of:



*the arrow indicates up to 4 substitutions in the positions indicated, and X^- an anion

Preferably, L_1 is selected from C2 to C20 hydrocarbyl chains, more preferably C6 to C12, most preferably C8 to C10.

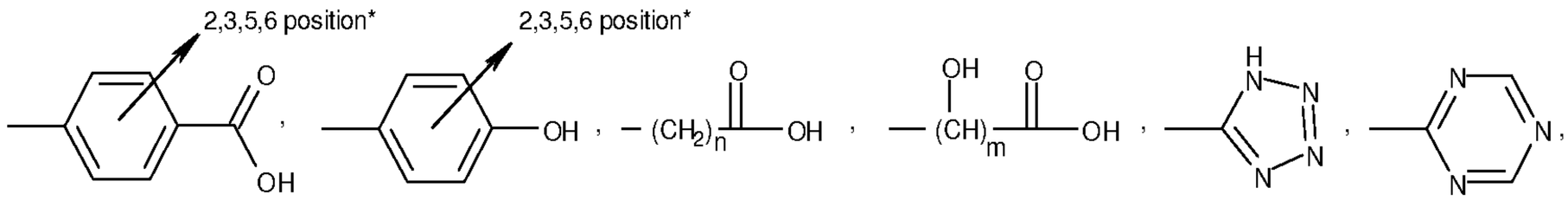
In a preferred embodiment: R_1 is R_3 or H or R', R_2 is R_4 or H or R', wherein each AA is independently selected from the group consisting of:

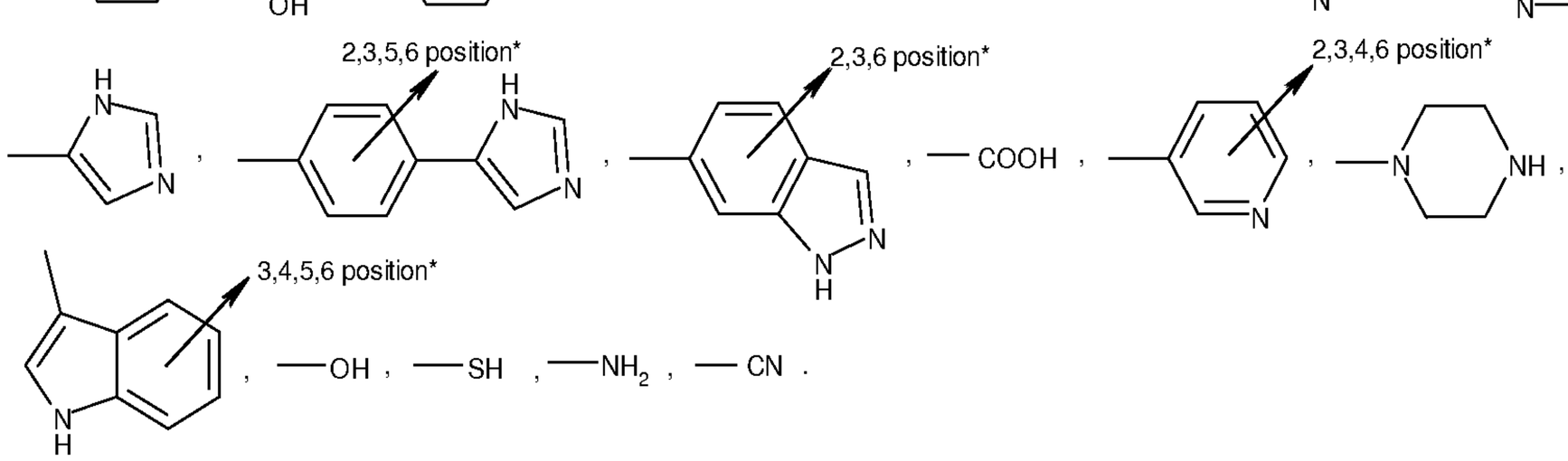


and R_3 and R_4 independently have the formula:

[IV] $(L')_o$-$(L'')_q$-R,

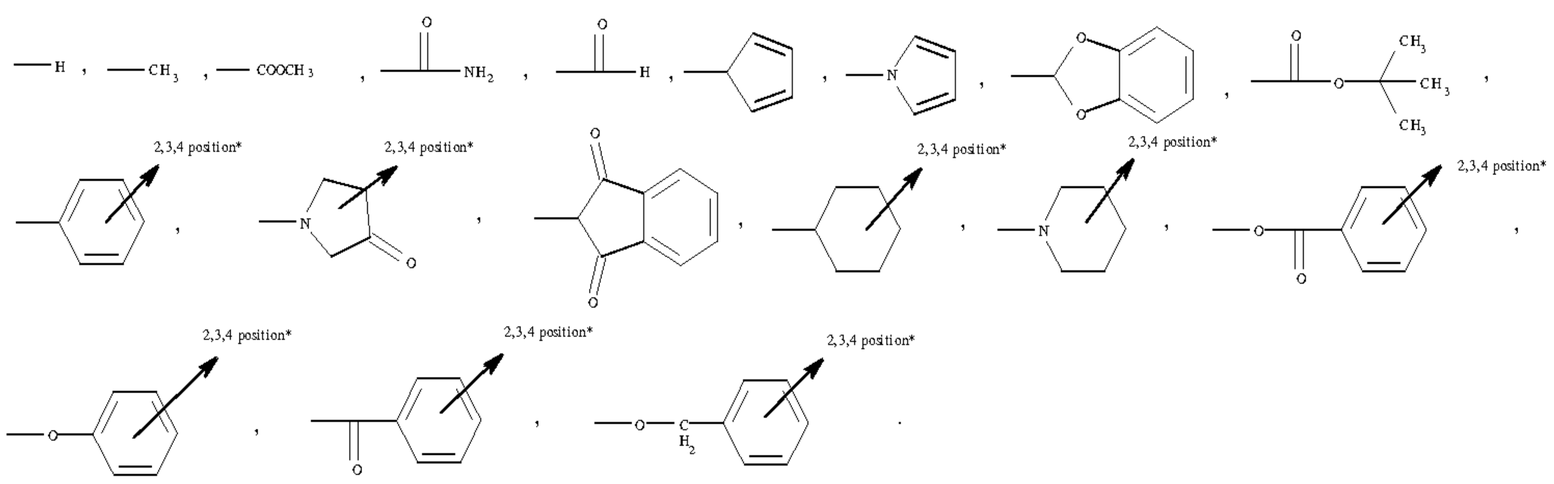
wherein: (o + q) is from 1 to 10; L' and L'' are linking groups, independently selected from the same groups as A, B, C and D in equation [III]; and R, R' and R'' are independently selected either from the pH-sensitive-groups consisting of:





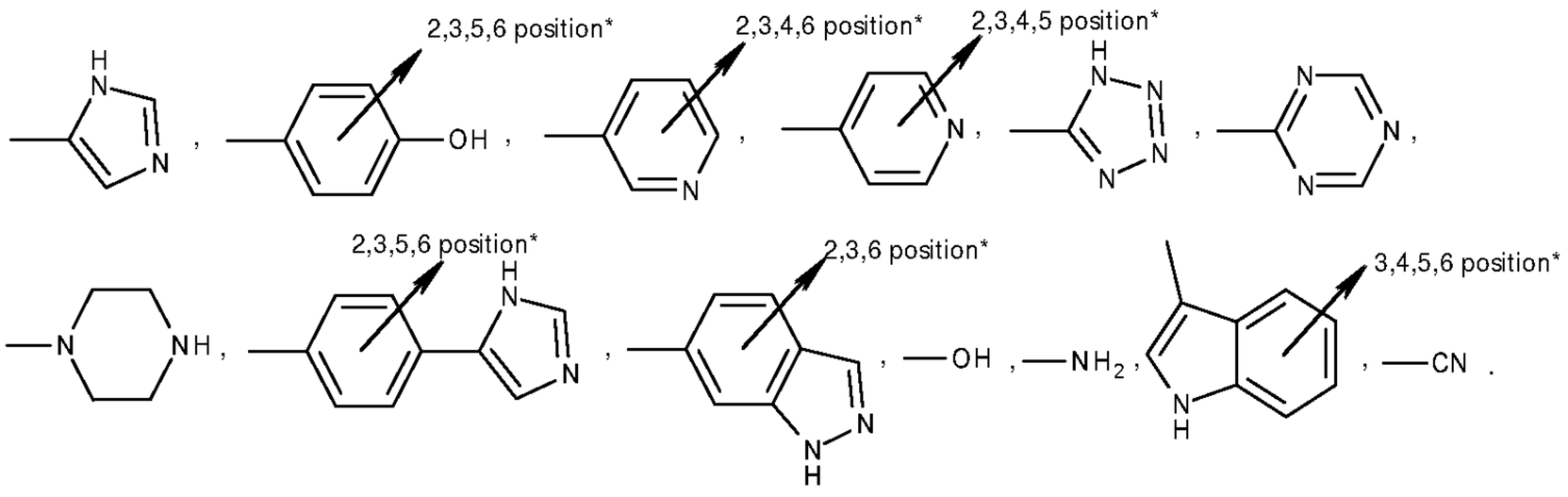
*the arrow indicates up to 4 substitutions in the positions indicated, n and m are integers from 1 to 20

or from the non-pH-sensitive groups consisting of:

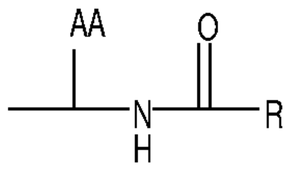


such that at least one of R, R' and R" comprises a pH-sensitive group. Preferably, R comprises the pH-sensitive group.

In other embodiments, at least some of R, R' and R" are independently selected from the group of pH-sensitive molecules consisting of:

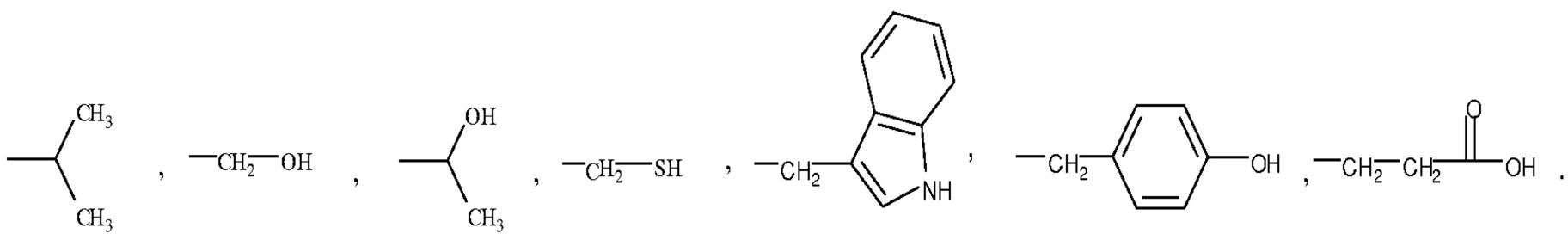


In a preferred embodiment, the pH tuneable amido gellant having structure [I] is characterized in that: L_1 is an aliphatic linking group with a backbone chain of from 2 to 20 carbon atoms, preferably $-(CH_2)_n-$ wherein n is selected from 2 to 20, and both R_1 and R_2 have the structure:

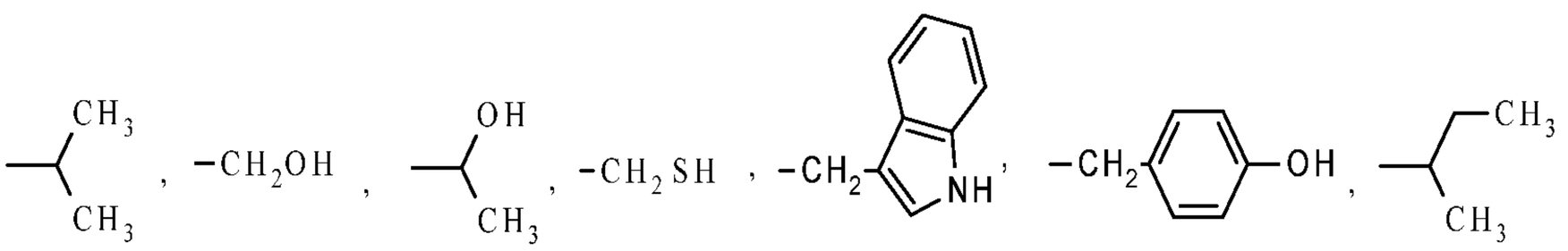


.

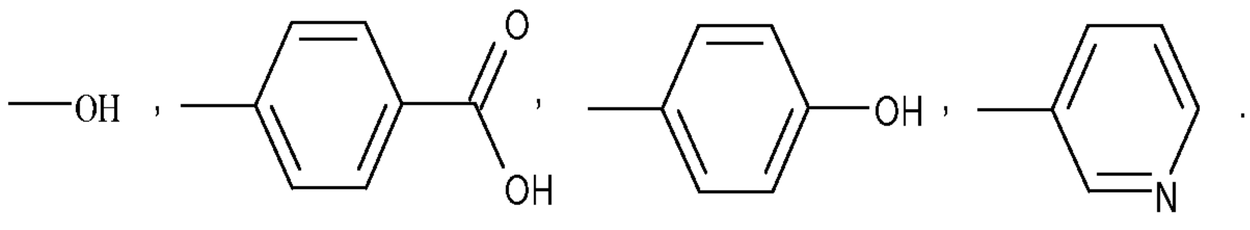
AA is preferably selected from the group consisting of:



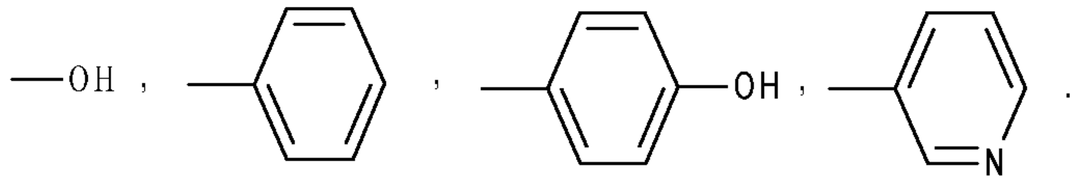
or from the group consisting of:



and R is preferably selected from the pH-sensitive groups consisting of:



or from the group:



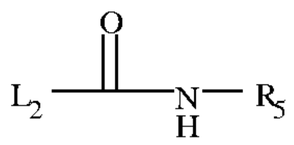
In another embodiment, two or more of L_1, L' and L" are the same group.

The pH tuneable amido gellant molecule described in formula [I] can be symmetric with respect to the L_1 entity or can be asymmetric. Without intending to be bound by theory, it is believed that symmetric pH tuneable amido gellant molecules allow for more orderly structured

networks to form, whereas compositions comprising one or more asymmetric pH tuneable amido gellant molecules can create disordered networks.

Suitable pH tuneable amido gellants having structure [I] may be selected from table 1 and table 2, and mixtures thereof. More preferably, the pH tuneable amido gellants, having structure [I], are selected from table 2, and mixtures thereof.

In another embodiment, the pH tuneable amido gellant has the structure [II]:



wherein R_5 is an aminofunctional moiety; L_2 is a backbone moiety having molecular weight from 14 to 500 g/mol; and at least one of L_2 or R_5 comprises a pH-sensitive group;

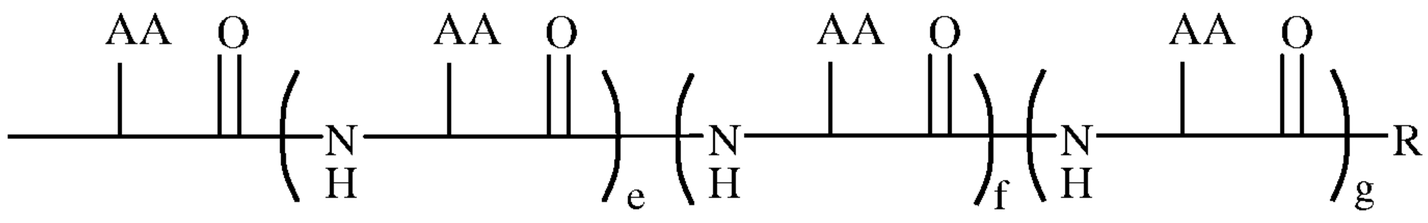
L_2 preferably has the formula:

[V] $L_2 = A_a\text{-}B_b\text{-}C_c\text{-}D_d\text{-}R'''$,

wherein: (a+b+c+d) is from 1 to 20; and R''' is either a pH-sensitive group or a non-pH-sensitive groups (selected from the same groups as R, R' and R" for structure [I]).

Preferably, L_2 is selected from C2 to C20 hydrocarbyl chains, more preferably C6 to C12, most preferably C8 to C10.

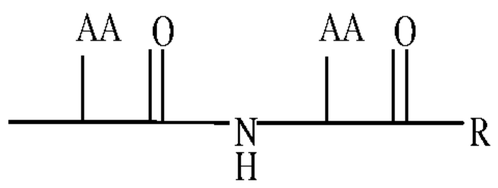
R_5 preferably has the formula:

[V] 
,

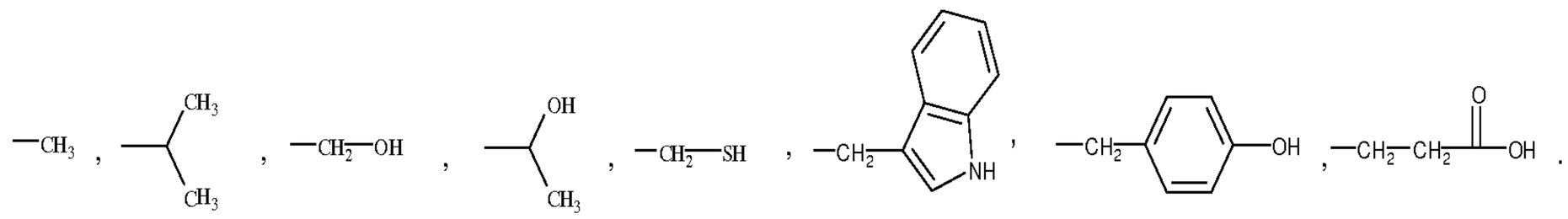
wherein: AA is independently selected from the same group of AA as for structure [I]; (e+f+g) is from 0 to 20, more preferably from 1 to 3.

