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(54) **Title**: POURABLE DETERGENT COMPOSITION

(57) **Abstract**: The invention relates to a pourable detergent composition comprising: · 30-75 wt.% glycerol; · 8-25 wt.% water; · 8-40 wt.% of one or more aminocarboxylate chelants; · 0.5-30 wt.% of one or more surfactants; wherein the combination of glycerol, water and aminocarboxylate chelant represents at least 60 wt.% of the composition. This pourable detergent composition has an exceptionally low water activity despite a considerable water content and is easy to manufacture. The invention further provides a process for the manufacture of the aforementioned pourable detergent composition.

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POURABLE DETERGENT COMPOSITION

TECHNICAL FIELD OF THE INVENTION

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The present invention relates to a pourable detergent composition. More particularly, the invention relates to a pourable detergent composition comprising glycerol, water, one or more aminocarboxylate chelants and one or more surfactants, wherein the combination of glycerol, water and aminocarboxylate chelant represents at least 60 wt.% of the composition.

10

The detergent composition of the present invention combines pourability with a very low water activity, despite the presence of a substantial amount of water.

15 BACKGROUND OF THE INVENTION

Detergent formulations typically contain a number of different active components, including surfactants, builders, enzymes and bleaching agents.

20 Surfactants are employed to release stains and soil and to disperse the released components into the cleaning liquid. Enzymes help to remove stubborn stains of proteins, starch and lipids by hydrolyzing these components. Bleaching agents are employed in detergent compositions to remove bleachable stains, such as those associated with tea, coffee, red wine, and various fruit and vegetable products, by oxidizing the components that make up these stains. Typical
25 bleaching agents for use in detergent formulations are chlorine- and peroxygen-based compounds, such as hypochlorite and percarbonate bleach, respectively.

Builders are incorporated in detergent formulations to complex magnesium and calcium ions as well as to maintain alkaline pH conditions. Phosphorous based builders, such as
30 phosphates, have been used for many years in a wide variety of detergent compositions. However, as part of an increasing trend towards environmentally friendly detergent compositions, alternative building agents have been developed and these alternative builders have found their way into commercial detergent products. The aminocarboxylate chelant L-glutamic-N,N-diacetate is an example of an environmentally friendly builder that is used in
35 commercial detergent products. Generally, aminocarboxylate chelants are present in

detergent formulations in the form of their (fully deprotonated) sodium salts. Aqueous solutions of aminocarboxylate salts are alkaline.

Liquid detergent formulations have been developed as these products offer the advantage

- 5 over powdered formulations that they are easy to dose, may contain higher concentrations of active ingredients, suffer less from moisture spoilage during storage and/or are more easily dispersed into aqueous cleaning liquid. In order to provide liquid detergent compositions that deliver cleaning, spotting and filming performance similar to that of a powdered formulation it is necessary to include components that remain undissolved in the liquid product matrix.
- 10 These undissolved components need to be homogeneously suspended throughout the product to guarantee a constant, optimum cleaning result. Although this may be achieved by instructing the user to shake the product before use, it is clearly preferable to provide the liquid detergent formulation in the form of a suspension that remains stable during the lifecycle of the product. This objective, however, is very difficult to achieve as suspensions
- 15 demix over time because suspended particles are subject to sedimentation and creaming/floating phenomena.

Bleaching agents and enzymes are moisture-sensitive detergent ingredients that lose their activity over time if the water activity of a detergent composition is too high.

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EP-A 1 129 160 describes liquid aqueous cleaning compositions containing water, glycerol, builder, enzyme and thickener.

WO 2007/141537 describes a liquid dishwashing formulation that contains water, GLDA, citric

- 25 acid, nonionic surfactant and enzymes.

WO 2013/092276 describes detergent formulations containing GLDA, water, citric acid, nonionic surfactant, coated spray-dried percarbonate, enzymes and other ingredients.

- 30 WO 2014/107578 describes detergent compositions containing water, glycerol, polyaminocarboxylic acid (chelating agent), nonionic surfactant, enzymes.

WO 2014/198547 describes a pourable thixotropic detergent composition comprising a

- continuous phase and at least 0.3 wt . % of suspended particles comprising water-soluble
- 35 surfactant, said continuous phase containing at least 10 wt .% of an aminocarboxylate chelant and at least 10 wt . % of water and said water-soluble surfactant being selected from aryl

sulfonate surfactant, alkyl sulfate surfactant and combinations thereof. Example 2 describes a liquid detergent formulation consisting of 96 wt.% of a premix and 4 wt.% of enzyme granulate. The premix comprises glycerol, water, aminocarboxylate chelant and surfactant.

- 5 US 2015/267153 describes a process for producing liquid low-water detergents or cleaning agents wherein at least one sulfo polymer and at least one builder component, are mixed together, wherein the at least one sulfo polymer is used in the form of an aqueous solution and the at least one builder component is used in solid form, wherein the builder component in solid form is selected from tripolyphosphate, MGDA, GLDA and combinations thereof. The
10 examples describe cleaning agents containing tripolyphosphate, glycerol and water.