At least one of AA, R or R''' comprises a pH sensitive group. Preferably, R comprises the pH sensitive group.

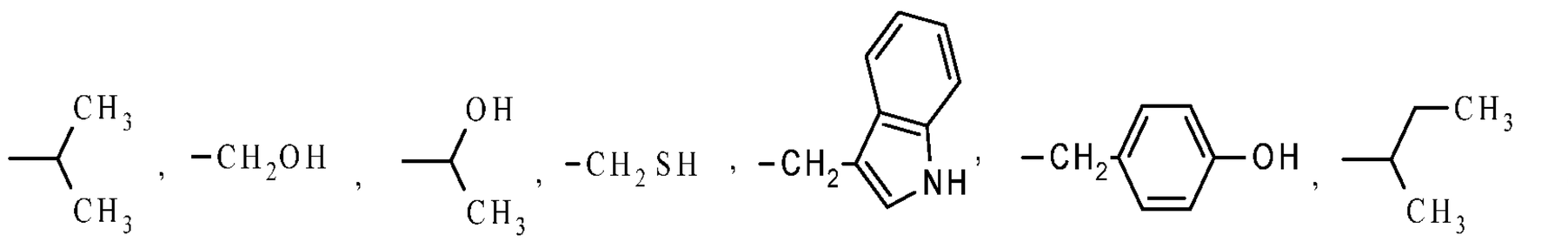
In a preferred embodiment, the pH tuneable amido gellant having structure [II] is characterized in that: L_2 is an aliphatic linking group with a backbone chain of from 2 to 20 carbon atoms, preferably $-(CH_2)_n-CH_3$ wherein n is selected from 2 to 20, and R_5 has the structure:



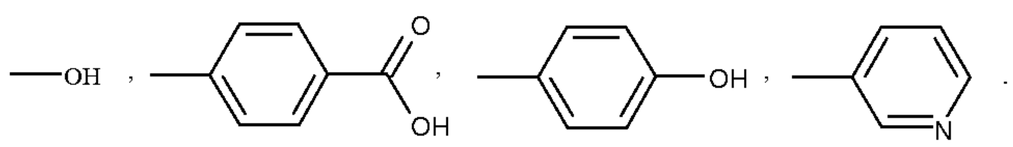
wherein: each AA is independently selected from the group consisting of:



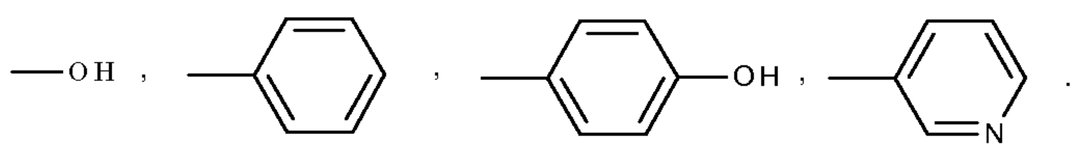
or from the group consisting of:



and R is selected from the pH-sensitive groups consisting of:



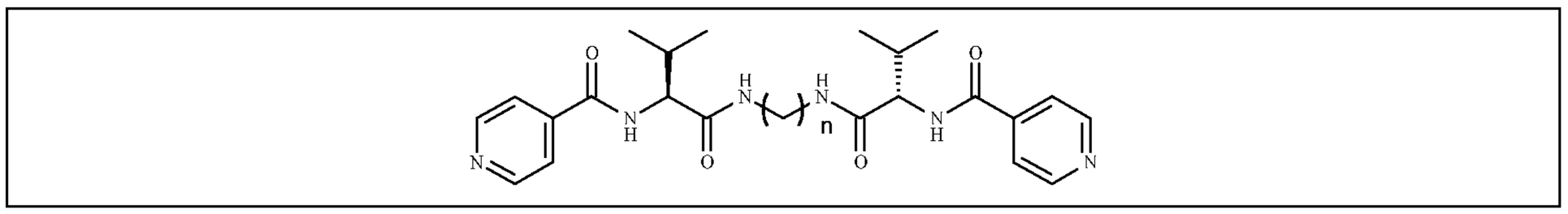
or from the group:

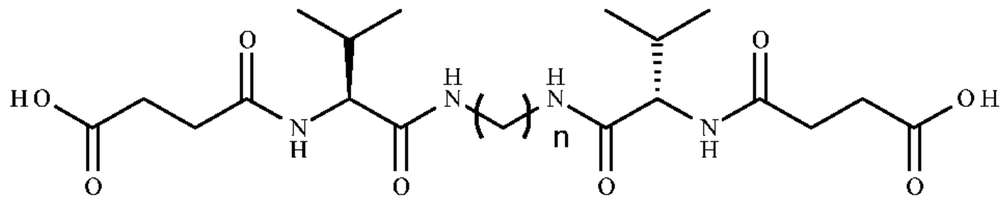
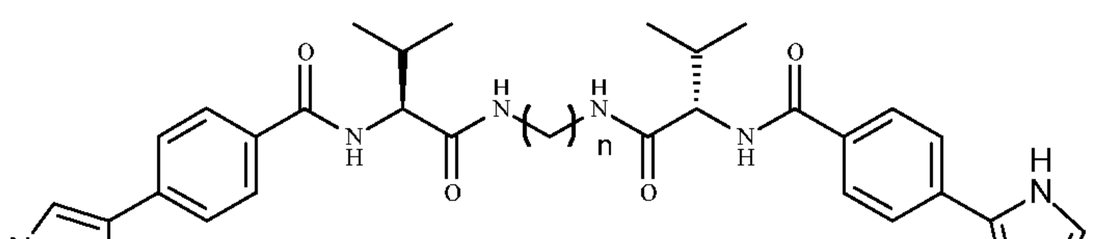


Suitable pH tuneable amido gellants having structure [II] include the structures selected from table 3, and mixtures thereof.

pH tuneable amido gellant examples of use in the present invention:

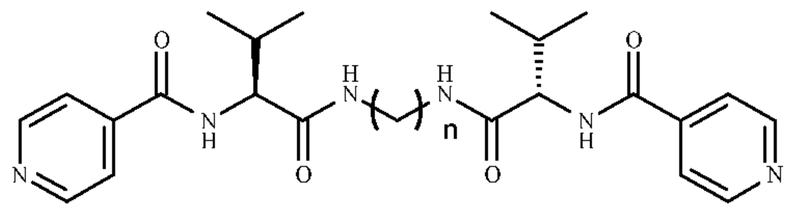
Table 1: Non-limiting examples of pH tuneable amido gellants having structure [I] of use in fluid detergent compositions of the invention:

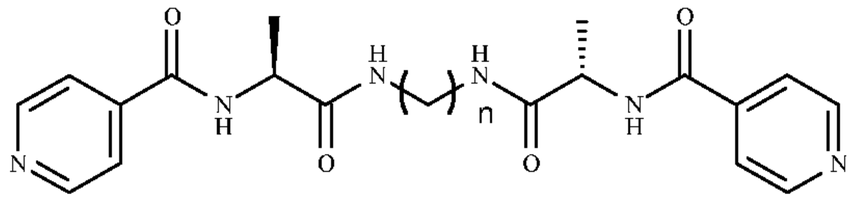
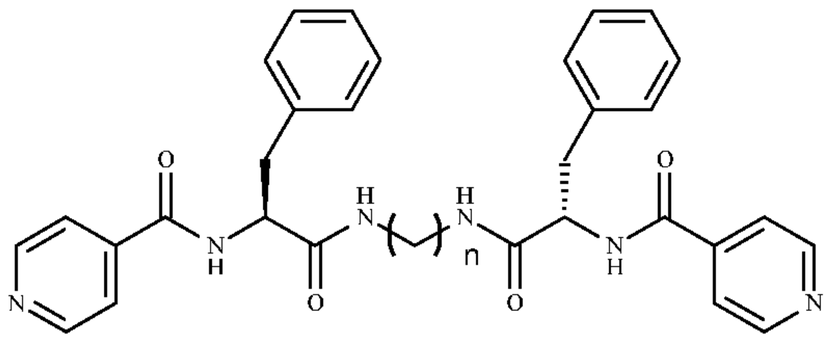


N,*N*'-(2*S*,2'*S*)-1,1'-(ethane-1,2-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide	*N*,*N*'-(2*S*,2'*S*)-1,1'-(propane-1,3-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide
N,*N*'-(2*S*,2'*S*)-1,1'-(butane-1,4-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide	*N*,*N*'-(2*S*,2'*S*)-1,1'-(pentane-1,5-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide
N,*N*'-(2*S*,2'*S*)-1,1'-(hexane-1,6-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide	*N*,*N*'-(2*S*,2'*S*)-1,1'-(heptane-1,7-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide
N,*N*'-(2*S*,2'*S*)-1,1'-(octane-1,8-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide	
	
	(6*S*,13*S*)-6,13-diisopropyl-4,7,12,15-tetraoxo-5,8,11,14-tetraazaoctadecane-1,18-dioic acid
(6*S*,14*S*')-6,14-diisopropyl-4,7,13,16-tetraoxo-5,8,12,15-tetraazanonadecane-1,19-dioic acid	(6*S*,15*S*)-6,15-diisopropyl-4,7,14,17-tetraoxo-5,8,13,16-tetraazaeicosane-1,20-dioic acid
(6*S*,16*S*)-6,16-diisopropyl-4,7,15,18-tetraoxo-5,8,14,17-tetraazaheneicosane-1,21-dioic acid	(6*S*,17*S*)-6,17-diisopropyl-4,7,16,19-tetraoxo-5,8,15,18-tetraazadocosane-1,22-dioic acid
(6*S*,18*S*)-6,18-diisopropyl-4,7,17,20-tetraoxo-5,8,16,19-tetraazatricosane-1,23-dioic acid	(6*S*,19*S*)-6,19-diisopropyl-4,7,18,21-tetraoxo-5,8,17,20-tetraazatetracosane-1,24-dioic acid
(6*S*,20*S*)-6,20-diisopropyl-4,7,19,22-tetraoxo-5,8,18,21-tetraazapentacosane-1,25-dioic acid	(6*S*,21*S*)-6,21-diisopropyl-4,7,20,23-tetraoxo-5,8,19,22-tetraazahexacosane-1,26-dioic acid
(6*S*,22*S*)-6,22-diisopropyl-4,7,21,24-tetraoxo-5,8,20,23-tetraazaheptacosane-1,27-dioic acid	(6*S*,23*S*)-6,23-diisopropyl-4,7,22,25-tetraoxo-5,8,21,24-tetraazaoctacosane-1,28-dioic acid
	

N,*N'*-(2*S*,2'*S*)-1,1'-(ethane-1,2-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)bis(4-(1*H*-imidazol-5-yl)benzamide)	*N*,*N'*-(2*S*,2'*S*)-1,1'-(propane-1,3-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)bis(4-(1*H*-imidazol-5-yl)benzamide)
N,*N'*-(2*S*,2'*S*)-1,1'-(butane-1,4-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)bis(4-(1*H*-imidazol-5-yl)benzamide)	*N*,*N'*-(2*S*,2'*S*)-1,1'-(pentane-1,5-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)bis(4-(1*H*-imidazol-5-yl)benzamide)
N,*N'*-(2*S*,2'*S*)-1,1'-(hexane-1,6-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)bis(4-(1*H*-imidazol-5-yl)benzamide)	*N*,*N'*-(2*S*,2'*S*)-1,1'-(heptane-1,7-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)bis(4-(1*H*-imidazol-5-yl)benzamide)
N,*N'*-(2*S*,2'*S*)-1,1'-(octane-1,8-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)bis(4-(1*H*-imidazol-5-yl)benzamide)	*N*,*N'*-(2*S*,2'*S*)-1,1'-(nonane-1,9-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)bis(4-(1*H*-imidazol-5-yl)benzamide)
N,*N'*-(2*S*,2'*S*)-1,1'-(decane-1,10-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)bis(4-(1*H*-imidazol-5-yl)benzamide)	*N*,*N'*-(2*S*,2'*S*)-1,1'-(undecane-1,11-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)bis(4-(1*H*-imidazol-5-yl)benzamide)
N,*N'*-(2*S*,2'*S*)-1,1'-(dodecane-1,12-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)bis(4-(1*H*-imidazol-5-yl)benzamide)	

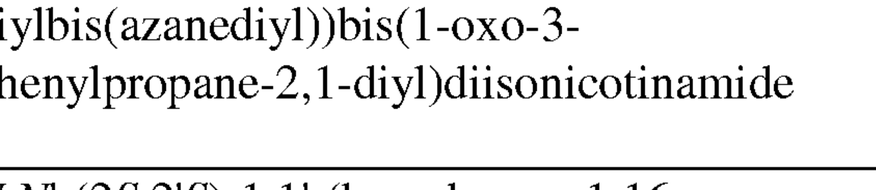
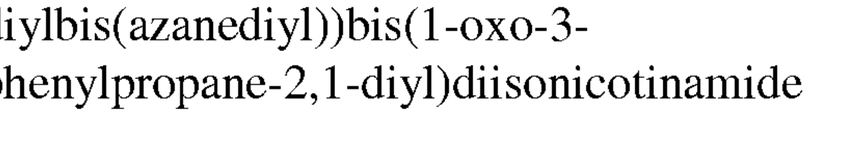
Table 2: Non-limiting examples of pH tuneable amido gellants having structure [I] of use in fluid detergent compositions of the invention:

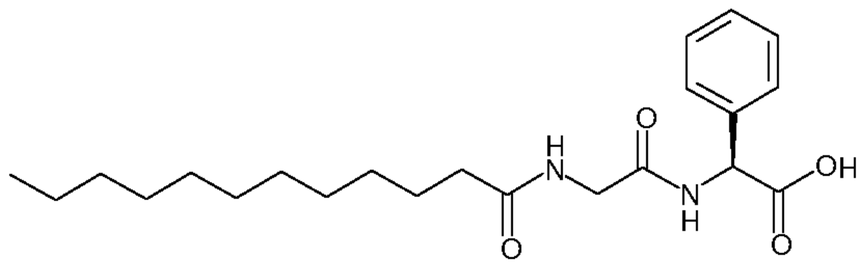
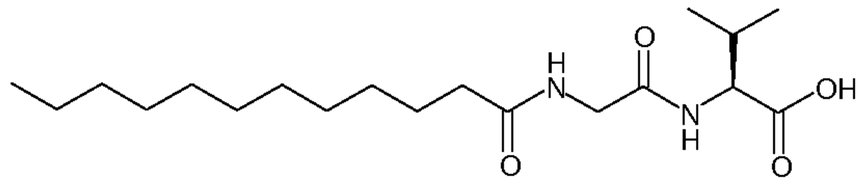
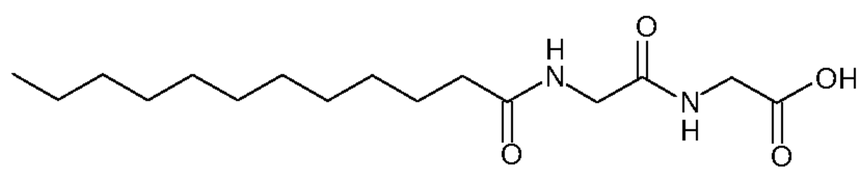
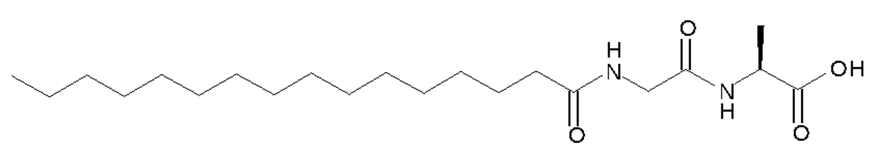
	
N,*N*'-(2*S*,2'*S*)-1,1'-(nonane-1,9-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide	*N*,*N*'-(2*S*,2'*S*)-1,1'-(decane-1,10-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide
N,*N*'-(2*S*,2'*S*)-1,1'-(undecane-1,11-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide	*N*,*N*'-(2*S*,2'*S*)-1,1'-(dodecane-1,12-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide
N,*N*'-(2*S*,2'*S*)-1,1'-(tridecane-1,13-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide	*N*,*N*'-(2*S*,2'*S*)-1,1'-(tetradecane-1,14-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide

N,*N*'-(2*S*,2'*S*)-1,1'-(hexadecane-1,16-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide	*N*,*N*'-(2*S*,2'*S*)-1,1'-(octadecane-1,18-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide
	
N,*N*'-(2*S*,2'*S*)-1,1'-(ethane-1,2-diylbis(azanediyl))bis(1-oxopropane-2,1-diyl)diisonicotinamide	*N*,*N*'-(2*S*,2'*S*)-1,1'-(propane-1,3-diylbis(azanediyl))bis(1-oxopropane-2,1-diyl)diisonicotinamide
N,*N*'-(2*S*,2'*S*)-1,1'-(butane-1,4-diylbis(azanediyl))bis(1-oxopropane-2,1-diyl)diisonicotinamide	*N*,*N*'-(2*S*,2'*S*)-1,1'-(pentane-1,5-diylbis(azanediyl))bis(1-oxopropane-2,1-diyl)diisonicotinamide
N,*N*'-(2*S*,2'*S*)-1,1'-(hexane-1,6-diylbis(azanediyl))bis(1-oxopropane-2,1-diyl)diisonicotinamide	*N*,*N*'-(2*S*,2'*S*)-1,1'-(heptane-1,7-diylbis(azanediyl))bis(1-oxopropane-2,1-diyl)diisonicotinamide
N,*N*'-(2*S*,2'*S*)-1,1'-(octane-1,8-diylbis(azanediyl))bis(1-oxopropane-2,1-diyl)diisonicotinamide	*N*,*N*'-(2*S*,2'*S*)-1,1'-(nonane-1,9-diylbis(azanediyl))bis(1-oxopropane-2,1-diyl)diisonicotinamide
N,*N*'-(2*S*,2'*S*)-1,1'-(decane-1,10-diylbis(azanediyl))bis(1-oxopropane-2,1-diyl)diisonicotinamide	*N*,*N*'-(2*S*,2'*S*)-1,1'-(undecane-1,11-diylbis(azanediyl))bis(1-oxopropane-2,1-diyl)diisonicotinamide
N,*N*'-(2*S*,2'*S*)-1,1'-(dodecane-1,12-diylbis(azanediyl))bis(1-oxopropane-2,1-diyl)diisonicotinamide	*N*,*N*'-(2*S*,2'*S*)-1,1'-(tridecane-1,13-diylbis(azanediyl))bis(1-oxopropane-2,1-diyl)diisonicotinamide
N,*N*'-(2*S*,2'*S*)-1,1'-(tetradecane-1,14-diylbis(azanediyl))bis(1-oxopropane-2,1-diyl)diisonicotinamide	*N*,*N*'-(2*S*,2'*S*)-1,1'-(hexadecane-1,16-diylbis(azanediyl))bis(1-oxopropane-2,1-diyl)diisonicotinamide
N,*N*'-(2*S*,2'*S*)-1,1'-(octadecane-1,18-diylbis(azanediyl))bis(1-oxopropane-2,1-diyl)diisonicotinamide	
	

	N,*N*'-(2*S*,2'*S*)-1,1'-(ethane-1,2-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)diisonicotinamide
N,*N*'-(2*S*,2'*S*)-1,1'-(propane-1,3-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)diisonicotinamide	*N*,*N*'-(2*S*,2'*S*)-1,1'-(butane-1,4-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)diisonicotinamide
N,*N*'-(2*S*,2'*S*)-1,1'-(pentane-1,5-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)diisonicotinamide	*N*,*N*'-(2*S*,2'*S*)-1,1'-(hexane-1,6-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)diisonicotinamide
N,*N*'-(2*S*,2'*S*)-1,1'-(heptane-1,7-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)diisonicotinamide	*N*,*N*'-(2*S*,2'*S*)-1,1'-(octane-1,8-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)diisonicotinamide
N,*N*'-(2*S*,2'*S*)-1,1'-(nonane-1,9-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)diisonicotinamide	*N*,*N*'-(2*S*,2'*S*)-1,1'-(decane-1,10-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)diisonicotinamide
N,*N*'-(2*S*,2'*S*)-1,1'-(undecane-1,11-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)diisonicotinamide	*N*,*N*'-(2*S*,2'*S*)-1,1'-(dodecane-1,12-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)diisonicotinamide
N,*N*'-(2*S*,2'*S*)-1,1'-(tridecane-1,13-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)diisonicotinamide	*N*,*N*'-(2*S*,2'*S*)-1,1'-(tetradecane-1,14-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)diisonicotinamide
N,*N*'-(2*S*,2'*S*)-1,1'-(hexadecane-1,16-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)diisonicotinamide	*N*,*N*'-(2*S*,2'*S*)-1,1'-(octadecane-1,18-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)diisonicotinamide

Table 3: Non-limiting examples of pH tuneable amido gellants having structure [I] of use in fluid detergent compositions of the invention:

(2*S*)-2-[[2-(dodecanoylamino)acetyl]amino]propanoic acid 	(2*S*)-2-[[2-[[2-(dodecanoylamino)acetyl]amino]acetyl]amino]propanoic acid 

(2*S*)-2-[[2-(dodecanoylamino)acetyl]amino]-2-phenyl-acetic acid 	(2*S*)-2-[[2-(dodecanoylamino)acetyl]amino]-3-methyl-butanoic acid 
(2*S*)-2-[[2-(dodecanoylamino)acetyl]amino]acetic acid 	(2*S*)-2-[[2-(hexadecanoylamino)acetyl]amino]propanoic acid 

In certain embodiments of both types of pH tuneable amido gellant structures, AA comprises at least one of: Alanine, ß-Alanine and substituted Alanines; Linear Amino-Alkyl Carboxylic Acid; Cyclic Amino-Alkyl Carboxylic Acid; Aminobenzoic Acid Derivatives; Aminobutyric Acid Derivatives; Arginine and Homologues; Asparagine; Aspartic Acid; p-Benzoyl-Phenylalanine; Biphenylalanine; Citrulline; Cyclopropylalanine; Cyclopentylalanine; Cyclohexylalanine; Cysteine, Cystine and Derivatives; Diaminobutyric Acid Derivatives; Diaminopropionic Acid; Glutamic Acid Derivatives; Glutamine; Glycine; Substituted Glycines; Histidine; Homoserine; Indole Derivatives; Isoleucine; Leucine and Derivatives; Lysine; Methionine; Naphthylalanine; Norleucine; Norvaline; Ornithine; Phenylalanine; Ring-Substituted Phenylalanines; Phenylglycine; Pipecolic Acid, Nipecotic Acid and Isonipecotic Acid; Proline; Hydroxyproline; Thiazolidine; Pyridylalanine; Serine; Statine and Analogues; Threonine; Tetrahydronorharman-3-carboxylic Acid; 1,2,3,4-Tetrahydroisoquinoline; Tryptophane; Tyrosine; Valine; and combinations thereof.

The pH tuneable amido gellant molecule may also comprise protective groups, preferably from 1 to 2 protective groups, preferably two protective groups. Examples of suitable protective groups are provided in "Protecting Groups", P.J. Kocienski, ISBN 313 135601 4, Georg Thieme Verlag, Stutgart; and "Protective Groups in Organic Chemistry", T.W. Greene, P.G.M. Wuts, ISBN 0-471-62301-6, John Wiley& Sons, Inc, New York.

The pH tuneable amido gellant preferably has a minimum gelling concentration (MGC) of from 0.1 to 100 mg/mL in the fluid detergent composition, at the target pH of the composition, preferably from 0.1 to 25 mg/mL, more preferred from 0.5 to 10mg/mL in accordance with the MGC Test Method. The MGC as used herein can be represented as mg/ml or as a wt %, where wt% is calculated as the MGC in mg/ml divided by 10. In one embodiment, when measured in the fluid detergent composition, the MGC is from 0.1 to 100 mg/mL, preferably from 0.1 to 25 mg/mL of said pH tuneable amido gellant, more preferably from 0.5 to 10 mg/mL, or at least 0.1 mg/mL, at least 0.3 mg/mL, at least 0.5 mg/mL, at least 1.0 mg/mL, at least 2.0 mg/mL, at least 5.0 mg/mL of pH tuneable amido gellant. While the invention includes fluid detergent compositions having a pH tuneable amido gellant concentration either above or below the MGC, the pH tuneable amido gellants of the invention result in particularly useful rheologies below the MGC.

2. Secondary External Structurants

In one embodiment, the pH tuneable amido gellant is combined with from 0.01 to 5% by weight of one or more additional external structurants. Without being limited by theory, it is believed that the use of an additional external structurant permits improved control of the time-dependent gelling. For example, while the pH tuneable amido gellant provides ultimately superior gelling, other external structurants may provide a temporary gel structure while the pH tuneable amido gellant is still undergoing gelling. Non-limiting examples of suitable secondary structurants are:

(i) Di-benzylidene Polyol Acetal Derivative: The fluid detergent composition may comprise from 0.01% to 1% by weight of a dibenzylidene polyol acetal derivative (DBPA), preferably from 0.05% to 0.8%, more preferably from 0.1% to 0.6%, most preferably from 0.3% to 0.5%. In one embodiment, the DBPA derivative may comprise a dibenzylidene sorbitol acetal derivative (DBS).

(ii) Bacterial Cellulose: The fluid detergent composition may also comprise from 0.005% to 1.0% by weight of a bacterial cellulose network. The term "bacterial cellulose" encompasses any type of cellulose produced via fermentation of a bacteria of the genus *Acetobacter* such as C*ELLULON® by* CPKelco U.S. and includes materials referred to popularly as microfibrillated cellulose, reticulated bacterial cellulose, and the like.

(iii) Coated Bacterial Cellulose: In one embodiment, the bacterial cellulose is at least partially coated with a polymeric thickener, for instance as prepared in accordance with the methods disclosed in US 2007/0027108 paragraphs 8 to 19. In one embodiment the at least partially coated bacterial cellulose comprises from 0.1% to 5%, preferably from 0.5% to 3.0 %, by weight of bacterial cellulose; and from 10% to 90% by weight of the polymeric thickener. Suitable bacterial cellulose include the bacterial cellulose described above and suitable polymeric thickeners include: carboxymethylcellulose, cationic hydroxymethylcellulose, and mixtures thereof.

(iv) Non-Polymeric Crystalline Hydroxyl-Functional Materials: In a preferred embodiment, the composition further comprises from 0.01 to 1% by weight of the composition of a non-polymeric crystalline, hydroxyl functional structurant. Such non-polymeric crystalline, hydroxyl functional structurants generally comprise a crystallizable glyceride which can be pre-emulsified to aid dispersion into the final fluid detergent composition. Preferred crystallizable glycerides include hydrogenated castor oil or "HCO" or derivatives thereof, provided that it is capable of crystallizing in the liquid detergent composition.

(v) Polymeric Structuring Agents: Fluid detergent compositions of the present invention may comprise from 0.01 to 5% by weight of a naturally derived and/or synthetic polymeric structurant. Examples of naturally derived polymeric structurants of use in the present invention include: hydroxyethyl cellulose, hydrophobically modified hydroxyethyl cellulose, carboxymethyl cellulose, polysaccharide derivatives and mixtures thereof. Examples of synthetic polymeric structurants of use in the present invention include: polycarboxylates, polyacrylates, hydrophobically modified ethoxylated urethanes, hydrophobically modified non-ionic polyols and mixtures thereof. In another preferred embodiment, the polyacrylate is a copolymer of unsaturated mono- or di-carbonic acid and C1-C30 alkyl ester of the (meth)acrylic acid.

<u>Water and/or non-aminofunctional organic solvent:</u>

The fluid detergent composition may be dilute or concentrated aqueous liquids. Alternatively, the fluid detergent composition may be almost entirely non-aqueous, and comprising a non-aminofunctional organic solvent. Such fluid detergent compositions may comprise very little water, for instance, that may be introduced with other raw materials. Preferably, the fluid detergent composition comprises from 1% to 95 % by weight of water and/or non-aminofunctional organic solvent. For concentrated detergents, the composition

comprises preferably from 5% to 70%, more preferably from 10% to 50%, most preferably from 15% to 45% by weight, water and/or non-aminofunctional organic solvent.

As used herein, "non-aminofunctional organic solvent" refers to any organic solvent which contains no amino functional groups. Preferred non-aminofunctional organic solvents include monohydric alcohols, dihydric alcohols, polyhydric alcohols, glycerol, glycols, polyalkylene glycols such as polyethylene glycol, and mixtures thereof. Highly preferred are mixtures of solvents, especially mixtures of two or more of the following: lower aliphatic alcohols such as ethanol, propanol, butanol, isopropanol; diols such as 1,2-propanediol or 1,3-propanediol; and glycerol. Also preferred are propanediol and mixtures thereof with diethylene glycol where the mixture contains no methanol or ethanol. Thus embodiments of fluid detergent compositions of the present invention may include embodiments in which propanediols are used but methanol and ethanol are not used.

Preferable non-aminofunctional organic solvents are liquid at ambient temperature and pressure (i.e. 21°C and 1 atmosphere), and comprise carbon, hydrogen and oxygen.

Adjuncts ingredients:

The fluid detergent composition of the present invention may also include conventional detergent ingredients selected from the group consisting of: cationic surfactants, amphoteric and/or zwitterionic surfactants, non-aminofunctional organic solvents, enzymes, enzyme stabilizers, amphiphilic alkoxylated grease cleaning polymers, clay soil cleaning polymers, soil release polymers, soil suspending polymers, bleaching systems, optical brighteners, hueing dyes, particulate material, perfume and other odour control agents, hydrotropes, suds suppressors, fabric care benefit agents, pH adjusting agents, dye transfer inhibiting agents, preservatives, non-fabric substantive dyes and mixtures thereof. Some of the optional ingredients which can be used are described in greater detail as follows:

1. Additional Surfactants

The fluid detergent compositions of the present invention may comprise additional surfactant selected from the group consisting: anionic, cationic, nonionic, amphoteric and/or zwitterionic surfactants and mixtures thereof.

Cationic surfactants: Suitable cationic surfactants can be water-soluble, water-dispersable or water-insoluble. Such cationic surfactants have at least one quaternized nitrogen and at least one long-chain hydrocarbyl group. Compounds comprising two, three or even four long-chain hydrocarbyl groups are also included. Examples include alkyltrimethylammonium

salts, such as C12 alkyltrimethylammonium chloride, or their hydroxyalkyl substituted analogs. Compositions known in the art may comprise, for example, 1% or more of cationic surfactants.

Amphoteric and/or zwitterionic surfactants: Suitable amphoteric or zwitterionic detersive surfactants of use in the fluid detergent compositions of the present invention include those which are known for use in hair care or other personal care cleansing. Non-limiting examples of suitable zwitterionic or amphoteric surfactants are described in U.S. Pat. Nos. 5,104,646 (Bolich Jr. et al.), 5,106,609 (Bolich Jr. et al.).

Amphoteric detersive surfactants suitable for use in the composition include those surfactants broadly described as derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical can be straight or branched chain and wherein one of the aliphatic substituents contains from 8 to 18 carbon atoms and one contains an anionic group such as carboxy, sulfonate, sulfate, phosphate, or phosphonate. Suitable amphoteric detersive surfactants for use in the present invention include, but are not limited to: cocoamphoacetate, cocoamphodiacetate, lauroamphoacetate, lauroamphodiacetate, and mixtures thereof.

Zwitterionic detersive surfactants suitable for use in the compositions are well known in the art, and include those surfactants broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight or branched chain, and wherein one of the aliphatic substituents contains from 8 to 18 carbon atoms and one contains an anionic group such as carboxy, sulfonate, sulfate, phosphate or phosphonate. Zwitterionics such as betaines are suitable for this invention.

Furthermore, amine oxide surfactants having the formula: $R(EO)_x(PO)_y(BO)_zN(O)(CH_2R')_2.qH_2O$ (I) are also useful in compositions of the present invention. R is a relatively long-chain hydrocarbyl moiety which can be saturated or unsaturated, linear or branched, and can contain from 8 to 20, preferably from 10 to 16 carbon atoms, and is more preferably C12-C16 primary alkyl. R' is a short-chain moiety preferably selected from hydrogen, methyl and $-CH_2OH$. When x+y+z is different from 0, EO is ethyleneoxy, PO is propyleneneoxy and BO is butyleneoxy. Amine oxide surfactants are illustrated by C12-C14 alkyldimethyl amine oxide.

Non-limiting examples of other anionic, zwitterionic, amphoteric or optional additional surfactants suitable for use in the compositions are described in McCutcheon's, Emulsifiers and

Detergents, 1989 Annual, published by M. C. Publishing Co., and U.S. Pat. Nos. 3,929,678, 2,658,072; 2,438,091; 2,528,378.

2. Enzymes

The fluid detergent compositions of the present invention may comprise from 0.0001 % to 8 % by weight of a detersive enzyme which provides cleaning performance and/or fabric care benefits. Such compositions have a neat pH of from 6 to 10.5. Suitable enzymes include proteases, amylases, cellulases, lipases, xylogucanases, pectate lyases, mannanases, bleaching enzymes, cutinases, and mixtures thereof. A preferred enzyme combination comprises a cocktail of conventional detersive enzymes such as lipase, protease, cellulase and amylase. Detersive enzymes are described in greater detail in U.S. Patent No. 6,579,839.

For the enzymes, accession numbers or IDs shown in parentheses refer to the entry numbers in the databases Genbank, EMBL and Swiss-Prot. For any mutations standard 1-letter amino acid codes are used with a * representing a deletion. Accession numbers prefixed with DSM refer to microorgansims deposited at Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH, Mascheroder Weg 1b, 38124 Brunswick (DSMZ).

Protease: The composition may comprise a protease. Suitable proteases include metalloproteases and/or serine proteases, including neutral or alkaline microbial serine proteases, such as subtilisins (EC 3.4.21.62). Suitable proteases include those of animal, vegetable or microbial origin. In one aspect, such suitable protease may be of microbial origin. The suitable proteases include chemically or genetically modified mutants of the aforementioned suitable proteases. In one aspect, the suitable protease may be a serine protease, such as an alkaline microbial protease or/and a trypsin-type protease. Examples of suitable neutral or alkaline proteases include:

(a) subtilisins (EC 3.4.21.62), including those derived from *Bacillus*, such as *Bacillus lentus, Bacillus alkalophilus* (P27963, ELYA_BACAO) , *Bacillus subtilis, Bacillus amyloliquefaciens* (P00782, SUBT_BACAM), *Bacillus pumilus (P07518) and Bacillus gibsonii* (DSM14391).

(b) trypsin-type or chymotrypsin-type proteases, such as trypsin (e.g. of porcine or bovine origin), including the Fusarium protease and the chymotrypsin proteases derived from *Cellumonas* (A2RQE2).

(c) metalloproteases, including those derived from *Bacillus amyloliquefaciens* (P06832,

NPRE_BACAM).

Preferred proteases include those derived from *Bacillus gibsonii* or *Bacillus Lentus* such as subtilisin *309* (P29600) and/or DSM 5483 (P29599).

Suitable commercially available protease enzymes include: those sold under the trade names Alcalase®, Savinase®, Primase®, Durazym®, Polarzyme®, Kannase®, Liquanase®, Liquanase Ultra®, Savinase Ultra®, Ovozyme®, Neutrase®, Everlase® and Esperase® by Novozymes A/S (Denmark); those sold under the tradename Maxatase®, Maxacal®, Maxapem®, Properase®, Purafect®, Purafect Prime®, Purafect Ox®, FN3® , FN4®, Excellase® and Purafect OXP® by Genencor International; those sold under the tradename Opticlean® and Optimase® by Solvay Enzymes; those available from Henkel/Kemira, namely BLAP (P29599 having the following mutations S99D + S101 R + S103A + V104I + G159S), and variants thereof including BLAP R (BLAP with S3T + V4I + V199M + V205I + L217D), BLAP X (BLAP with S3T + V4I + V205I) and BLAP F49 (BLAP with S3T + V4I + A194P + V199M + V205I + L217D) all from Henkel/Kemira; and KAP (Bacillus alkalophilus subtilisin with mutations A230V + S256G + S259N) from Kao.