SUMMARY OF THE INVENTION

- 15 The present inventors have developed a pourable detergent composition that offers the advantages of a liquid detergent composition, that has an exceptionally low water activity despite a considerable water content, and that is easy to manufacture.

The pourable detergent composition of the present invention comprises:

- 20 • 30-75 wt.% glycerol;
• 8-25 wt.% water;
• 8-40 wt.% of one or more aminocarboxylate chelants;
• 0.5-30 wt.% of one or more surfactants;

wherein the combination of glycerol, water and aminocarboxylate chelant represents at least
25 60 wt.% of the composition.

- Although the inventors do not wish to be bound by theory, it is believed that the combination glycerol, and aminocarboxylate chelant is capable of reducing the water activity of the detergent composition to very low levels, despite the presence of at least 8 wt.% water. The
30 combination of glycerol and water enables the preparation of a detergent composition that is pourable and homogeneous. The detergent compositions of the present invention further offer the advantage that a wide range of detergent ingredients can be incorporated therein in either dispersed or dissolved form.

The invention also provides a process of preparing the aforementioned pourable detergent composition, said method comprising the steps of:

- combining glycerol and water to prepare a liquid mixture; and
- adding the one or more aminocarboxylate chelants to the liquid mixture.

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DETAILED DESCRIPTION OF THE INVENTION

A first aspect of the present invention relates to a pourable detergent composition comprising:

- 10
- 30-75 wt.% glycerol;
 - 8-25 wt.% water;
 - 8-40 wt.% of one or more aminocarboxylate chelants;
 - 0.5-30 wt.% of one or more surfactants;

wherein the combination of glycerol, water and aminocarboxylate chelant represents at least
15 60 wt.% of the composition.

The term "pourable" as used herein refers to a composition that is able to flow under ambient conditions. Thixotropic compositions that can be rendered pourable by shear thinning are also regarded as pourable.

20

The term "thixotropic" as used herein refers to compositions (e.g. gels or fluids) that are viscous under quiescent conditions and that become less viscous when shaken, agitated, or otherwise stressed. In thixotropic compositions, this so called "shear thinning effect" is reversible, i.e. the composition will return to a more viscous state once it is no longer

25 subjected to shear stress.

The term "particles" as used herein, unless indicated otherwise, refers to a particulate matter in liquid or solid form, preferably solid form.

30 The term "aminocarboxylate chelant" as used herein refers to compounds containing one or more nitrogen atoms connected through carbon atoms to one or more carboxyl groups, which form strong complexes with metal ions by donation of electron pairs from the nitrogen and oxygen atoms to the metal ion to form multiple chelate rings.

Whenever reference is made herein to water content, unless indicated otherwise, said water content includes unbound (free) as well as bound water.

Whenever a parameter, such as a concentration or a ratio, is said to be less than a certain upper limit it should be understood that in the absence of a specified lower limit the lower limit for said parameter is 0.

Whenever an amount or concentration of a component is quantified herein, unless indicated otherwise, the quantified amount or quantified concentration relates to said component *per se*, even though it may be common practice to add such a component in the form of a solution or of a blend with one or more other ingredients.

The detergent composition of the present invention preferably contains water and the one or more aminocarboxylate chelants in a weight ratio of not more than 2:1, preferably of not more than 1.5:1, most preferably of not more than 1.2:1. Water and the one or more aminocarboxylate chelants are typically contained in the detergent composition in a weight ratio of at least 1:3, more preferably of at least 1:2 and most preferably of at least 1:1.8.

Glycerol and water are preferably contained in the pourable detergent composition in a weight ratio that lies within the range of 2:3 to 1:6, more preferably within the range of 1:2 to 1:5, most preferably within the range of 1:2.2 to 1:4.

The pourable detergent composition preferably contains up to 60 wt.%, more preferably 33-55 wt.% and most preferably 35-48 wt.% glycerol.

The water content of the detergent composition preferably is in the range of 10-22 wt.%, more preferably in the range of 11-20 wt.% and most preferably in the range of 12-18 wt.%.

The detergent composition typically has a water activity of 0.2 to 0.6 at 20°C. More preferably, the water activity of the detergent composition at 20°C is in the range of 0.3 to 0.5, most preferably of 0.35 to 0.45.

The pourable detergent composition preferably contains at least 10 wt.%, more preferably 12-30 wt.% and most preferably 13-25 wt.% of the one or more aminocarboxylate chelants.

Preferably the one or more aminocarboxylate chelants are selected from glutamic acid N,N-diacetic acid (GLDA), methylglycinediacetic acid (MGDA), iminodisuccinic acid (IDS), ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), hydroxyethyliminodiacetic acid (HEIDA), Nitrilotriacetic acid (NTA), aspartic acid

5 diethoxysuccinic acid (AES), aspartic acid-N, -diacetic acid (ASDA), hydroxyethylenediaminetetraacetic acid (HEDTA), hydroxyethylethylenediaminetriacetic acid (HEEDTA), iminodifumaric (IDF), iminoditartaric acid (IDT), iminodimaleic acid (IDMAL), iminodimalic acid (IDM), ethylenediaminedifumaric acid (EDDF), ethylenediaminedimalic acid (EDDM), ethylenediamineditartaric acid (EDDT), ethylenediaminedisuccinic acid (EDDS),

10 ethylenediaminedimaleic acid and (EDDMAL), dipicolinic acid, and their salts.