Since certain pH tuneable amido-gellants may be hydrolyzed by protease enzymes, it is preferred that the protease enzyme is inhibited, such as through the use of a suitable enzyme stabilizer, unless the protease enzyme is encapsulated.

Amylase: Suitable amylases are alpha-amylases, including those of bacterial or fungal origin. Chemically or genetically modified mutants (variants) are included. A preferred alkaline alpha-amylase is derived from a strain of *Bacillus*, such as *Bacillus licheniformis*, *Bacillus amyloliquefaciens*, *Bacillus stearothermophilus*, *Bacillus subtilis*, or other *Bacillus sp.*, such as *Bacillus sp*. NCIB 12289, NCIB 12512, NCIB 12513, sp 707, DSM 9375, DSM 12368, DSMZ no. 12649, KSM AP1378, KSM K36 or KSM K38. Preferred amylases include:

(a) alpha-amylase derived from *Bacillus licheniformis* (P06278, AMY_BACLI), and variants thereof, especially the variants with substitutions in one or more of the following positions: 15, 23, 105, 106, 124, 128, 133, 154, 156, 181, 188, 190, 197, 202, 208, 209, 243, 264, 304, 305, 391, 408, and 444.

(b) AA560 amylase (CBU30457, HD066534) and variants thereof, especially the variants with one or more substitutions in the following positions: 26, 30, 33, 82, 37, 106, 118, 128, 133, 149, 150, 160, 178, 182, 186, 193, 203, 214, 231, 256, 257, 258, 269, 270, 272, 283, 295, 296, 298, 299, 303, 304, 305, 311, 314, 315, 318, 319, 339, 345, 361, 378, 383, 419, 421, 437, 441,

444, 445, 446, 447, 450, 461, 471, 482, 484, preferably that also contain the deletions of D183* and G184*.

(c) variants exhibiting at least 90% identity with the wild-type enzyme from *Bacillus SP722* (CBU30453, HD066526), especially variants with deletions in the 183 and 184 positions.

Suitable commercially available alpha-amylases are Duramyl®, Liquezyme® Termamyl®, Termamyl Ultra®, Natalase®, Supramyl®, Stainzyme®, Stainzyme Plus®, Fungamyl® and BAN® (Novozymes A/S), Bioamylase® and variants thereof (Biocon India Ltd.), Kemzym® AT 9000 (Biozym Ges. m.b.H, Austria), Rapidase® , Purastar®, Optisize HT Plus®, Enzysize®, Powerase® and Purastar Oxam®, Maxamyl® (Genencor International Inc.) and KAM® (KAO, Japan). Preferred amylases are Natalase®, Stainzyme® and Stainzyme Plus®.

Cellulase: The composition may comprise a cellulase. Suitable cellulases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Suitable cellulases include cellulases from the genera *Bacillus, Pseudomonas, Humicola, Fusarium, Thielavia, Acremonium*, e.g., the fungal cellulases produced from *Humicola insolens, Myceliophthora thermophila* and *Fusarium oxysporum.*

Commercially available cellulases include Celluzyme®, and Carezyme® (Novozymes A/S), Clazinase®, and Puradax HA® (Genencor International Inc.), and KAC-500(B)® (Kao Corporation).

In one aspect, the cellulase can include microbial-derived endoglucanases exhibiting endo-beta-1,4-glucanase activity (E.C. 3.2.1.4), including a bacterial polypeptide endogenous to a member of the genus *Bacillus* which has a sequence of at least 90%, 94%, 97% and even 99% identity to the amino acid sequence SEQ ID NO:2 in US 7,141,403) and mixtures thereof. Suitable endoglucanases are sold under the tradenames Celluclean® and Whitezyme® (Novozymes A/S, Bagsvaerd, Denmark).

Preferably, the composition comprises a cleaning cellulase belonging to Glycosyl Hydrolase family 45 having a molecular weight of from 17kDa to 30 kDa, for example the endoglucanases sold under the tradename Biotouch® NCD, DCC and DCL (AB Enzymes, Darmstadt, Germany).

Highly preferred cellulases also exhibit xyloglucanase activity, such as Whitezyme®.

Lipase: The composition may comprise a lipase. Suitable lipases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of

useful lipases include lipases from *Humicola* (synonym *Thermomyces*), e.g., from *H. lanuginosa* (*T. lanuginosus*), or from *H. insolens*, a Pseudomonas lipase, e.g., from *P. alcaligenes* or *P. pseudoalcaligenes*, *P. cepacia*, *P. stutzeri*, *P. fluorescens, Pseudomonas* sp. strain SD 705, *P. wisconsinensis*, a *Bacillus* lipase, e.g., from *B. subtilis*, *B. stearothermophilus* or *B. pumilus*.

The lipase may be a "first cycle lipase", preferably a variant of the wild-type lipase from *Thermomyces lanuginosus* comprising T231R and N233R mutations. The wild-type sequence is the 269 amino acids (amino acids 23 – 291) of the Swissprot accession number Swiss-Prot O59952 (derived from *Thermomyces lanuginosus* (*Humicola lanuginosa*)). Preferred lipases would include those sold under the tradenames Lipex®, Lipolex® and Lipoclean® by Novozymes, Bagsvaerd, Denmark.

Preferably, the composition comprises a variant of *Thermomyces lanuginosa* (O59952) lipase having >90% identity with the wild type amino acid and comprising substitution(s) at T231 and/or N233, preferably T231R and/or N233R.

In another aspect, the composition comprises a variant of *Thermomyces lanuginosa* (O59952) lipase having >90% identity with the wild type amino acid and comprising substitution(s):

(a) S58A +V60S + I83T +A150G +L227G +T231R +N233R +I255A +P256K;

(b) S58A +V60S + I86V +A150G +L227G +T231R +N233R +I255A +P256K;

(c) S58A +V60S + I86V +T143S +A150G +L227G +T231R +N233R +I255A +P256K;

(d) S58A +V60S + I86V +T143S +A150G +G163K +S216P +L227G +T231R +N233R +I255A +P256K;

(e) E1* +S58A +V60S + I86V +T143S +A150G +L227G +T231R +N233R +I255A +P256K;

(f) S58A +V60S + I86V +K98I +E99K +T143S +A150G +L227G +T231R +N233R +I255A +P256K;

(g) E1N +S58A +V60S + I86V +K98I +E99K +T143S +A150G +L227G +T231R +N233R +I255A +P256K +L259F;

(h) S58A +V60S + I86V +K98I +E99K +D102A +T143S +A150G +L227G +T231R +N233R +I255A +P256K;

(i) N33Q +S58A +V60S + I86V +T143S +A150G +L227G +T231R +N233R +I255A +P256K;

(j) E1* +S58A +V60S + I86V +K98I +E99K +T143S +A150G +L227G +T231R +N233R

+I255A +P256K;

(k) E1N +S58A +V60S + I86V +K98I +E99K +T143S +A150G +S216P +L227G +T231R +N233R +I255A +P256K;

(l) D27N +S58A +V60S + I86V +G91N +N94R +Dl U N +T143S +A150G +L227G +T231R +N233R +I255A +P256K;

(m) E1N +S58A +V60S + I86V +K98I +E99K +T143S +A150G +E210A +S216P +L227G +T231R +N233R +1255A +P256K;

(n) A150G +E210V +T231R +N233R +I255A +P256K; and

(o) I202L +E210G +T231R +N233R +I255A +P256K.

When lipase is present, it is preferred that the pH tuneable amido-gellant comprises no ester-bonds, since some di-amido gellants that comprise ester-bonds may be hydrolyzed by the lipase enzyme, unless the lipase enzyme is encapsulated.

Xyloglucanase: Suitable xyloglucanase enzymes have enzymatic activity towards both xyloglucan and amorphous cellulose substrates, wherein the enzyme is a glycosyl hydrolase (GH) is selected from GH families 5, 12, 44 or 74. Preferably, the glycosyl hydrolase is selected from GH family 44. Suitable glycosyl hydrolases from GH family 44 are the XYG1006 glycosyl hydrolase from *Paenibacillus polyxyma* (ATCC 832) and variants thereof.

Pectate lyase: Suitable pectate lyases are either wild-types or variants of Bacillus-derived pectate lyases (CAF05441, AAU25568) sold under the tradenames Pectawash®, Pectaway® and X-Pect® (from Novozymes A/S, Bagsvaerd, Denmark).

Mannanase: Suitable mannanases are sold under the tradenames Mannaway® (from Novozymes A/S, Bagsvaerd, Denmark), and Purabrite® (Genencor International Inc., Palo Alto, California).

Bleaching enzyme: Suitable bleach enzymes include oxidoreductases, for example oxidases such as glucose, choline or carbohydrate oxidases, oxygenases, catalases, peroxidases, like halo-, chloro-, bromo-, lignin-, glucose- or manganese-peroxidases, dioxygenases or laccases (phenoloxidases, polyphenoloxidases). Suitable commercial products are sold under the Guardzyme® and Denilite® ranges from Novozymes. Advantageously, additional, preferably organic, particularly preferably aromatic compounds are incorporated with the bleaching enzyme; these compounds interact with the bleaching enzyme to enhance the activity of the oxidoreductase (enhancer) or to facilitate the electron flow (mediator) between the oxidizing enzyme and the stain typically over strongly different redox potentials.

Other suitable bleaching enzymes include perhydrolases, which catalyse the formation of peracids from an ester substrate and peroxygen source. Suitable perhydrolases include variants of the Mycobacterium smegmatis perhydrolase, variants of so-called CE-7 perhydrolases, and variants of wild-type subtilisin Carlsberg possessing perhydrolase activity.

Cutinase: Suitable cutinases are defined by E.C. Class 3.1.1.73, preferably displaying at least 90%, or 95%, or most preferably at least 98% identity with a wild-type derived from one of *Fusarium solani*, *Pseudomonas Mendocina* or *Humicola Insolens*.

Identity: The relativity between two amino acid sequences is described by the parameter "identity". For purposes of the present invention, the alignment of two amino acid sequences is determined by using the Needle program from the EMBOSS package (http://emboss.org) version 2.8.0. The Needle program implements the global alignment algorithm described in Needleman, S. B. and Wunsch, C. D. (1970) J. Mol. Biol. 48, 443-453. The substitution matrix used is BLOSUM62, gap opening penalty is 10, and gap extension penalty is 0.5.

Enzymes, particularly protease and lipase, may be encapsulated. Suitable encapsulated enzymes may be prepared by methods such as:

(i) interfacial condensation polymerization, including capsules formed by the reaction of acid chlorides with compounds containing at least two amine groups and polycondensation reaction of formaldehyde with melamine. Examples of such methods are disclosed in USP 4,906,396, USP 6,221,829, USP 6,359,031, US 6,242,405 and WO 07/100501 A2.

(ii) sol-gel processes including capsules made by reaction of aminoalkylsilane precursors and aminoalkyl-trialkoxysilane, and one or more alkoxysilane precursors, examples of which are disclosed in WO 05/028603 A1 and WO 05/028604 A1; and

(iii) polyectrolyte precipitation, including capsules formed by reaction of chitosan and alginate or using biopolymer gels such as gellan. Examples of such methods are disclosed in EP 1,502,645 A1.

(iv) Spray drying, including capsules derived from spray drying mixtures comprising at least one cellulosic polymer selected from the group consisting of hydroxypropyl methylcellulose phthalate (HPMCP), cellulose acetate phthalate (CAP), and mixtures thereof. Such polymers include polymers that are commercially available under the trade names NF Hypromellose Phthalate

(HPMCP) (Shin-Etsu), cellulose ester NF or cellulose cellacefate NF (CAP) from G.M. Chemie Pvt Ltd, Mumbai, 400705, India and Eastman Chemical Company, Kingsport, USA. Examples of such methods are disclosed in WO/2011/005943.

The encapsulated protease may comprise at least 0.5%, or at least 1%, or at least 2%, or at least 5%, or at least 10%, or even at least 20% by weight active protease enzyme.

Encapsulated proteases may comprise from about 5% to about 90% active protease by weight.

Encapsulated proteases may be incorporated into the compositions of the present invention, based on total cleaning composition weight, at a level of from 0.001% to about 30%, or from about 0.005% to about 25%, or from about 0.05% to about 10% or even from about 0.01% to about 2%.

Without wishing to be bound by theory, it is believed that having a low particle size facilitates the liquid phase's ability to suspend the particles, thereby keeping the liquid phase as homogenous as possible. When said encapsulated proteases are in the form of enzyme microcapsules, said microcapsules typically have a particle size of from about 100 microns to about 0.05 microns, from about 80 microns to about 0.05 microns, or even from about 50 microns to about 0.05 microns. Thus, in one aspect, such microcapsules are sized such that they are not typically visible to a consumer when such microcapsules are incorporated into a cleaning composition.

Preferably, the encapsulated protease releases at least 80% of its protease load within 10 minutes, within 5 minutes, or even within 2 minutes upon dilution in the wash. These release rates are preferably achievable at ambient temperatures under a 100 fold dilution at 20 °C with stirring at 150 rpm. Protease activity can be determined by any standard method such as use of protease analysis kits available from Sigma Aldrich, Milwaukee, Wisconsin, USA or ASTM method D0348-89 (2003). Without wishing to be bound by theory, it is believed that a better cleaning profile is obtained as the time that the enzymes have to interact with the soil is increased.

Encapsulated proteases may be enzyme granulates/prills, having an average particle size of 200 – 1000 microns. Such enzyme granules/prills may be made in accordance with the teachings of USP 4,106,991, USP 4,242,219, USP 4,689,297, USP 5,324,649 and USP 7,018,821 B2. In one aspect, such enzyme granulates/prills may comprise a dye and/or pigment.

In one aspect, such enzyme granulates/prills may comprise a coating comprising hydroxpropylmethylcellulose and/or polyvinylalcohol and derivatives thereof.

3. Enzyme Stabilizers

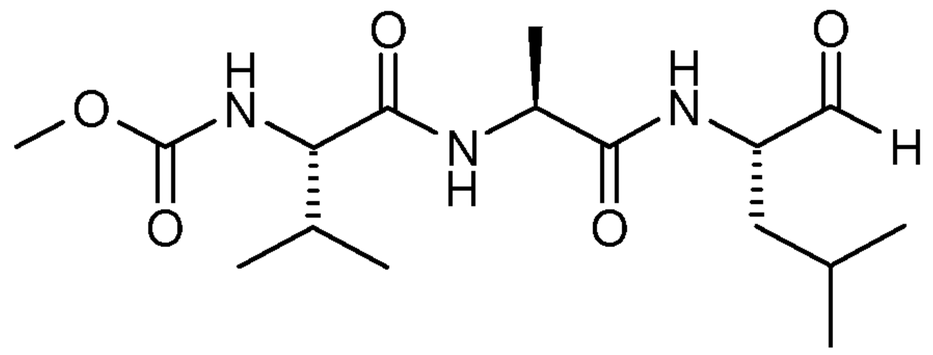
Suitable mass efficient reversible protease inhibitors for the inhibition of serine proteases would include derivates of boronic acid, especially derivatives of phenyl boronic acid and peptide aldehydes, including tripeptide aldehydes. Examples of such compounds are disclosed in WO 98/13458 A1, WO 07/113241 A1, and USP 5,972,873.

The stabilizer may be selected from the group consisting of thiophene-2 boronic acid, thiophene-3 boronic acid, acetamidophenyl boronic acid, benzofuran-2 boronic acid, naphtalene-1 boronic acid, naphtalene-2 boronic acid, 2-fomyl phenyl boronic acid (2-FPBA), 3-FBPA, 4-FPBA, 1-thianthrene boronic acid, 4-dibenzofuran boronic acid, 5-methylthiophene-2 boronic, acid, thionaphtrene boronic acid, furan-2 boronic acid, furan-3 boronic acid, 4,4 biphenyldiboronic acid, 6-hydroxy-2-naphtalene, 4-(methylthio) phenyl boronic acid, 4 (trimethylsilyl)phenyl boronic acid, 3-bromothiophene boronic acid, 4-methylthiophene boronic acid, 2-naphtyl boronic acid, 5-bromothiphene boronic acid, 5-chlorothiophene boronic acid, dimethylthiophene boronic acid, 2-bromophenyl boronic acid, 3-chlorophenyl boronic acid, 3-methoxy-2-thiophene, p-methyl-phenylethyl boronic acid, 2-thianthrene boronic acid, di-benzothiophene boronic acid, 4-carboxyphenyl boronic acid, 9-anthryl boronic acid, 3,5 dichlorophenyl boronic, acid, diphenyl boronic acidanhydride, o-chlorophenyl boronic acid, p-chlorophenyl boronic acid m-bromophenyl boronic acid, p-bromophenyl boronic acid, p-fluorophenyl boronic acid, p-tolyl boronic acid, o-tolyl boronic acid, octyl boronic acid, 1,3,5 trimethylphenyl boronic acid, 3-chloro-4-flourophenyl boronic acid, 3-aminophenyl boronic acid, 3,5-bis-(trifluoromethyl) phenyl boronic acid, 2,4 dichlorophenyl boronic acid, 4-methoxyphenyl boronic acid and mixtures thereof. Further suitable boronic acid derivatives suitable as stabilizers are described in USP 4,963,655, USP 5,159,060, WO 95/12655, WO 95/29223, WO 92/19707, WO 94/04653, WO 94/04654, USP 5,442,100, USP 5,488,157 and USP 5,472,628.

Suitable mass efficient reversible protease inhibitors may comprise 4-formyl phenyl boronic acid.

The mass efficient reversible protease inhibitor may comprise a reversible peptide protease inhibitor. Examples of suitable reversible peptide protease inhibitors and processes for making same may be found in USP 6,165,966 and WO 98/13459 A1..

Suitable tripeptide enzyme inhibitors may have the following structure:



The mass efficient reversible protease inhibitor may comprise a protease inhibitor of the protein type such as RASI, BASI, WASI (bifunctional alpha-amylase/subtilisin inhibitors of rice, barley and wheat) as disclosed in WO09/095425 or SSI (streptomyces subtilisin inhibitor) and variants thereof as disclosed in Protein Engineering Design & Selection, vol 17 no.4, p.333-339, 2004.