More preferably, the one or more aminocarboxylate chelants are selected from GLDA, MGDA, IDS, HEIDA, EDDS and NTA, and their salts. In an even more preferred embodiment, the one or more aminocarboxylate chelants are selected from GLDA, MGDA, IDS and their

15 salts. Most preferably, the the one or more aminocarboxylate chelants are selected from GLDA and salts thereof.

The GLDA employed in the present composition preferably is an alkali metal salt of glutamic-N,N-diacetic acid. More preferably, the GLDA employed is a sodium salt of glutamic-N,N-diacetic acid. Most preferably, the GLDA employed is a tetra sodium salt of glutamic-N,N-

20 diacetic acid.

The combination of glycerol, water and the one or more aminocarboxylate chelants typically represent at least 63 wt.%, preferably at least 65 wt.% of the detergent composition.

25 *Surfactants*

The present detergent composition contains one or more surfactants. Surfactants, within the invention, are components within the classification as described in "Surfactant Science Series", Vol.82, Handbook of detergents, part A: Properties, chapter 2 (Surfactants, classification), G. Broze (ed.). Typically, the detergent composition contains 0.5-30 wt.%,

30 preferably 1-20 wt.%, more preferably 1.3-10 wt.% of one or more surfactants. In a preferred embodiment, the surfactants are selected from one or more non-ionic surfactants.

According to a particularly preferred embodiment, the composition contains 0.1-15 wt.%, more preferably 0.5-10 wt.% and most preferably 1-5 wt.% of a nonionic surfactant or a

35 mixture of two or more non-ionic surfactants. Examples of nonionic surfactants that may be employed in the present composition include the condensation products of hydrophobic alkyl,

alkenyl, or alkyl aromatic compounds bearing functional groups having free reactive hydrogen available for condensation with hydrophilic alkylene oxide, such as ethylene oxide, propylene oxide, butylene oxide, polyethylene oxide or polyethylene glycol to form nonionic surfactants.

Examples of such functional groups include hydroxy, carboxy, mercapto, amino or amido

5 groups.

Examples of useful hydrophobes of commercial nonionic surfactants include C8-C18 alkyl fatty alcohols, C8-C14 alkyl phenols, C8-C18 alkyl fatty acids, C8-C18 alkyl mercaptans, C8-C18 alkyl fatty amines, C8-C18 alkyl amides and C8-C18 alkyl fatty alkanolamides.

10 Accordingly, suitable ethoxylated fatty alcohols may be chosen from ethoxylated cetyl alcohol, ethoxylated ketostearyl alcohol, ethoxylated isotridecyl alcohol, ethoxylated lauric alcohol, ethoxylated oleyl alcohol and mixtures thereof. Examples of suitable nonionic surfactants for use in the invention are found in the low- to non-foaming ethoxylated/ propoxylated straight-

15 chain alcohols of the Plurafac™ LF series, supplied by the BASF and the Synperonic™ NCA series supplied by Croda. Also of interest are the end-capped ethoxylated alcohols available as the SLF 18 series from BASF and the alkylpolyethylene glycol ethers made from a linear, saturated C16-C18 fatty alcohol of the Lutensol™ AT series, supplied by BASF. Other suitable nonionics to apply in the composition of the invention are modified fatty alcohol polyglycoethers available as Dehypon™ 3697 GRA or Dehypon™ Wet from BASF/Cognis.

20 Also suitable for use herein are nonionics from the Lutensol™ TO series of BASF, which are alkylpolyethylene glycol ethers made from a saturated iso-C13 alcohol. Amineoxide surfactants may also be used in the present invention as anti- redeposition surfactant.

Examples of suitable amineoxide surfactants are C10-C15 alkyl dimethylamine oxide and C10-C15 acylamido alkyl dimethylamine oxide. The inventors have found that, a detergent
25 composition that is not only chemically but also physically very stable can be produced if the nonionic surfactant employed is solid at ambient temperature. Thus, advantageously, the present composition contains 0.1 -30 wt.%, more preferably 0.5-20 wt.%, further preferred 1-10 wt.%, and most preferably 1 -5 wt.% of nonionic surfactant that is solid at 25°C.

30 If an anionic surfactant is used, the total amount present preferably is less than 5 wt.%, and more preferably not more than 2 wt.%. Furthermore, if an anionic surfactant is present, it is preferred that an antifoam agent to suppress foaming is present. Examples of suitable anionic surfactants are methylester sulphonates or sodium lauryl sulphate. It is preferred that no anionic surfactant is present in the composition of the current invention.

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Structuring biopolymer

In accordance with a particularly advantageous embodiment, the detergent composition of the present invention contains a structuring biopolymer. The inventors have found that the use of biopolymer that is capable of structuring water (e.g. through gelation) makes it possible to
5 prepare a fluid product with excellent rheological properties.

Preferably, the fluid product contains at least 0.1% of structuring biopolymer by weight of water. Even more preferably, the product contains 0.2-3%, most preferably 0.3-2% of structuring biopolymer by weight of water. Examples of structuring biopolymers that can be
10 employed include xanthan gum, locust bean gum, guar gum, gum Arabic, gellan gum, carrageenan, carboxymethyl cellulose, microcrystalline cellulose, microfibrinous cellulose and combinations thereof. More preferably, the structuring biopolymer is selected from xanthan gum, guar gum, carboxymethyl cellulose, microfibrinous cellulose and combinations thereof. Most preferably, the structuring biopolymer is xanthan gum.

Builders

In addition to the one or more aminocarboxylate chelants, the pourable detergent composition may contain additional water-softening builders. Traditionally phosphorous based builders, such as phosphates have been used as builders, but due to environmental pressures other
20 builders are preferred. These include organic builders such as citrate and inorganic builders such as carbonates, in particular sodium carbonate.

Citrate is preferably contained in the pourable detergent composition in a concentration of 0.1-4 wt.%, more preferably of 0.2-2 wt.%, most preferably of 0.25-1.2 wt.% citric acid
25 equivalent.

According to a particularly preferred embodiment, the detergent composition contains 3-30 wt.%, more preferably 5-25 wt.%, most preferably 7-20 wt.% of sodium carbonate.

Silicates

Silicates may be added to the formulation. Silicates can act as builder, buffering agent or article care agent. Preferred silicates are sodium silicate such as sodium disilicate, sodium metasilicate and crystalline phyllosilicates and mixtures thereof. Silicates are preferably used in the detergent composition in a concentration of 0.5 to 8%, more preferably of 0.8 to 6% by
35 weight of the composition.

Enzymes

Examples of enzymes suitable for use in the cleaning compositions of this invention include lipases, cellulases, peroxidases, proteases (proteolytic enzymes), amylases (amylolytic enzymes) and others which degrade, alter or facilitate the degradation or alteration of

5 biochemical soils and stains encountered in cleansing situations so as to remove more easily the soil or stain from the object being washed to make the soil or stain more removable in a subsequent cleansing step. Both degradation and alteration can improve soil removal.

Preferably, the one or more active enzymes contained in the present composition are

10 selected from protease, amylase, cellulase, peroxidase, mannanase, pectate lyase and lipase. Most preferably, the active enzyme is selected from protease, amylase and combinations thereof.

The composition of the present invention typically contains at least 10 mg/kg, more preferably

15 at least 20 mg/kg, even more preferably at least 50 mg/kg and most preferably at least 100 mg/kg of active enzyme. The concentration of active enzyme preferably does not exceed 50 g/kg, more preferably it does not exceed 40 g/kg and most preferably it does not exceed 30 g/kg.

20 According to a particularly preferred embodiment, the composition contains at least 10 mg/kg, more preferably at least 20 mg/kg and most preferably at least 50 mg/kg of active amylase.

According to another especially preferred embodiment, the composition contains at least 100 mg/kg, more preferably at least 200 mg/kg and most preferably at least 400 mg/kg of active

25 protease.

Enzymes may be added in liquid or in encapsulated form. Examples of encapsulated enzymes are enzyme granule types D, E and HS by Genencor and granule types, T, GT, TXT and Evity™ of Novozymes.

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The proteolytic enzymes in this invention include metal loproteases and serine proteases, including neutral or alkaline microbial serine protease, such as subtilisins (EC 3.4.21 .62).

The proteolytic enzymes for use in the present invention can be those derived from bacteria of fungi. Chemically or genetically modified mutants (variants) are included. Preferred

35 proteolytic enzymes are those derived from

Bacillus, such as B. lentus, B. gibsonii, B. subtilis, B. licheniformis, B. alkalophilus, B. amyloliquefaciens and Bacillus pumilus, of which B. lentus and B. gibsonii are most preferred. Examples of such proteolytic enzymes are Excellase™, Properase™, Purafect™, Purafect™ Prime, Purafect™ Ox by Genencor; and those sold under the trade names Blaze™, 5 Ovozyme™, Savinase™, Alcalase™, Everlase™, Esperase™, Relase™, Polarzyme™, Liquinase™ and Coronase™ by Novozymes.

The amylolytic enzymes for use in the present invention can be those derived from bacteria or fungi. Chemically or genetically modified mutants (variants) are included. Preferred amylolytic 10 enzyme is an alpha-amylase derived from a strain of Bacillus, such as B. subtilis, B. licheniformis, B. amyloliquefaciens or B. stearothermophilus. Examples of such amylolytic enzymes are produced and distributed under the trade name of Stainzyme™, Stainzyme™ Plus, Termamyl™, Natalase™ and Duramyl™ by Novozymes; as well as Powerase™, Purastar™, Purastar™ OxaM by Genencor. Stainzyme™, Stainzyme™ Plus and Powerase™ 15 are the preferred amylases.