4. Polymer Deposition Aids

Preferably, the fluid detergent composition comprises from 0.1% to 7%, more preferably from 0.2% to 3%, of a polymer deposition aid. As used herein, "polymer deposition aid" refers to any cationic polymer or combination of cationic polymers that significantly enhance deposition of a care benefit agents onto substrates (such as fabric) during washing (such as laundering). Suitable polymer deposition aids can comprise a cationic polysaccharide and/or a copolymer. "Fabric care benefit agent" as used herein refers to any material that can provide fabric care benefits. Non-limiting examples of fabric care benefits include, but are not limited to: fabric softening, color protection, color restoration, pill/fuzz reduction, anti-abrasion and anti-wrinkling. Non-limiting examples of fabric care benefit agents include: silicone derivatives, oily sugar derivatives, dispersible polyolefins, polymer latexes, cationic surfactants and combinations thereof.

5. Cleaning Polymers

The detergent compositions herein may optionally contain from 0.01 to 10% by weight of one or more cleaning polymers that provide for broad-range soil cleaning of surfaces and fabrics and/or suspension of the soils. Any suitable cleaning polymer may be of use. Useful cleaning polymers are described in US 2009/0124528A1. Non-limiting examples of useful categories of cleaning polymers include: amphiphilic alkoxylated grease cleaning polymers; clay soil cleaning polymers; soil release polyers; and soil suspending polymers.

6. Bleaching systems

One embodiment is a composition, wherein the composition is a fluid laundry bleach additive comprising from 0.1% to 12 % by weight of a bleach or bleach system, preferably a peroxide bleach, and further comprises a neat pH of from 2 to 6. Another embodiment is a fluid laundry detergent composition comprising: from 0.1% to 12 % by weight of the bleach, and a composition pH of from 6.5 to 10.5. Suitable hydrogen peroxide sources are described in detail in Kirk Othmer's Encyclopedia of Chemical Technology, 4th Ed (1992, John Wiley & Sons), Vol. 4, pp. 271-300 "Bleaching Agents (Survey)", and include the various forms of sodium perborate and sodium percarbonate, including various coated and modified forms. For example, hydrogen peroxide itself; perborates, e.g., sodium perborate (any hydrate but preferably the mono- or tetra-hydrate); sodium carbonate peroxyhydrate or equivalent percarbonate salts; sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, or sodium peroxide can be used herein. Also useful are sources of available oxygen such as persulfate bleach (e.g., OXONE™, manufactured by DuPont). Sodium perborate monohydrate and sodium percarbonate are particularly preferred. Compositions of the present invention may also comprise as the bleaching agent a chlorine-type bleaching material. Such agents are well known in the art, and include for example sodium dichloroisocyanurate ("NaDCC"). However, chlorine-type bleaches are less preferred for compositions comprising enzymes. They bleaching systems of use in the present invention may also include ingredients selected from the group consisting of: bleach activators, hydrogen peroxide, hydrogen peroxide sources, organic peroxides, metal-containing bleach catalysts, transition metal complexes of macropolycyclic rigid ligands, other bleach catalysts, preformed peracids, photobleaches and mixtures thereof.

Bleach Activators: The peroxygen bleach component in the composition can be formulated with an activator (peracid precursor), present at levels of from 0.01 to 15 %, preferably from 0.5 to 10 %, more preferrably from 1% to 8 % by weight of the composition. Preferred activators are selected from the group consisting of: tetraacetyl ethylene diamine (TAED), benzoylcaprolactam (BzCL), 4-nitrobenzoylcaprolactam, 3-chlorobenzoylcaprolactam, benzoyloxybenzenesulphonate (BOBS), nonanoyloxybenzenesulphonate (NOBS), phenyl benzoate (PhBz), decanoyloxybenzenesulphonate (C_{10}-OBS), benzoylvalerolactam (BZVL), octanoyloxybenzenesulphonate (C_8-OBS), perhydrolyzable esters and mixtures thereof, alternatively benzoylcaprolactam and benzoylvalerolactam, 4-[N-(nonaoyl) amino hexanoyloxy]-benzene sulfonate sodium salt (NACA-OBS) (See U.S. 5,523,434),

dodecanoyloxy-benzenesulphonate (LOBS or C_{12}-OBS), 10-undecenoyloxybenzenesulfonate (UDOBS or C_{11}-OBS with unsaturation in the 10 position), and decanoyloxybenzoic acid (DOBA) and mixtures thereof. Non-limiting examples of suitable bleach activators, including quaternary substituted bleach activators, are described in US 6,855,680.

Hydrogen Peroxides sources: Suitable examples include inorganic perhydrate salts, including alkali metal salts such as sodium salts of perborate (usually mono- or tetra-hydrate), percarbonate, persulphate, perphosphate, persilicate salts and mixtures thereof. When employed, inorganic perhydrate salts are typically present in amounts of from 0.05% to 40%, preferably from 1% to 30% by weight of the composition.

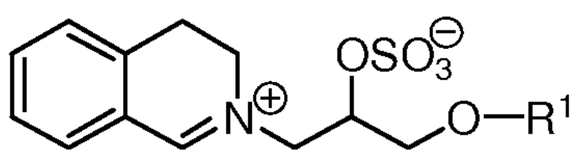
Organic Peroxides: Diacyl Peroxides that do not cause visible spotting or filming are particularly preferred. One example is dibenzoyl peroxide. Other suitable examples are illustrated in Kirk Othmer, Encyclopedia of Chemical Technology at 27-90, v. 17, John Wiley and Sons, (1982).

Metal-containing Bleach Catalysts: Preferred bleach catalysts include manganese and cobalt-containing bleach catalysts. Other suitable metal-containing bleach catalysts include catalyst systems comprising a transition metal cation of defined bleach catalytic activity, such as copper, iron, titanium, ruthenium tungsten, molybdenum, or manganese cations; an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminum cations; and a sequestrate having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra (methylenephosphonic acid) and water-soluble salts thereof. Suitable catalyst systems are disclosed in US 4,430,243.

Transition Metal Complexes of Macropolycyclic Rigid Ligands: The fluid detergent compositions herein may also include bleach catalysts comprising a transition metal complex of a macropolycyclic rigid ligand. The amount used is preferably more than 1 ppb, more preferably 0.001 ppm or more, even more preferably from 0.05 ppm to 500 ppm (wherein "ppb" denotes parts per billion by weight and "ppm" denotes parts per million by weight).

Other Bleach Catalysts: Other bleach catalysts such as organic bleach catalysts and cationic bleach catalysts are suitable for the fluid detergent compositions of the invention. Organic bleach catalysts are often referred to as bleach boosters. The fluid detergent compositions herein may comprise one or more organic bleach catalysts to improve low temperature bleaching. Preferred organic bleach catalysts are zwitterionic bleach catalysts,

including aryliminium zwitterions. Suitable examples include 3-(3,4-dihydroisoquinolinium) propane sulfonate and 3,4-dihydro-2-[2-(sulfooxy)decyl]isoquinolimium. Suitable aryliminium zwitterions include:



wherein R^1 is a branched alkyl group containing from 9 to 24 carbons or linear alkyl group containing from 11 to 24 carbons. Preferably, each R^1 is a branched alkyl group containing from 9 to 18 carbons or linear alkyl group containing from 11 to 18 carbons, more preferably each R^1 is selected from the group consisting of 2-propylheptyl, 2-butyloctyl, 2-pentylnonyl, 2-hexyldecyl, n-dodecyl, n-tetradecyl, n-hexadecyl, n-octadecyl, iso-nonyl, iso-decyl, iso-tridecyl and iso-pentadecyl. Other suitable examples of organic bleach catalysts can be found in US 5,576,282 and US 5,817,614, EP 923,636 B1, WO 2001/16263 A1, WO 2000/42156 A1, WO 2007/001262 A1.

Suitable examples of cationic bleach catalysts are described in US 5,360,569, US 5,442,066, US 5,478,357, US 5,370,826, US 5,482,515, US 5,550,256, WO 95/13351, WO 95/13352, and WO 95/13353.

Preformed peracids: The preferred preformed peracid is Phthalimido peroxycaproic acid (PAP). Other suitable preformed peracids include, but are not limited to, compounds selected from the group consisting of: percarboxylic acids and salts, percarbonic acids and salts, perimidic acids and salts, peroxymonosulfuric acids and salts, and mixtures thereof. In compositions such as bleach containing fluid laundry detergents, the preformed peracid may be present at a level of from 0.1% to 25%, preferably from 0.5% to 20%, more preferably from 1% to 10%, most preferably from 2% to 4% by weight of the composition. Alternatively, higher levels of peracid may be present. For instance, compositions such as fluid laundry bleach additives may comprise from 10% to 40%, preferably from 15% to 30%, more preferably from 15% to 25% by weight preformed peracid.

7. Optical brighteners

These are also known as fluorescent whitenening agents for textiles. Preferred levels are from 0.001% to 1% by weight of the fluid detergent composition. Suitable brighteners are

disclosed in EP 686691B and include hydrophobic as well as hydrophilic types. Brightener 49 is preferred for use in the present invention.

8. Hueing Dyes

Hueing dyes or fabric shading dyes are useful adjuncts in fluid detergent compositions. Suitable dyes include blue and/or violet dyes having a hueing or shading effects. The fluid detergent compositions herein may comprise from 0.00003% to 0.1%, preferably from 0.00008% to 0.05%, more preferably from 0.0001% to 0.04% by weight of the fabric hueing dye.

9. Particulate material

The fluid detergent composition may include particulate material such as clays, suds suppressors, encapsulated sensitive ingredients, e.g., perfumes including perfume microcapsules, bleaches and enzymes in encapsulated form; or aesthetic adjuncts such as pearlescent agents including mica, pigment particles, or the like. Suitable levels are from 0.0001% to 5%, or from 0.1% to 1% by weight of the fluid detergent composition.

10. Perfume and odour control agents

In preferred embodiments, the fluid detergent composition comprises a perfume. If present, perfume is typically incorporated at a level from 0.001 to 10%, preferably from 0.01% to 5%, more preferably from 0.1% to 3% by weight of the composition. The perfume may comprise a perfume microcapsule and/or a perfume nanocapsule. In other embodiments, the fluid detergent composition comprises odour control agents such as uncomplexed cyclodextrin as described in US 5,942,217.

11. Hydrotropes

The fluid detergent composition optionally comprises a hydrotrope in an effective amount, i.e. up to 15%, preferably 1 % to 10 %, more preferably 3 % o 6 % by weight, so that the fluid detergent compositions are compatible in water. Suitable hydrotropes for use herein include anionic-type hydrotropes, particularly sodium, potassium, and ammonium xylene sulfonate, sodium, potassium and ammonium toluene sulfonate, sodium potassium and ammonium cumene sulfonate, and mixtures thereof, as disclosed in US 3,915,903.

Unit Dose Detergent:

In some embodiments of the present invention, the fluid detergent composition is enclosed within a water soluble pouch material. Preferred polymers, copolymers or derivatives thereof suitable for use in pouch materials are selected from the group: polyvinyl alcohols,

polyvinyl pyrrolidone, polyalkylene oxides, acrylamide, acrylic acid, cellulose, cellulose ethers, cellulose esters, cellulose amides, polyvinyl acetates, polycarboxylic acids and salts, polyaminoacids or peptides, polyamides, polyacrylamide, copolymers of maleic/acrylic acids, polysaccharides including starch and gelatin, natural gums such as xanthum and carragum. More preferred polymers are selected from polyacrylates and water-soluble acrylate copolymers, methylcellulose, carboxymethylcellulose sodium, dextrin, ethylcellulose, hydroxyethyl cellulose, hydroxypropyl methylcellulose, maltodextrin, polymethacrylates, and most preferably selected from polyvinyl alcohols, polyvinyl alcohol copolymers and hydroxypropyl methyl cellulose (HPMC), and combinations thereof.

Process of Making:

The present invention also includes a process for making a fluid detergent composition incorporating a pH tuneable amido gellant, comprising the steps of:

a) preparing a structurant premix comprising the pH tuneable amido gellant, wherein the structurant premix is at a pH such that the pH tuneable amido gellant is in its ionic, non-viscosity building, form;

b) combining the structurant premix with a detergent feed, said detergent feed comprising an anionic and/or nonionic surfactant;

c) adjusting the pH of the combined fluid detergent composition as needed, such that the fluid detergent composition is at a pH at which the pH tuneable amido gellant is in its nonionic, viscosity building, form.

The fluid detergent compositions comprising a pH tuneable amido gellant is preferably processed such that the temperatures of the structurant premix and/or the ingredient stream are maintained at less than 50 °C, preferably less than 30°C; particularly if the fluid detergent composition further incorporates temperature-sensitive ingredients such as enzymes or perfumes.

Test Methods:

1. Turbidity (NTU):

Turbidity (measured in NTU: Nephelometric Turbidity Units) according to the present invention is measured using a Hach 2100P turbidity meter calibrated according to the procedure provided by the manufacture. The sample vials are filled with 15ml of representative sample and capped and cleaned according to the operating instructions. If necessary, the samples are

degassed to remove any bubbles either by applying a vacuum or using an ultrasonic bath (see operating manual for procedure). The turbidity is measured using the automatic range selection.

2. Minimum gelling concentration (MGC)

MGC is calculated by a tube inversion method based on R.G. Weiss, P. Terech; "Molecular Gels: Materials with self-assembled fibrillar structures" 2006 springer, p 243. In order to determine the MGC, three screenings are done:

a) First screening: prepare several vials increasing the pH tuneable amido gellant concentration from 0.5 % to 5.0 weight % in 0.5% steps, at the target pH.
b) Determine in which interval the gel is formed (one inverted sample still flowing and the next one is already a strong gel). In case no gel is formed at 5%, higher concentrations are used.
c) Second screening: prepare several vials increasing the pH tuneable amido gellant concentration in 0.1 weight % steps in the interval determined in the first screening, at the target pH.
d) Determine in which interval the gel is formed (one inverted sample still flowing and the next one is already a strong gel)
e) Third screening: in order to have a very precise percentage of the MGC, run a third screening in 0.025 weight % steps in the interval determined in the second screening, at the target pH.
f) The Minimum Gelling Concentration (MGC) is the lowest concentration which forms a gel in the third screening (does not flow on inversion of the sample).

For each screening, samples are prepared and treated as follows: 8mL vials (Borosilacate glass with Teflon™ cap, ref. B7857D, Fisher Scientific Bioblock) are filled with 2.0000±0.0005 g (KERN ALJ 120-4 analytical balance with ± 0.1mg precision) of the fluid (comprising the fluid detergent composition and pH tuneable amido gellant) for which we want to determine the MGC. The vial is sealed with the screw cap and left for 10 minutes in an ultrasound bath (Elma Transsonic™ T 710 DH, 40 kHz, 9.5L, at 25 °C and operating at 100% power) in order to disperse the solid in the liquid. Complete dissolution is then achieved by heating, using a heating gun (Bosch PHG-2), and gentle mechanical stirring of the vials. It is crucial to observe a completely clear solution. Handle vials with care. While they are manufactured to resist high temperatures, a high solvent pressure may cause the vials to explode. Vials are cooled to 25°C, for 10min in a

thermostatic bath (Compatible Control Thermostats with controller CC2, D77656, Huber). Vials are inverted, left inverted for 1 minute, and then observed for which samples do not flow. After the third screening, the concentration of the sample that does not flow after this time is the MGC. For those skilled in the art, it is obvious that during heating solvent vapours may be formed, and upon cooling down the samples, these vapours can condense on top of the gel. When the vial is inverted, this condensed vapour will flow. This is discounted during the observation period. If no gels are obtained in the concentration interval, higher concentrations must be evaluated.

3. pH measurement of a liquid detergent composition

pH measurement of a liquid detergent composition may be measured using test method EN 1262.

4. Rheology

An AR-G2 rheometer from TA Instruments is used for rheological measurements.

Plate: 40mm standard steel parallel plate, 300μm gap.

1. Gel strength: The gel strength is measured using a stress sweep test whereby the oscillation stress is increased from 0.001Pa to 10Pa, taking 10 points per decade at 20°C and at a frequency of 1Hz. We use G' and G" within the linear viscoelastic region and the oscillation stress at the point where G' and G" cross over as a measure for the gel strength, as shown in Figure 1.

2. Recovery of structure: first we apply a pre-shear of 30s-1 at 20°C for 60s, after which we follow how the structure recovers applying a time sweep test with an oscillation stress of 0.02Pa and a single frequency of 1Hz at 20°C for 10 minutes. As a measure of the restructuring kinetics, we use G' and G" cross over, as shown in the Figure 2.

EXAMPLES

Example 1: A liquid laundry detergent composition according to the present invention is prepared as follows:

Step 1: A structurant premix A1 is prepared by dissolving 0.20 grams *N,N'*-(2S,2'S)-1,1'-(hexane-1,6-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide in 12.0

grams of 50% citric acid aqueous solution (prepared by dissolving 6.0 grams of citric acid solid in 6.0 grams deionized water) at 25°C.

Step 2: A detergent feed B1 having the composition described in Table 4 is prepared.

Table 4: Composition of detergent feed B1

Ingredient	Detergent Feed B1
	Grams
Linear Alkylbenzene sulfonic acid (LAS)	12.0
C12-14 alkyl ethoxy 3 sulfate Mono Ethanol Amine salt	9.3
C12-14 alkyl 7-ethoxylate	8.0
1,2-propanediol	9.8
C12-18 Fatty Acid	10.0
Grease Cleaning Alkoxylated Polyalkylenimine Polymer[1]	0.9
PEG PVAc Polymer[2]	0.9
Soil Suspending Alkoxylated Polyalkylenimine Polymer[3]	2.2
Hydroxyethane diphosphonic acid	1.6
FWA	0.23
Ethanol	1.5
Boric acid	0.5
MEA	Up to pH 8
Water up to	66 grams

[1] 600 g/mol molecular weight polyethylenimine core with 24 ethoxylate groups per -NH and 16 propoxylate groups per -NH.

[2] PEG-PVA graft copolymer is a polyvinyl acetate grafted polyethylene oxide copolymer having a polyethylene oxide backbone and multiple polyvinyl acetate side chains. The molecular weight of the polyethylene oxide backbone is 6000 and the weight ratio of the polyethylene

oxide to polyvinyl acetate is 40 to 60 and no more than 1 grafting point per 50 ethylene oxide units.

[3] 600 g/mol molecular weight polyethylenimine core with 20 ethoxylate groups per -NH.

Step 3: 12.4 grams of structurant premix A1 is mixed with 66 grams of detergent feed B1 at 600rpm for 10 min, at 25°C, and the resulting mixture is adjusted to pH 8 with MEA.

Step 4: The pH sensitive ingredients (1.5 grams protease, 0.7 grams amylase, 0.1 grams mannanase, 0.1 grams xyloglucanase, 0.4 grams pectate lyase and 1.7 grams of perfume) and deionized water (to bring the final weight up to 100 grams) are added under gentle stirring, at 500-600rpm for 10 min.

Example 2 – Unit Dose Laundry detergent

A laundry unit dose comprising the fluid detergent composition of the present invention is prepared as follows:

Step 1: A structurant premix A2 is prepared by fully dissolving 0.20 grams *N,N'*-(2S,2'S)-1,1'-(octane-1,8-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide in 1.0 grams of citric acid and 3 grams of deionized water at 25°C.

Step 2: A detergent feed B2 having the composition described in Table 5 is prepared.

Table 5: Composition of detergent feed B2

Ingredient	Detergent Feed B2
	% of base @100% active
1,2-Propanediol	15
MEA	10
Glycerol	5
Hydroxyethane diphosphonic acid	1
Potassium sulfite	0.2
C12-45 alkyl 7-ethoxylate	20
Linear Alkylbenzene sulfonic acid	24.5
FWA	0.2
C12-18 Fatty Acid	16

Ethoxysulfated Hexamethylene Diamine Dimethyl Quat	2.9
Soil Suspending Alkoxylated Polyalkylenimine Polymer[3]	1
$MgCl_2$	0.2
Water and minors	Up to 100%

Step 3: 4.2 grams of structurant premix A2 are mixed with 34.5 grams of detergent feed B2 at 600rpm for 10 min, at 25ºC, for 5 minutes. The resulting mixture is adjusted to pH 8 with MEA and pH sensitive ingredients listed in Table 6 are added at 600rpm, 25ºC, and mixed for 2 minutes:

Table 6: pH sensitive ingredients.

Ingredient	
	% of base @100% active
Protease enzyme	1.4
Mannanase enzyme	0.1
Amylase enzyme	0.2

The fluid detergent composition is then packed into a polyvinyl alcohol pouch.

Examples 3A to 3E: Fluid Detergent Fabric Care Compositions comprising amido-gellants of the present invention:

Step 1: A structurant premix A3 is prepared by dissolving 5 grams *N,N'*-(2S,2'S)-1,1'-(dodecane-1,12-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide in 95 grams of 25% sulfuric acid aqueous solution (Sigma-Aldrich) at 25°C.

Step 2: A detergent feed B3A to B3E having the composition described in Table 7 is prepared.

Table 7: Composition of detergent feed B3A to B3E

Ingredient	B3A	B3B	B3C	B3D	B3E
	Wt%	Wt%	Wt%	Wt%	Wt%
C12-15 alkyl polyethoxylate (3.0) sulfate	6.7	6.5	7.8	6.4	5.7

C11.8 linear alkylbenzene sulfonc acid	19.4	18.9	19.0	14.6	16.4
C14-15 alkyl 7-ethoxylate	11.8	11.5	3.9	4.8	16.4
C12-14 alkyl 7-ethoxylate	-	0.9	1.0	1.1	0.9
1,2 Propane diol	7.0	5.2	8.2	9.1	6.9
Ethanol	1.8	1.7	2.0	2.3	1.7
Di Ethylene Glycol	-	3.4	-	-	-
Na Cumene Sulfonate	5.3	5.2	6.1	6.8	5.2
C12-18 Fatty Acid	4.6	4.5	6.7	5.9	4.5
Citric acid	4.6	4.5	7.6	9.8	4.5
Fluorescent Whitening Agent	0.18	-	0.20	0.23	0.17
Diethylene Triamine Penta Acetic acid	-	0.860	-	-	-
Diethylene Triamine Penta Methylene Phosphonic acid	0.53	0.17	0.61	0.68	0.52
Soil Suspending Alkoxylated Polyalkylenimine Polymer[1]	1.4	0.9	-	-	1.4
Zwitterionic ethoxylated quaternized sulfated hexamethylene diamine[2]	1.8	1.7	1.8	2.3	1.7
Grease Cleaning Alkoxylated Polyalkylenimine Polymer[3]	0.7	0.7	-	0.5	-
PEG-PVAc Polymer[4]	-	0.9	-	-	-
Monoethanolamine Borate	3.5	1.7	4.1	4.6	3.4
4 – Formyl Phenyl Boronic Acid	-	0.05	-	-	-
Sodium formate	0.7	0.7	0.8	0.9	0.7
Calcium chloride	0.09	0.09	0.10	0.11	0.09
Acticide™ MBS 2550	0.010	0.010	0.010	0.010	0.010
Water	up to 100%	up to 100%	up to 100%	up to 100%	up to 100%

[1] 600 g/mol molecular weight polyethylenimine core with 20 ethoxylate groups per -NH.

Available from BASF (Ludwigshafen, Germany)

[2] Described in WO 01/05874 and available from BASF (Ludwigshafen, Germany)

[3] 600 g/mol molecular weight polyethylenimine core with 24 ethoxylate groups per -NH and 16 propoxylate groups per -NH. Available from BASF (Ludwigshafen, Germany).

[4] PEG-PVA graft copolymer is a polyvinyl acetate grafted polyethylene oxide copolymer having a polyethylene oxide backbone and multiple polyvinyl acetate side chains. The molecular weight of the polyethylene oxide backbone is about 6000 and the weight ratio of the polyethylene oxide to polyvinyl acetate is about 40 to 60 and no more than 1 grafting point per 50 ethylene oxide units. Available from BASF (Ludwigshafen, Germany).

Step 3: Structurant premix A3 (amounts listed in Table 8) is mixed with 70 grams of detergent feeds B3A to B3E at 400rpm for 10 min, at 35°C.

Table 8: addition of premix A3

Ingredient	3A	3B	3C	3D	3E
	grams	grams	grams	grams	grams
Premix A3	5	3	4	6	3.6

The resulting mixture is adjusted to pH 8 with sodium hydroxide 20% and pH sensitive ingredients listed in Table 9 are added at 600rpm, 25°C, and mixed for 5 minutes.

Table 9: pH sensitive ingredients.

Ingredient	**3A**	**3B**	**3C**	**3D**	**3E**
	Wt%	**Wt%**	**Wt%**	**Wt%**	**Wt%**
Protease (40.6mg/g/)[1]	0.5	0.5	0.5	0.5	0.5
Natalase™ 200L (29.26mg/g)[2]	0.1	0.1	0.1	0.1	0.1
Termamyl™ Ultra (25.1mg/g)[2]	0.05	0.05	0.05	0.05	0.05
Mannaway™ 25L (25mg/g)[2]	0.05	0.05	0.05	0.05	0.05
Lipase (16.91 mg/g)[2]	0.5	-	0.25	-	0.5
Lipolex®[2]	-	0.2	-	-	-
Lipex®[2]	-	-	-	0.25	-
Whitezyme™ (20mg/g)[2]	0.05	0.05	0.05	0.05	0.05
Perfume Microcapsules[3]	-	-	-	0.2	-

Mica	-	-	-	-	0.05
Silicone suds suppressor	-	0.1	-	-	-
Water, perfumes, dyes, neutralizers, and other optional components (pH to 8.0 – 8.2)	to 100%	to 100%	to 100%	to 100%	to 100%

[1] Available from Genencor International, South San Francisco, CA.

[2] Available from Novozymes, Denmark.

[3] Perfume microcapsules can be prepared as follows: 25 grams of butyl acrylate-acrylic acid copolymer emulsifier (Colloid C351, 25% solids, pka 4.5-4.7, Kemira Chemicals, Inc. Kennesaw, Georgia U.S.A.) is dissolved and mixed in 200 grams deionized water. The pH of the solution is adjusted to pH of 4.0 with sodium hydroxide solution. 8 grams of partially methylated methylol melamine resin (Cymel™ 385, 80% solids, Cytec Industries West Paterson, New Jersey, U.S.A.) is added to the emulsifier solution. 200 grams of perfume oil is added to the previous mixture under mechanical agitation and the temperature is raised to 50°C. After mixing at higher speed until a stable emulsion is obtained, the second solution and 4 grams of sodium sulfate salt are added to the emulsion. This second solution contains 10 grams of butyl acrylate-acrylic acid copolymer emulsifier (Colloid C351, 25% solids, pka 4.5-4.7, Kemira), 120 grams of distilled water, sodium hydroxide solution to adjust pH to 4.8, 25 grams of partially methylated methylol melamine resin (Cymel 385, 80% solids, Cytec). This mixture is heated to 70°C and maintained overnight with continuous stirring to complete the encapsulation process. 23 grams of acetoacetamide (Sigma-Aldrich, Saint Louis, Missouri, U.S.A.) is added to the suspension.

Examples 4A to 4S: Hand-dish washing fluid detergent compositions comprising amido-gellants.

Hand-dish washing liquid detergent compositions may be prepared by mixing together the ingredients listed in the proportions shown:

Table 10: Hand-dish washing fluid detergent compositions comprising amido-gellants

	Ex 4A	Ex 4B	Ex 4C	Ex 4D	Ex 4E	Ex 4F
Alkyl Ethoxy Sulfate AE0.6S	22.0	19.0	27.0	20.0	22.0	22.0
Linear C12-C14 Amine oxide	6.0	4.5	-	-	6.0	5.0
C9-C11 alkyl EO8 ethoxylate	7.0	-	-	-	-	-
L-Glutamic acid-N,N-di(acetic acid) tetrasodium salt	1.0	-	-	0.1	-	-
Sodium Citrate	-	1.0	-	0.5	0.8	-
Solvent: ethanol, isopropylalcohol,..	2.5	4.0	3.0	2.0	3.0	2.5
Polypropylene glycol Mw2000	1.0	0.5	1.0	-	2.0	1.0
Sodium Chloride	0.5	1.0	1.0	0.5	0.5	0.5
N,N'-(2S,2'S)-1,1'-(dodecane-1,12-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide	0.05	0.20	0.10	0.15	0.25	0.20

Minors and Balance with water up to 100%

Table 11: Hand-dish washing fluid detergent compositions comprising amido-gellants

	Ex 4G	Ex 4H	Ex 4I	Ex 4J
Alkyl Ethoxy Sulfate AE1.0S	13	16	17	20
C12-C14 Amine oxide	4.5	5.5	4.0	4.5
C9-C11 alkyl EO8 ethoxylate	4	4	-	-
L-Glutamic acid-N,N-di(acetic acid) tetrasodium salt	0.7	-	-	-
Sodium Citrate	-	-	0.2	-
Solvent: ethanol, isopropylalcohol,..	2.0	2.0	2.0	1.5
Polypropylene glycol Mw2000	0.5	0.3	0.5	0.8
Sodium Chloride	0.5	0.8	0.4	0.5
N,N'-(2S,2'S)-1,1'-(dodecane-1,12-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide	0.30	0.20	0.50	0.25

Minors and Balance with water up to 100%

Table 12: Hand-dish washing fluid detergent compositions comprising amido-gellants

	Ex 4K	Ex 4L	Ex 4M	Ex 4N	Ex 4O
Linear Alkylbenzene Sulfonate	21.0	21.0	12.0	13.0	-
Alkyl Ethoxy Sulfate AE1.0S	-	-	14.0	5.0	17.0
C12-14 alpha olefin sulfonate	-	-	-	-	6.0
Coco amido propyl Amine Oxide	-	-	-	1.0	5.0
alkylpolyglucoside	-	2.0	-	-	-
C9-C11 alkyl EO8 ethoxylate	5.0	4.0	8.0	4.0	3.0
L-Glutamic acid-N,N-di(acetic acid) tetrasodium salt	0.5	-	-	-	-
N,N'-(2S,2'S)-1,1'-(dodecane-1,12-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide	0.15	0.15	0.10	0.20	0.10

Minors and Balance with water up to 100%

Table 13: Hand-dish washing fluid detergent compositions comprising amido-gellants

	Ex 4P	Ex 4Q	Ex 4R	Ex 4S
Alkyl Ethoxy Sulfate AE2.0S	17.0	12.0	24.0	29.0
C12-14 alpha olefin sulfonate	-	-	1.0	-
Paraffin Sulfonate (C15)	9.0	1.0	1.0	-
Coco amido propyl amine oxide	-	6.0	-	1.0
C12-C14 Akylpolyglucoside	-	3.0	2.0	-
C9-C11 alkyl EO8 ethoxylate	8.0	2.0	-	-
L-Glutamic acid-N,N-di(acetic acid) tetrasodium salt	0.5	-	0.5	-
Polypropylene glycol MW2000	1.0	1.0	-	0.5
N,N'-(2S,2'S)-1,1'-(dodecane-1,12-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide	0.10	0.25	0.10	0.15

Minors and Balance with water up to 100%

N,N'-(2S,2'S)-1,1'-(dodecane-1,12-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide has been added as Premix A3 prepared in example 3. Afterwards, pH was adjusted with 20% sodium hydroxide aqueous solution to pH 9 (for examples 4A to 4J) and pH 8 (examples 4K to 4S).

Examples 5A, 5B and 5C: compacted laundry fluid detergent compositions (25mL dosage) comprising amido-gellants:

Step 1: A structurant premix A5 is prepared by dissolving 10 grams *N,N'*-(2S,2'S)-1,1'-(dodecane-1,12-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide in 90 grams 20% C_{11-8} HLAS in 1,2-propanediol solution (prepared by adding 20 grams C_{11-8} HLAS to 80 grams 1,2-propanediol at 50°C) at 45°C.

Step 2: Detergent feeds B5A and B5B having the composition described in Table 14 are prepared.

Table 14: Composition of detergent feeds B5A, B5B, B5C

	5A	**5B**	**5C**
Ingredients	**Weight%**		
Monoethanolamine: C_{12-15} EO·3·SO_3H	40.5	43.3	41.5
Monoethanolamine: C_{16-17} highly soluble alkyl sulfate	6.5	7.4	7.0
C_{12-14} dimethylamine-N-oxide	1.9	2.1	2.0
Ethoxylated Polyethyleneimine[1]	4.3	4.9	4.3
Citric acid	-	2.5	1.0
Amphiphilic alkoxylated grease cleaning polymer[2]	4.3	3.1	4.3

C_{12-18} Fatty acid	3.3	-	3.3
Suds suppression polymer	0.1	0.1	0.1
C_{11-8} HLAS	14.7	12.4	13.0
Hydroxy Ethylidene 1,1 Di Phosphonic acid	-	1.2	-
Tiron	2.2	-	2.2
Brightener	0.1	0.2	0.1
Water	5.1	6.2	4.8
Minors (antioxidant, sulfite, aesthetics,…)	1.6	1.9	2.0
Buffers (monoethanolamine)	To pH 8.0		
Solvents (1,2 propanediol, ethanol)	To 100 parts		

[1] Polyethyleneimine (MW=600grams/mol) with 20 ethoxylate groups per –NH (BASF, Germany)

[2] PG617 or PG640 (BASF, Germany)

Step 3: Structurant premix A5 (amounts listed in Table 15) are mixed with detergent feeds B5A and B5B at 500rpm for 10 min, at 45ºC, for 5 minutes, then, product is cooled to 35ºC and pH is adjusted to pH 8 with monoethanolamine. Then, product is cooled to 25ºC and perfume and/or perfume microcapsules are added according to table 15.

Table 15: addition of premix A5 and formula finishing

	5A	**5B**	**5C**
Ingredients	**Weight%**		
Detergent feed	75	75	75
Premix A5	2.5	3.0	6.0
Monoethanolamine	To pH 8.0		
Perfume	1.5	1.7	1.3

Perfume microcapsules[1]	2.3	-	1.5
Solvents (1,2 propanediol)	To 100 parts		

[1] as described in example 3

Examples 6A and 6B: laundry fluid detergent composition comprising amido-gellants: Detergent feeds 6A and 6B, having the compositions described in Table 16, are prepared. Then A3 premix is added and pH is adjusted to 8 with sodium hydroxide 20%.

Table 16: laundry fluid detergent composition comprising amido-gellants

Ingredient	6A	6B
	Wt%	Wt%
C12-14 alkyl polyethoxylate (3.0) sulfate	3.8	3.5
C_{11-8} HLAS	3.7	4.0
C12-14 alkyl 7-ethoxylate	1.4	1.4
1,2 Propane diol	0.18	0.25
Glycerine	2.00	2.00
Diethylene triamine penta acetate	0.48	0.48
Phenoxyethanol	0.1	0.1
Citric acid	1.70	2.5
Fluorescent Whitening Agent	0.057	-
Dodecyldimethylamine N-oxide	0.4	0.4
Zwitterionic ethoxylated quaternized sulfated hexamethylene diamine[1]	0.25	0.25
Perfume	0.43	0.30
PEG-PVAc Polymer[2]	0.5	0.5
Silicone suds supressor	0.0025	0.0025
Boric Acid	1.20	1.20
Calcium chloride	0.06	0.06
Acticide MBS 2550	0.01	0.01
Premix A3	5.0	10.0

Sodium hydroxide 20%	To pH 8	To pH 8
Water	up to 100%	up to 100%

[1] Described in WO 01/05874 and available from BASF (Ludwigshafen, Germany)

[2] PEG-PVA graft copolymer is a polyvinyl acetate grafted polyethylene oxide copolymer having a polyethylene oxide backbone and multiple polyvinyl acetate side chains. The molecular weight of the polyethylene oxide backbone is 6000 and the weight ratio of the polyethylene oxide to polyvinyl acetate is 40 to 60 and no more than 1 grafting point per 50 ethylene oxide units.