In accordance with a particularly preferred embodiment of the invention, the composition contains active protease and the protease activity of the freshly prepared composition decreases by not more than 70%, more preferably by not more than 50% and most preferably by not more than 20% when the composition is stored in a closed container for 8 weeks at 20 20 °C. Well known enzyme stabilizers such as polyalcohols/borax, calcium, formate or protease inhibitors like 4-formylphenyl boronic acid may also be present in the composition.

Bleach

The present detergent composition preferably contains at least 0.3 wt.%, more preferably 1- 25 15 wt.% and most preferably 2-12 wt.% of bleaching agent.

The bleaching agent may suitably comprise a chlorine-, or bromine-releasing agent or a peroxygen compound. Preferably, the bleaching agent is selected from peroxides (including peroxide salts such as sodium percarbonate), organic peracids, salts of organic peracids and 30 combinations thereof. More preferably, the bleaching agent is a peroxide. Most preferably, the bleaching agent is a percarbonate.

Examples of peroxides are acids and corresponding salts of monopersulphate, perborate monohydrate, perborate tetrahydrate, and percarbonate. Organic peracids useful herein 35 include alkyl peroxy acids and aryl peroxyacids such as peroxybenzoic acid and ring substituted peroxybenzoic acids (e.g. peroxy-alpha- naphthoic acid), aliphatic and substituted

aliphatic monoperoxy acids (e.g. peroxy lauric acid and peroxy stearic acid), and phthaloyl amido peroxy caproic acid (PAP).

Typical diperoxy acids useful herein include alkyl diperoxy acids and aryl diperoxy acids, such as 1,12 di-peroxy-dodecanedioic acid (DPDA), 1,9 diperoxyazelaic acid, diperoxybrassylic acid, diperoxysebacic acid and diperoxy-isophthalic acid, and 2 decyldiperoxybutane 1,4 dioic acid.

The detergent composition of the present invention preferably contains bleaching agent in the form of particles. More preferably, the composition contains 0.3-15 wt.%, more preferably 0.5-10 wt.% of particles of bleaching agent.

According to a preferred embodiment, the particles of bleaching agent are coated particles comprising one or more core particles that contain the bleaching agent, which one or more core particles are enclosed by a water-soluble coating. The water-soluble coating advantageously comprises a coating agent selected from alkali sulphate, alkali carbonate or alkali chloride and combinations thereof.

The detergent composition may contain one or more bleach activators such as peroxyacid bleach precursors. Peroxyacid bleach precursors are well known in the art. As non-limiting examples can be named N,N,N',N'-tetraacetyl ethylene diamine (TAED), sodium nonanoyloxybenzene sulphonate (SNOBS), sodium benzoyloxybenzene sulphonate (SBOBS) and the cationic peroxyacid precursor (SPCC) as described in US-A-4,751,015.

If desirable, a bleach catalyst, such as the manganese complex, e.g. Mn-Me TACN, as described in EP-A-0458397, or the sulphonimines of US-A-5,041,232 and US-A- 5,047,163, can be incorporated. Cobalt or iron catalysts can also be used.

Dispersing polymers

The detergent composition may suitably contain one or more dispersing polymers. Dispersing polymers as referred to in this invention are chosen from the group of anti-spotting agents and/or anti-scaling agents.

Examples of suitable anti-spotting polymeric agents include hydrophobically modified polycarboxylic acids such as Acusol™ 460 ND (ex Dow) and Alcosperse™ 747 by AkzoNobel, whereas also synthetic clays, and preferably those synthetic clays which have a

high surface area are very useful to prevent spots, in particular those formed where soil and dispersed remnants are present at places where the water collects on the glass and spots formed when the water subsequently evaporates.

- 5 Examples of suitable anti-scaling agents include organic phosphonates, amino carboxylates, polyfunctionally-substituted compounds, and mixtures thereof.

Particularly preferred anti-scaling agents are organic phosphonates such as alpha-hydroxy-2 phenyl ethyl diphosphonate, ethylene diphosphonate, hydroxy 1,1 - hexylidene, vinylidene 1
10 ,1 -diphosphonate, 1,2-dihydroxyethane 1,1 -diphosphonate and hydroxy-ethylene 1,1 - diphosphonate. Most preferred is hydroxy-ethylene 1,1 - diphosphonate (EDHP) and 2-phosphono-butane, 1,2,4-tricarboxylic acid (Bayhibit ex Bayer). Suitable anti-scaling agents are water soluble dispersing polymers prepared from an allyloxybenzenesulfonic acid monomer, a methallyl sulfonic acid monomer, a copolymerizable nonionic monomer and a
15 copolymerizable olefinically unsaturated carboxylic acid monomer as described in US 5 547 612 or known as acrylic sulphonated polymers as described in EP 851 022. Polymers of this type include polyacrylate with methyl methacrylate, sodium methallyl sulphonate and sulphophenol methallyl ether such as Alcosperse™ 240 supplied (AkzoNobel). Also suitable is a terpolymer containing polyacrylate with 2-acrylamido-2 methylpropane sulphonic acid
20 such as Acumer 3100 supplied by Dow. As an alternative, polymers and co-polymers of acrylic acid having a molecular weight between 500 and 20,000 can also be used, such as homo-polymeric polycarboxylic acid compounds with acrylic acid as the monomeric unit. The average weight of such homo-polymers in the acid form preferably ranges from 1,000 to 100,000 particularly from 3,000 to 10,000 e.g. Sokalan™ PA 25 from BASF or Acusol™ 425
25 from Dow.