Example 7: Hand-dish washing fluid detergent compositions comprising amido-gellant. Hand-dish washing liquid detergent compositions may be prepared by mixing together the ingredients listed in the proportions shown:

Table 17: Hand-dish washing fluid detergent compositions comprising amido-gellant

	7
Alkyl Ethoxy Sulfate AE2.0S	18.0
Coco amido propyl Betaine	5.0
Polypropylene glycol MW2000	0.5
N,*N*'-(2*S*,2'*S*)-1,1'-(octane-1,8-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)bis(4-hydroxybenzamide)	0.25

Minors, citric acid and Balance with water up to 100% and pH 5.5.

Example 8: A liquid laundry detergent composition according to the present invention is prepared as follows:

Step 1: A structurant premix A1 is prepared by dissolving 0.20 grams *N,N'*-(2S,2'S)-1,1'-(dodecane-1,12-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide in 12.0 grams of 50% citric acid aqueous solution (prepared by dissolving 6.0 grams of citric acid solid in 6.0 grams deionized water) at 25°C.

Step 2: A detergent feed B1 having the composition described in Table 18 is prepared.

Table 18: Composition of detergent feed B1

Ingredient	Detergent Feed B1
	Grams
Linear Alkylbenzene sulfonic acid (LAS)	12.0
C12-14 alkyl ethoxy 3 sulfate Mono Ethanol Amine salt	9.3
C12-14 alkyl 7-ethoxylate	8.0
1,2-propanediol	9.8
C12-18 Fatty Acid	10.0
Grease Cleaning Alkoxylated Polyalkylenimine Polymer[1]	0.9
PEG PVAc Polymer[2]	0.9
Soil Suspending Alkoxylated Polyalkylenimine Polymer[3]	2.2
Hydroxyethane diphosphonic acid	1.6
FWA	0.23
Ethanol	1.5
Boric acid	0.5
MEA	Up to pH 8
Water up to	66 grams

[1] 600 g/mol molecular weight polyethylenimine core with 24 ethoxylate groups per -NH and 16 propoxylate groups per -NH.

[2] PEG-PVA graft copolymer is a polyvinyl acetate grafted polyethylene oxide copolymer having a polyethylene oxide backbone and multiple polyvinyl acetate side chains. The molecular weight of the polyethylene oxide backbone is 6000 and the weight ratio of the polyethylene oxide to polyvinyl acetate is 40 to 60 and no more than 1 grafting point per 50 ethylene oxide units.

[3] 600 g/mol molecular weight polyethylenimine core with 20 ethoxylate groups per -NH.

Step 3: 12.4 grams of structurant premix A1 is mixed with 66 grams of detergent feed B1 at 600rpm for 10 min, at 25°C, and the resulting mixture is adjusted to pH 8 with MEA.

Step 4: The pH sensitive ingredients (1.5 grams protease, 0.7 grams amylase, 0.1 grams mannanase, 0.1 grams xyloglucanase, 0.4 grams pectate lyase and 1.7 grams of perfume) and deionized water (to bring the final weight up to 100 grams) are added under gentle stirring, at 500-600rpm for 10 min.

Rheology Data

Table 19:

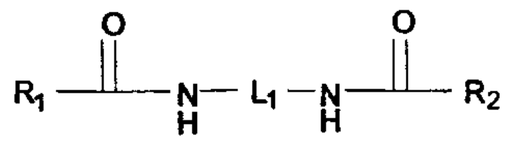
Example n.	Gel strength			Recovery
	G' (Pa)	G'' (Pa)	Oscillation stress (Pa)	Time (s)
1	90	27	6.3	<6
5A	70	40	6.3	52
5C	8140	1540	>10	<6
6A	60	25	1.3	<6
6B	3030	730	8	<6
8	45	5	>10	<6

The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as "40 mm" is intended to mean "about 40 mm".

CLAIMS:

1. A fluid detergent composition comprising:

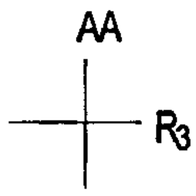
a) from 1% to 70% by weight of a surfactant selected from the group: anionic, nonionic surfactants and mixtures thereof; and

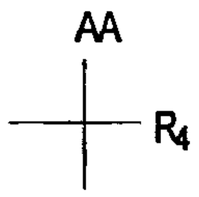
b) from 0.01 wt% to 10 wt% of a pH tuneable amido-gellant as an external structuring system having a formula 

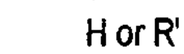
wherein:

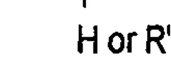
at least one of L_1, R_1 or R_2 comprises a pH-sensitive group;

L_1 is a backbone moiety having molecular weight from 14 to 500 g/mol;

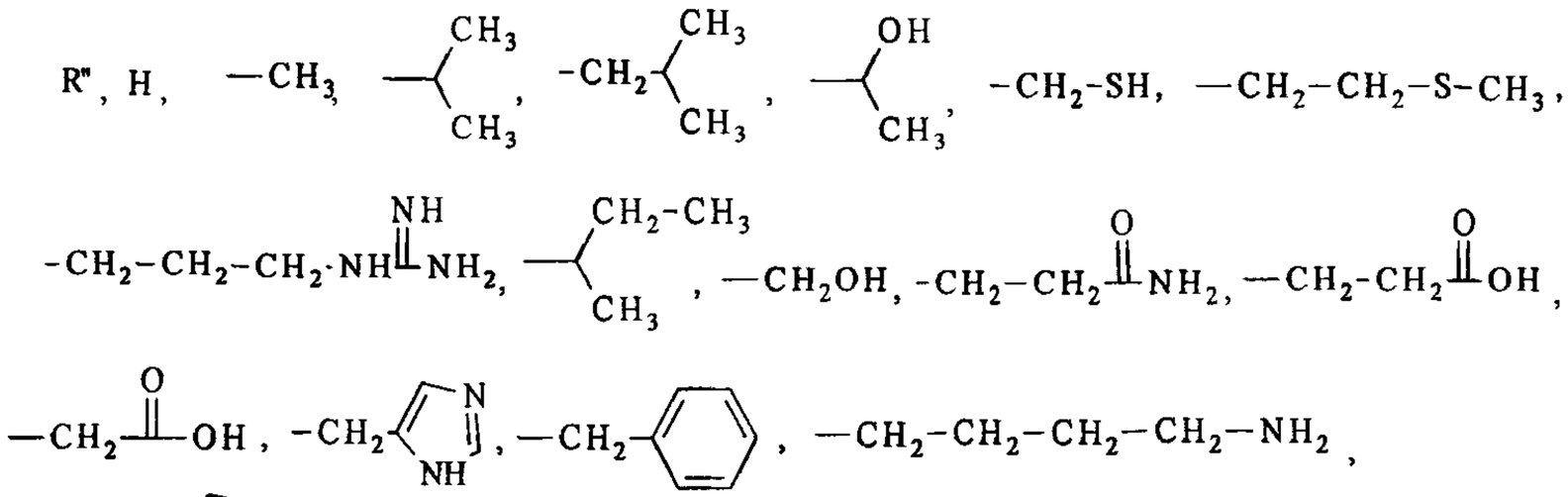




R_1 is R_3 or 

, R_2 is R_4 or 

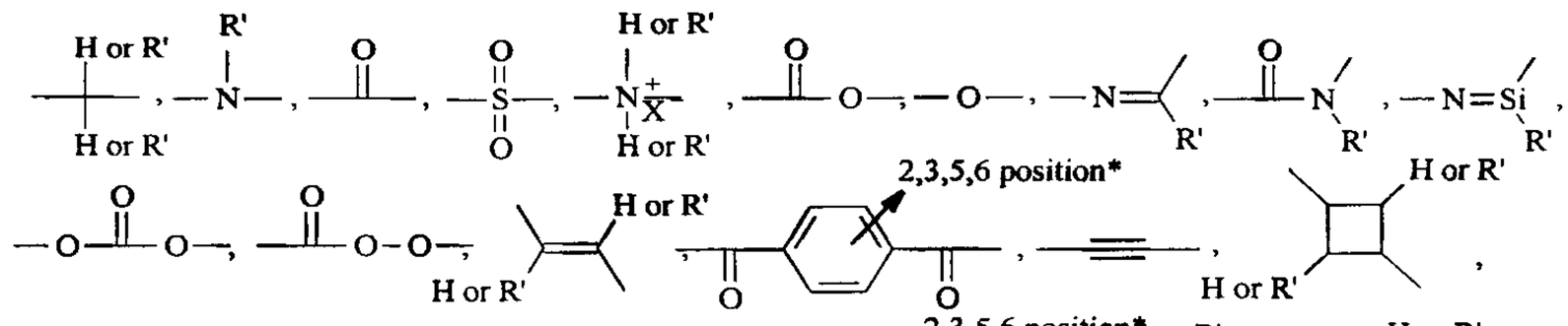
, wherein each AA is independently selected from the group consisting of:

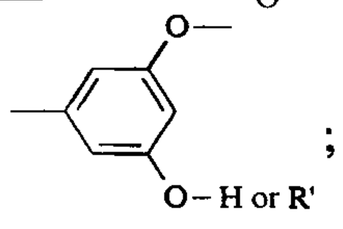


R_3 and R_4 independently have the formula:

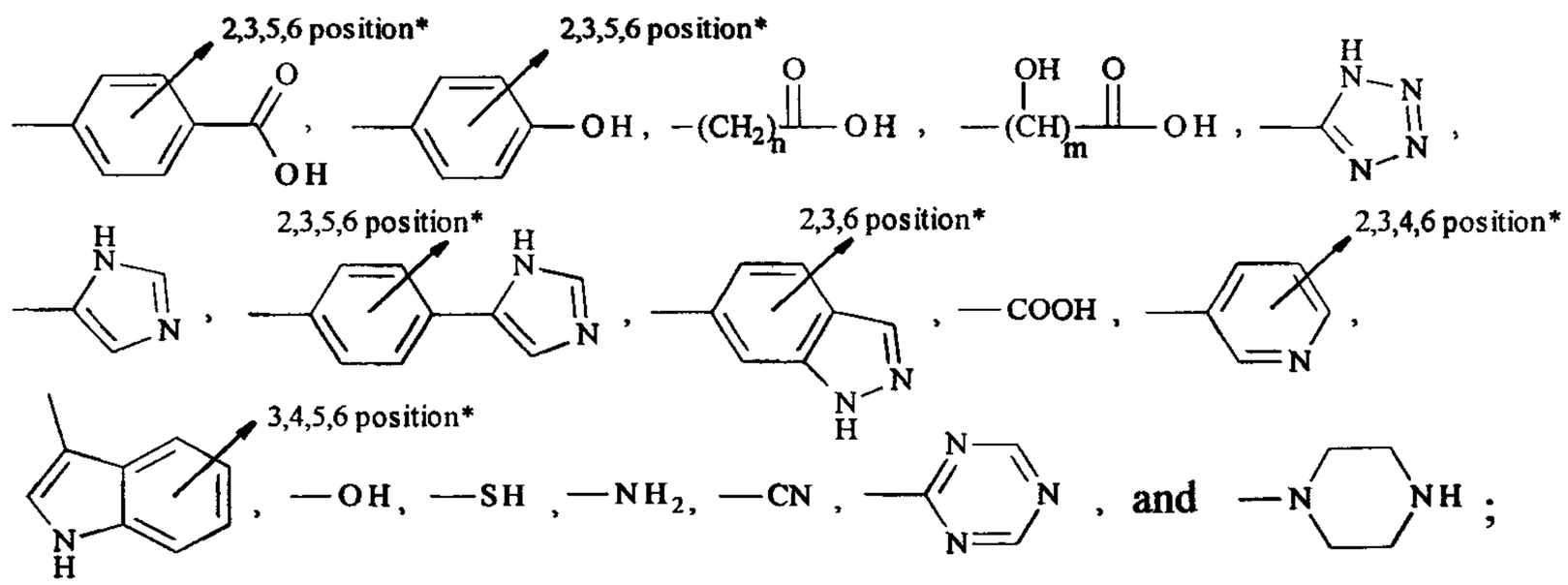
$(L')_o$-$(L'')_q$-R,

wherein: (o + q) is from 1 to 10; L' and L" are independently selected from:



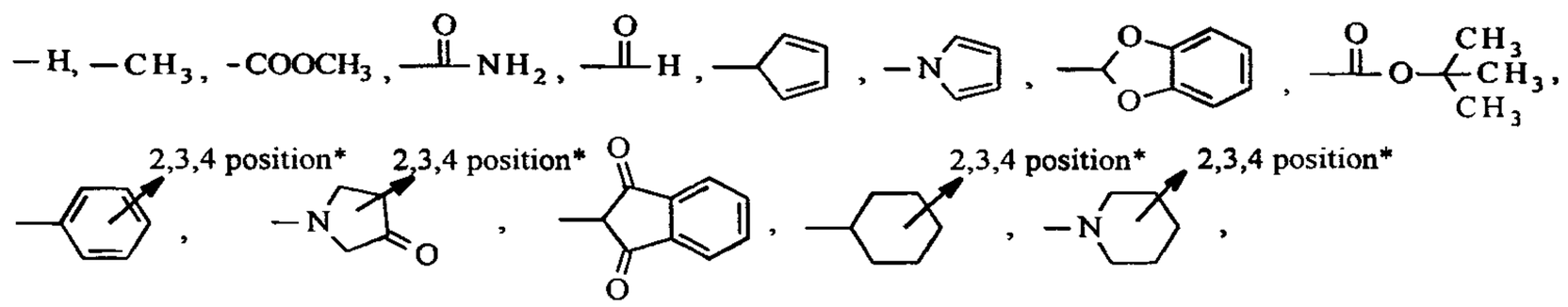
and  ;

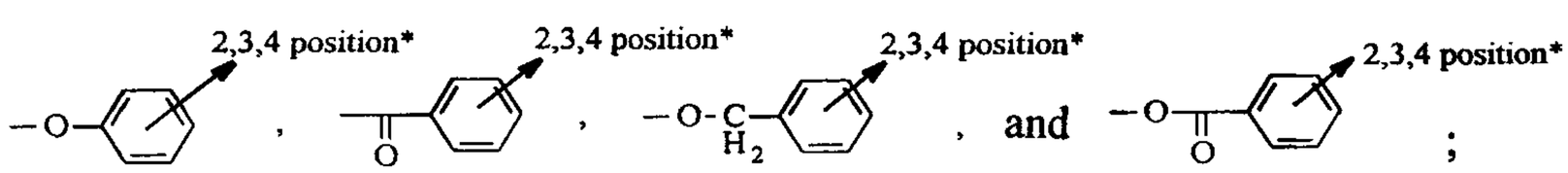
and R, R' and R" are independently selected either from pH-sensitive-groups consisting of:



wherein n and m are integers from 1 to 20;

or from non-pH-sensitive groups consisting of:





such that at least one of R, R' and R" comprises a pH-sensitive group;

wherein the pH tuneable amido-gellant has a pKa of from 1 to 30.

2. The fluid detergent composition according to claim 1, wherein the pH tuneable amido-gellant has a pKa of from 1.5 to 14.

3. The fluid detergent composition according to claim 1 or 2, wherein the pH tuneable amido-gellant has a molecular weight from 150 to 1500 g/mol.

4. The fluid detergent composition according to any one of claims 1 to 3, wherein the pH tuneable amido-gellant has a minimum gelling concentration (MGC) of from 0.1 to 100mg/mL, at the pH of the composition.

5. The fluid detergent composition according to any one of claims 1 to 4, wherein the pH tuneable amido gellant is selected from the group: *N*,*N*'-(2*S*,2'*S*)-1,1'-(ethane-1,2-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(propane-1,3-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide;*N*,*N*'-(2*S*,2'*S*)-1,1'-(butane-1,4-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(pentane-1,5-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(hexane-1,6-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(heptane-1,7-diylbis(azanediyl))bis(3-

methyl-1-oxobutane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(octane-1,8-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide; (6*S*,13*S*')-6,13-diisopropyl-4,7,12,15-tetraoxo-5,8,11,14-tetraazaoctadecane-1,18-dioic acid; (6*S*,14*S*')-6,14-diisopropyl-4,7,13,16-tetraoxo-5,8,12,15-tetraazanonadecane-1,19-dioic acid; (6*S*,15*S*')-6,15-diisopropyl-4,7,14,17-tetraoxo-5,8,13,16-tetraazaeicosane-1,20-dioic acid; (6*S*,16*S*')-6,16-diisopropyl-4,7,15,18-tetraoxo-5,8,14,17-tetraazaheneicosane-1,21-dioic acid; (6*S*,17*S*')-6,17-diisopropyl-4,7,16,19-tetraoxo-5,8,15,18-tetraazadocosane-1,22-dioic acid; (6*S*,18*S*')-6,18-diisopropyl-4,7,17,20-tetraoxo-5,8,16,19-tetraazatricosane-1,23-dioic acid; (6*S*,19*S*')-6,19-diisopropyl-4,7,18,21-tetraoxo-5,8,17,20-tetraazatetracosane-1,24-dioic acid; (6*S*,20*S*')-6,20-diisopropyl-4,7,19,22-tetraoxo-5,8,18,21-tetraazapentacosane-1,25-dioic acid; (6*S*,21*S*')-6,21-diisopropyl-4,7,20,23-tetraoxo-5,8,19,22-tetraazahexacosane-1,26-dioic acid; (6*S*,22*S*')-6,22-diisopropyl-4,7,21,24-tetraoxo-5,8,20,23-tetraazaheptacosane-1,27-dioic acid; (6*S*,23*S*')-6,23-diisopropyl-4,7,22,25-tetraoxo-5,8,21,24-tetraazaoctacosane-1,28-dioic acid; *N*,*N*'-(2*S*,2'*S*)-1,1'-(ethane-1,2-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)bis(4-(1H-imidazol-5-yl)benzamide); *N*,*N*'-(2*S*,2'*S*)-1,1'-(propane-1,3-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)bis(4-(1H-imidazol-5-yl)benzamide *N*,*N*'-(2*S*,2'*S*)-1,1'-(butane-1,4-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)bis(4-(1H-imidazol-5-yl)benzamide); *N*,*N*'-(2*S*,2'*S*)--1,1'-(pentane-1,5-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)bis(4-(1H-imidazol-5-yl)benzamide); *N*,*N*'-(2*S*,2'*S*)-1,1'-(hexane-1,6-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)bis(4-(1H-imidazol-5-yl)benzamide); *N*,*N*'-(2*S*,2'*S*)--1,1'-(heptane-1,7-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)bis(4-(1H-imidazol-5-yl)benzamide); *N*,*N*'-(2*S*,2'*S*)-1,1'-(octane-1,8-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)bis(4-(1H-imidazol-5-yl)benzamide); *N*,*N*'-(2*S*,2'*S*)-1,1'-(nonane-1,9-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)bis(4-(1H-imidazol-5-yl)benzamide); *N*,*N*'-(2*S*,2'*S*)-1,1'-(decane-1,10-diylbis(azanediyl))bis(3-

methyl-1-oxobutane-2,1-diyl)bis(4-(1H-imidazol-5-yl)benzamide); *N*,*N*'-(2*S*,2'*S*)-1,1'-(undecane-1,11-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)bis(4-(1H-imidazol-5-yl)benzamide); *N*,*N*'-(2*S*,2'*S*)-1,1'-(dodecane-1,12-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)bis(4-(1H-imidazol-5-yl)benzamide); N,N'-(2S,2'S)-1,1'-(nonane-1,9-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(decane-1,10-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(undecane-1,11-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(dodecane-1,12-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(tridecane-1,13-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(tetradecane-1,14-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(hexadecane-1,16-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(octadecane-1,18-diylbis(azanediyl))bis(3-methyl-1-oxobutane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(ethane-1,2-diylbis(azanediyl))bis(1-oxopropane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(propane-1,3-diylbis(azanediyl))bis(1-oxopropane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(butane-1,4-diylbis(azanediyl))bis(1-oxopropane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(pentane-1,5-diylbis(azanediyl))bis(1-oxopropane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(hexane-1,6-diylbis(azanediyl))bis(1-oxopropane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(heptane-1,7-diylbis(azanediyl))bis(1-oxopropane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(octane-1,8-diylbis(azanediyl))bis(1-oxopropane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(nonane-1,9-diylbis(azanediyl))bis(1-oxopropane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(decane-1,10-diylbis(azanediyl))bis(1-oxopropane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(undecane-1,11-diylbis(azanediyl))bis(1-oxopropane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-