Also suitable are polycarboxylates co-polymers derived from monomers of acrylic acid and maleic acid, such as CP 5 from BASF. The average molecular weight of these polymers in the acid form preferably ranges from 4,000 to 70,000. Modified polycarboxylates like
30 Sokalan™CP42, Sokalan™ CP50 from BASF or Alcoguard™ 4160 from AkzoNobel may also be used.

Mixture of anti-scaling agents may also be used. Particularly useful is a mixture of organic phosphonates and polymers of acrylic acid. It is preferable if the level of dispersing polymers
35 ranges from 0.2 to 10 wt.% of the total composition, preferably from 0.5 to 8 wt.%, and further preferred from 1 to 6 wt.%.

Other ingredients Glass corrosion inhibitors can prevent the irreversible corrosion and iridescence of glass surfaces in machine dishwasher detergents. The claimed composition may suitably contain glass corrosion inhibitors. Suitable glass corrosion agents can be selected from the group consisting of salts of zinc, bismuth, aluminum, tin, magnesium, calcium, strontium, titanium, zirconium, manganese, lanthanum, mixtures thereof and precursors thereof. Most preferred are salts of bismuth, magnesium or zinc or combinations thereof. Preferred levels of glass corrosion inhibitors in the present composition are 0.01 -2 wt.%, more preferably 0.01 - 0.5 wt.%.

Anti-tarnishing agents may prevent or reduce the tarnishing, corrosion or oxidation of metals such as silver, copper, aluminium and stainless steel. Anti-tarnishing agents such as benzotriazole or bis-benzotriazole and substituted or substituted derivatives thereof and those described in EP 723 577 (Unilever) may also be included in the composition. Other anti-tarnishing agents that may be included in the detergent composition are mentioned in WO 94/26860 and WO 94/26859. Suitable redox active agents are for example complexes chosen from the group of cerium, cobalt, hafnium, gallium, manganese, titanium, vanadium, zinc or zirconium, in which the metal are in the oxidation state of II, III, IV V or VI.

Optionally other components may be added to the formulation such as perfume, colorant or preservatives. The desired viscosity profile of the detergent composition depends on the end use of the product. It may be a liquid, gel or a paste depending on the application. Another aspect of the present invention relates to a water-soluble sachet that is filled with a composition as defined herein before.

Rheology

According to a particularly preferred embodiment of the present invention the detergent composition is a thixotropic composition.

The term "thixotropic" means that the product is viscous under quiescent conditions and become less viscous when shaken, agitated, or otherwise stressed. In thixotropic compositions, this so called "shear thinning effect" is reversible, i.e. the composition will return to a more viscous state once it is no longer subjected to shear stress. This thixotropic behavior of the detergent composition can be demonstrated by measuring the storage modulus (G') and the loss modulus (G'') of the product as a function of angular frequency (ω) on a rheometer in oscillatory mode. Both G' and G'' of the fluid product increase as a function

of angular frequency (ω), be it that G'' increases at a faster rate than G' . At very low angular frequency (ω) G'' of the fluid product is lower than G' , but at an ω in the range of 0.05-50 rad/s G'' surpasses G' .

- 5 Both the storage modulus (G') and the loss modulus (G'') of the fluid product are determined at 20°C using Anton Paar® MCR 302 rheometer, using plate-plate geometry, spindle PP50/S (sandblasted) and a gap size of 3mm. The program settings applied are as follows:
 - A Strain γ is chosen in the Linear Visco-elastic range of the product (LVER is determined by an Amplitude Sweep). The strain is kept constant on 0.1%.
 - 10 • An increasing ramp log of angular frequency ω is set on the sample from low to high frequency, starting at 0.01 rad/s. The end ω is 100 rad/s unless the sample is very stiff.
 - The setting in which the measuring points are gathered is the 'no time settings'. In this modus the apparatus waits for a steady state situation before it takes his measuring point.
 - Every decade six measuring points are taken.
- 15 Using oscillatory rheology, it is possible to quantify both the viscous-like and the elastic-like properties of a material at different time scales. The basic principle of an oscillatory rheometer is to induce a sinusoidal shear deformation in the sample and measure the resultant stress response; the time scale probed is determined by the frequency of oscillation, ω , of the shear deformation. A sample is placed between two plates. While the top plate remains stationary, a
 - 20 motor rotates the bottom plate, thereby imposing a time dependent strain $\gamma(t) = \gamma \cdot \sin(\omega t)$ on the sample. Simultaneously, the time dependent stress $\sigma(t)$ is quantified by measuring the torque that the sample imposes on the top plate.

Measuring this time dependent stress response at a single frequency immediately reveals key
 25 differences between materials. If the material is an ideal elastic solid, then the sample stress is proportional to the strain deformation, and the proportionality constant is the shear modulus of the material. The stress is always exactly in phase with the applied sinusoidal strain deformation.

- 30 In contrast, if the material is a purely viscous fluid, the stress in the sample is proportional to the rate of strain deformation, where the proportionality constant is the viscosity of the fluid. The applied strain and the measured stress are out of phase, with a phase angle $\delta = \pi/2$.

Viscoelastic materials show a response that contains both in-phase and out-of-phase
 35 contributions. These contributions reveal the extents of solid-like and liquid-like behavior. As a

consequence, the total stress response shows a phase shift δ with respect to the applied strain deformation that lies between that of solids and liquids, $0 < \delta < \pi/2$. The viscoelastic behaviour of the system at ω is characterised by the storage modulus, $G'(\omega)$, and the loss modulus, $G''(\omega)$, which respectively characterise the solid-like and fluid-like contributions to the measured stress response. For a sinusoidal strain deformation $\gamma(t) = \gamma_0 \sin(\omega t)$, the stress response of a viscoelastic material is given by $\sigma(t) = G'(\omega)\gamma_0 \sin(\omega t) + G''(\omega)\gamma_0 \cos(\omega t)$.

Whether the product behaves more solid-like or more liquid-like depends on the time scale at which it is deformed. At the lowest accessible frequencies the fluid product of the present invention has a loss modulus that is lower than the storage modulus, indicating solid-like behavior, while at the highest frequencies accessed the loss modulus dominates the response, indicating viscous-like behavior.

In accordance with a particularly advantageous embodiment of the present invention the detergent composition is a thixotropic composition having a storage modulus at 20°C ($G'(\omega)$) and a loss modulus at 20°C ($G''(\omega)$), both moduli measured as a function of angular frequency (ω) on a rheometer in oscillatory mode operating at a strain of 0.1%, wherein:

- $G''(\omega) > G'(\omega)$ at angular frequencies (ω) in the range of 50 to 100 rad/s, and
- $G''(\omega) < G'(\omega)$ at angular frequencies (ω) in the range of 0.01-0.05 rad/s.

Especially preferred is a detergent composition having a storage modulus (G') and a loss modulus (G'') that meet at least one of the following conditions:

- $G''(\omega) > G'(\omega)$ at angular frequencies (ω) in the range of 30 to 100 rad/s, more preferably in the range of 10 to 100 rad/s;
- $G''(\omega) < G'(\omega)$ at angular frequencies (ω) in the range of 0.01 to 0.2 rad/s, more preferably in the range of 0.01 to 0.5 rad/s.

The pourable detergent composition typically has a storage modulus (G') at 0.2 rad/s in the range of 1 to 100 Pa, more preferably in the range of 8 to 30 Pa, most preferably in the range of 10 to 20 Pa.

The loss modulus (G'') of the pourable detergent composition at 0.2 rad/s preferably is in the range of 1 to 100 Pa, more preferably in the range of 3 to 60 Pa, most preferably in the range of 8 to 30 Pa.

Manufacture

Another aspect of the invention relates to a process of preparing a detergent composition as disclosed herein, which method comprises the steps of:

- combining glycerol and water to prepare a liquid mixture; and
- 5 • mixing the one or more aminocarboxylate chelants with the liquid mixture to form a homogenous fluid.

In a preferred embodiment the one or more aminocarboxylate chelants are added to the liquid under reduced pressure, e.g. a pressure of less than 900 mbar, to minimize formation of air
10 bubbles.

In accordance with another preferred embodiment one or more particulate detergent ingredients are added to the homogenous fluid. Examples of particulate detergent ingredients that may be added at this stage include bleaching agent, bleach activator, enzymes and
15 surfactants.

Packaging

The pourable detergent composition is in particular suitable to be packaged in a container comprising a container wall and an outlet, such as a bottle, to allow adaptation of the dose to the amount of soil on the dish ware. Such a container or bottle is suitable for multiple use. In a
20 preferred embodiment, the container has at least one translucent outer wall. In another embodiment, the pourable detergent composition can be packaged in a container suitable for single use.

In accordance with this embodiment, such a single use container holds one unit of the detergent formulation and is at least partly made from water-soluble material. Examples of
25 containers that may be used in accordance with this embodiment are sachets (pouches) and capsules.