(dodecane-1,12-diylbis(azanediyl))bis(1-oxopropane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(tridecane-1,13-diylbis(azanediyl))bis(1-oxopropane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(tetradecane-1,14-diylbis(azanediyl))bis(1-oxopropane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(hexadecane-1,16-diylbis(azanediyl))bis(1-oxopropane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(octadecane-1,18-diylbis(azanediyl))bis(1-oxopropane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(ethane-1,2-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(propane-1,3-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(butane-1,4-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(pentane-1,5-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(hexane-1,6-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)diisonicotinamide *N*,*N*'-(2*S*,2'*S*)-1,1'-(heptane-1,7-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(octane-1,8-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(nonane-1,9-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(decane-1,10-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(undecane-1,11-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(dodecane-1,12-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(tridecane-1,13-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(tetradecane-1,14-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(hexadecane-1,16-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)diisonicotinamide; *N*,*N*'-(2*S*,2'*S*)-1,1'-(octadecane-1,18-diylbis(azanediyl))bis(1-oxo-3-phenylpropane-2,1-diyl)diisonicotinamide; and mixtures thereof.

6. The fluid detergent composition according to any one of claims 1 to 5, wherein the composition additionally comprises: from 0.0001 % to 8 % by weight of a detersive enzyme, and has a neat pH from 6.5 to 10.5.

7. The fluid detergent composition according to claim 6, wherein the detersive enzyme is selected from the group consisting of: proteases, amylases, cellulases, lipases, xylogucanases, pectate lyases, mannanases, bleaching enzymes, cutinases, and mixtures thereof.

8. The fluid detergent composition according to any one of claims 1 to 7, wherein the composition is a fluid laundry detergent composition additionally comprising: from 0.1% to 12 % by weight of the bleach or bleach system, and exhibits a neat pH of from 6.5 to 10.5.

9. The fluid detergent composition according to any one of claims 1 to 7, wherein the composition is a fluid laundry bleach additive additionally comprising: from 0.1% to 12 % by weight of a bleach or bleach system, and exhibits a neat pH of from 2 to 6.

10. The fluid detergent composition according to any one of claims 1 to 9, wherein the surfactant is an anionic surfactant selected from the group consisting of: C_{11}-C_{18} alkyl benzene sulfonates, C_{10}-C_{20} branched-chain and random alkyl sulfates, C_{10}-C_{18} alkyl ethoxy sulfates, mid-chain branched alkyl sulfates, mid-chain branched alkyl alkoxy sulfates, C_{10}-C_{18} alkyl alkoxy carboxylates comprising 1-5 ethoxy units, modified alkylbenzene sulfonate, C_{12}-C_{20} methyl ester sulfonate, C_{10}-C_{18} alpha-olefin sulfonate, C_6-C_{20} sulfosuccinates, and mixtures thereof.

11. The fluid detergent composition according to any one of claims 1 to 10, wherein the composition additionally comprises an adjunct ingredient selected from the group consisting of: cationic surfactants, amphoteric or zwitterionic surfactants, non-

aminofunctional organic solvents, enzymes, enzyme stabilizers, amphiphilic alkoxylated grease cleaning polymers, clay soil cleaning polymers, soil release polymers, soil suspending polymers, bleaching systems, optical brighteners, hueing dyes, particulate material, perfume and other odour control agents, hydrotropes, suds suppressors, fabric care benefit agents, pH adjusting agents, dye transfer inhibiting agents, preservatives, non-fabric substantive dyes and mixtures thereof.

12. The fluid detergent composition according to any one of claims 1 to 11, wherein said fluid detergent composition is enclosed within a water soluble pouch material.

13. A process for making a fluid detergent composition as defined in any one of claims 1 to 12, comprising the steps of:

a) preparing a structurant premix comprising the pH tuneable amido gellant, wherein the structurant premix is at a pH such that the pH tuneable amido gellant is in its ionic, non-viscosity building, form;

b) combining the structurant premix with a detergent feed, said detergent feed comprising the anionic and/or nonionic surfactant; and

c) adjusting the pH of the combined fluid detergent composition as needed, such that the fluid detergent composition is at a pH at which the pH tuneable amido gellant is in its nonionic, viscosity building, form.

14. The process according to claim 13, for making a fluid detergent composition wherein the temperatures of the structurant premix and/or the detergent feed are maintained at less than 50 °C.

15. The process according to claim 13, for making a fluid detergent composition wherein the temperatures of the structurant premix and/or the detergent feed are maintained at less than 30°C.

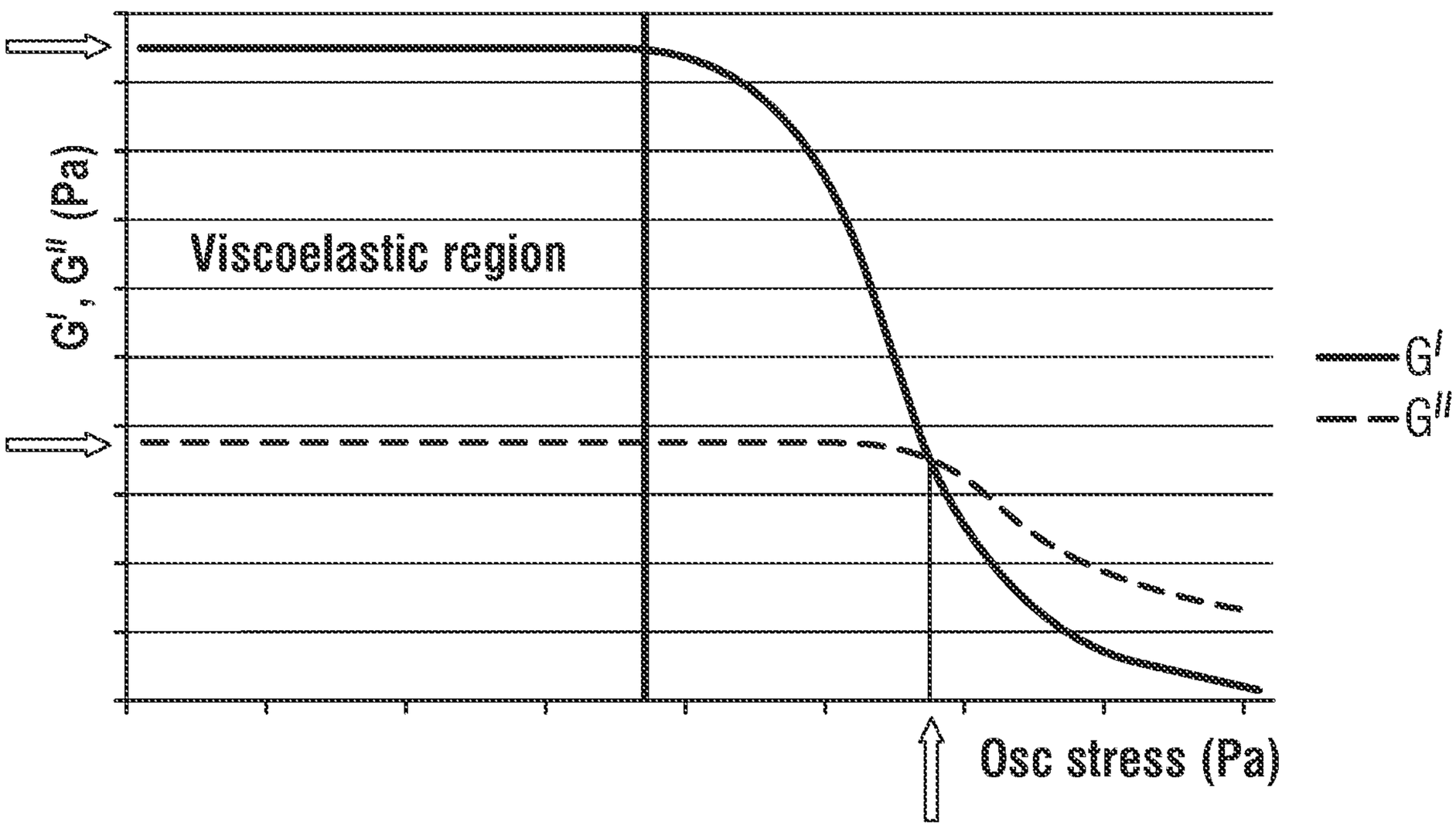


Fig. 1

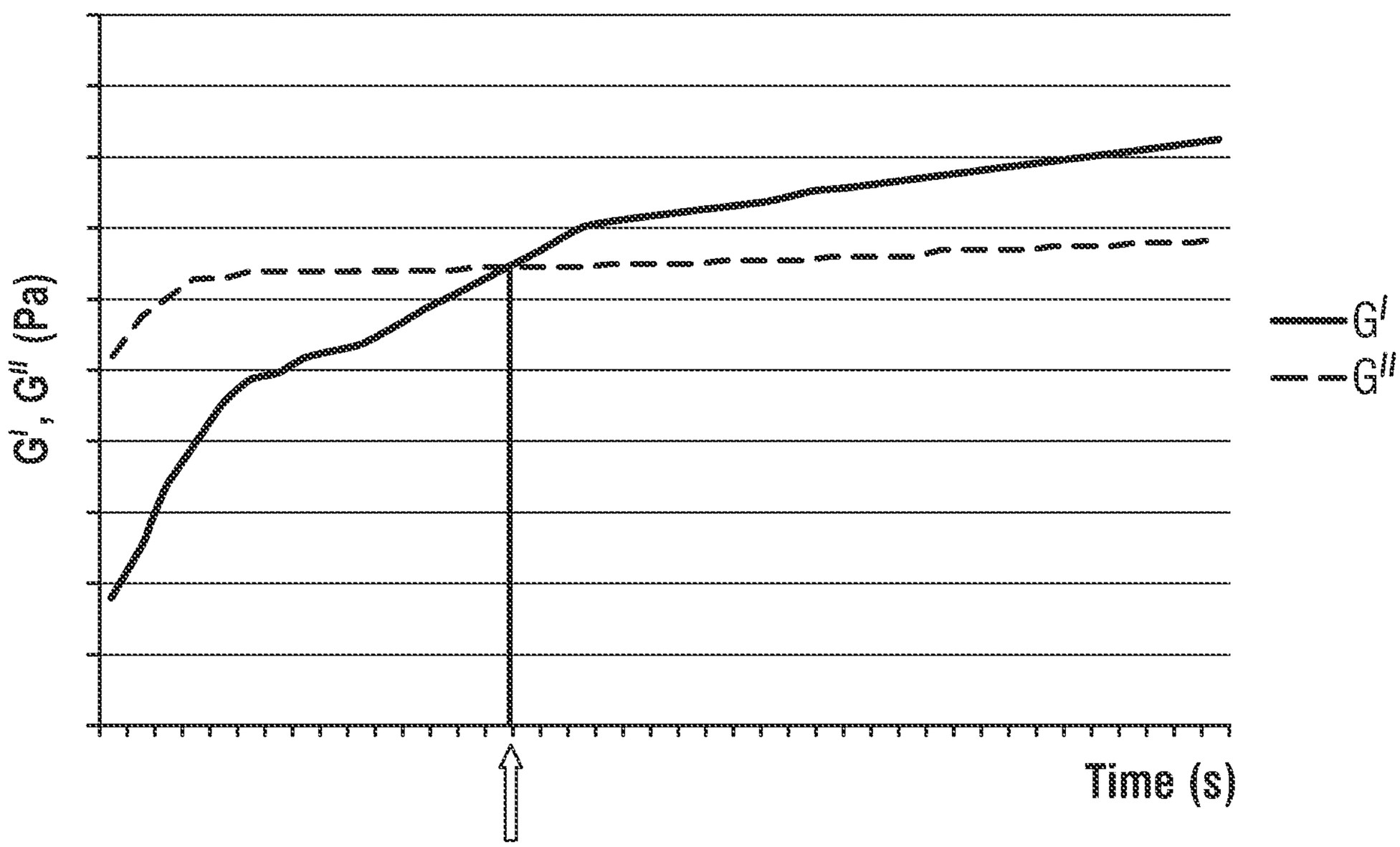
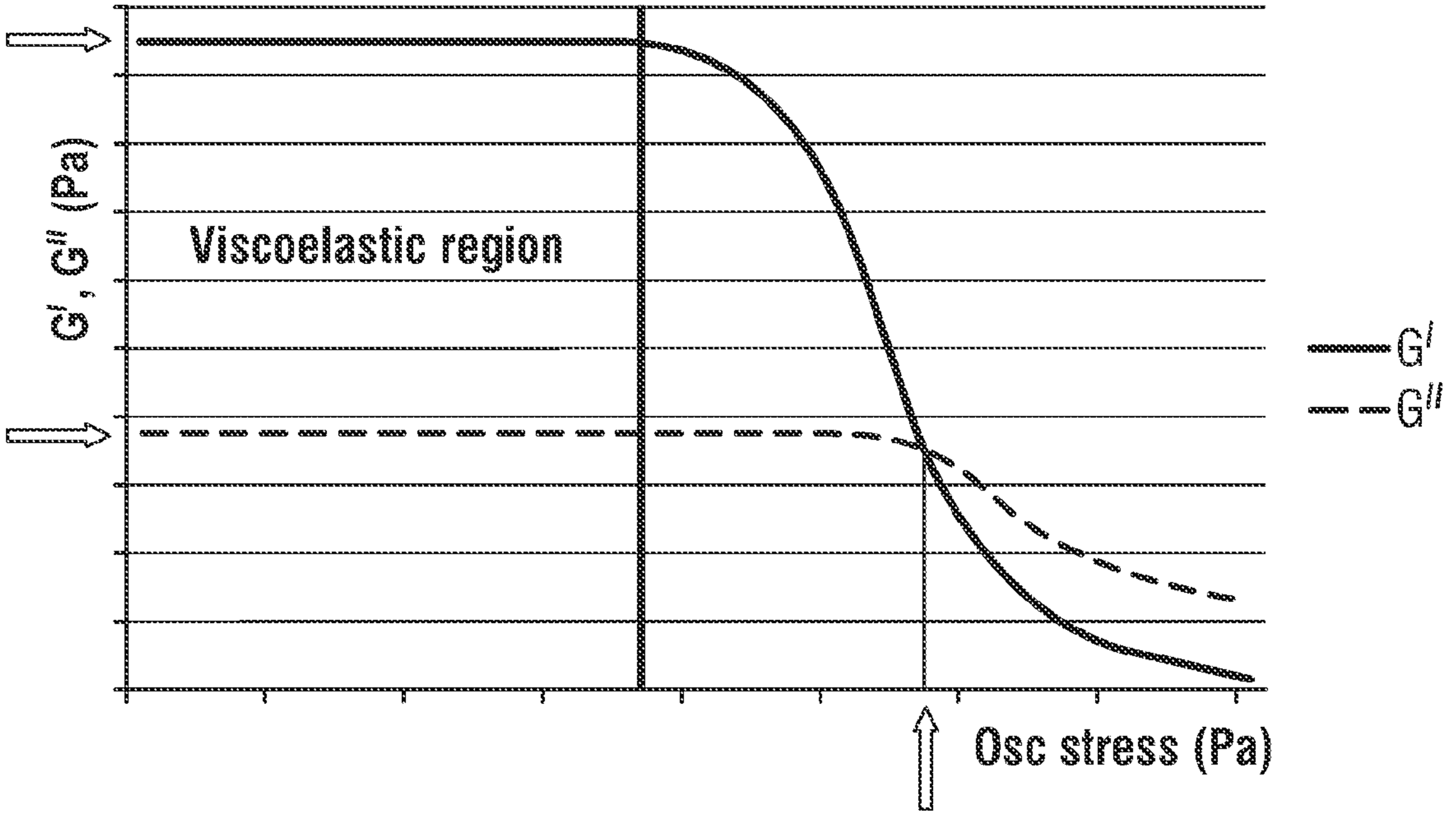


Fig. 2


G', G'' (Pa)
Viscoelastic region
G'
G''
Osc stress (Pa)