Suitably, the single use container is not only water-insoluble, but also water-permeable. More particularly, it is preferred that the container is made of a water-permeable and water-soluble
30 polymer selected from polyvinyl alcohol, cellulose ethers, polyethylene oxide, starch, polyvinylpyrrolidone, polyacrylamide, polyvinyl methyl ether-maleic anhydride, polymaleic anhydride, styrene maleic anhydride, hydroxyethylcellulose, methylcellulose, polyethylene glycols, carboxymethylcellulose, polyacrylic acid salts, alginates, acrylamide copolymers, guar gum, casein, ethylene-maleic anhydride resin series, polyethylene imine, ethyl
35 hydroxyethylcellulose, ethyl methylcellulose, hydroxyethyl methylcellulose and combinations

thereof. Even more preferably, the single use container is made of polyvinyl alcohol, polyethelene oxide, polyvinylpyrrolidone and combinations thereof.

In another preferred embodiment, the single use container is made of a water-permeable and water-insoluble polymer selected from butyral resin, polyvinyl acetal, poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate), polyvinyl butyrate, polyvinyl acetate and combinations and comonomers thereof.

Most preferably, the single use container is made of polyvinyl alcohol, a copolymer of polyvinyl alcohol and combinations thereof. Polyvinyl alcohols preferred have a weight average molecular weight between 1,000 and 300,000, more preferably, between 2,000 and 150,000, and most preferably, between 3,000 and 100,000.

According to a preferred embodiment, the container comprises 5-40 ml, more preferably 8-30-ml and most preferably 10-20-ml of the detergent formulation.

The invention is further illustrated by the following non-limiting examples.

EXAMPLES

Example 1

A thixotropic machine dishwashing product was prepared on the basis of the recipe that is shown in Table 1.

Table 1

Ingredients	Wt. %
Glycerol	60.56
Citric Acid (50% aqueous solution)	2.5
Dissolvine™ GL 47-S ¹	10.79
Dissolvine™ PD-S ²	14.84
Demi water	9.31
Xanthan Gum	0.39
Lutensol™ AT80 (nonionic surfactant)	1.22

¹ Contains appr. 48 wt.% GLDA and 45 wt.% water

² Contains appr. 85 wt.% GLDA and 9 wt.% water

The product was prepared as follows: a liquid premix was made by mixing glycerol and xanthan gum to a homogeneous suspension. Next, demi water was added under constant

stirring. After that Dissolvine™ GL 47-S and citric acid were dosed at ambient temperature. Next, Dissolvine™ PD-S was mixed in. Finally, the nonionic surfactant was added to the mix under stirring. All ingredients were mixed in under vacuum to minimize formation of air bubbles.

5

The rheological properties of the thixotropic detergent composition, measured 7 hours from production, are summarized in Table 2.

Table 2

ω (in rad/s)	G' (in Pa)	G'' (in Pa)
0.05	16.5	4.6
0.1	19	5.5
0.5	25	9
1	30	12.6
3.2	37	23.5
10	51	48.2
32	72	108
100	57	255

10

Example 2

Thixotropic machine dishwashing compositions were prepared on the basis of the recipes shown in Table 3

15

Table 3

Ingredients	Wt. %	
	1	2
Glycerol	60.8	37.4
Citric Acid (50% aqueous solution)	2.5	4.0
Dissolvine™ GL 47-S	10.8	17.3
Dissolvine™ PD-S 2	14.9	23.8
Demi water	9.4	15.0
Xanthan Gum	0.4	0.6
Lutensol™ AT80 (nonionic surfactant)	1.2	1.9

The compositions were prepared in batches of 3 kg in a Unimix (ex Haagen & Rinau) mixer, that was operated under vacuum at 70 rpm, whilst keeping the temperature of the mixer

20 contents at 20°C. The mixing procedure used was as follows:

- introduce glycerol and xanthan and mix for 20 minutes;
- add demi water and continue mixing for 20 minutes;
- add citric acid solution and Dissolvine™ GL 47-S and continue mixing for 5 minutes;

- add Dissolvine™ PD-S 2 and continue mixing for 40 minutes;
- add Lutensol™ AT80 and continue mixing for 65 minutes.

The compositions so obtained were viscous, semi-transparent liquids. Both compositions
5 could rapidly be dissolved in tap water of 40°C. Composition 1 had a water activity of 0.42
whereas composition 2 had a water activity of 0.54.

CLAIMS

1. A pourable detergent composition comprising:
 - 30-75 wt.% glycerol;
 - 8-25 wt.% water;
 - 8-40 wt.% of one or more aminocarboxylate chelants;
 - 0.5-30 wt.% of one or more surfactants;wherein the combination of glycerol, water and aminocarboxylate chelant represents at least 60 wt.% of the composition.
2. Detergent composition according to claim 1, wherein the composition contains water and the one or more aminocarboxylate chelants in a weight ratio of not more than 2:1.
3. Detergent composition according to claim 1 or 2, wherein the one or more aminocarboxylate chelants are selected from GLDA, MGDA, IDS and combinations thereof.
4. Detergent composition according to claim 3, wherein the aminocarboxylate chelant is GLDA.
5. Detergent composition according to any one of the preceding claims, wherein the composition contains water and glycerol in a weight ratio water to glycerol in the range of 2:3 to 1:6.
6. Detergent composition according to any one of the preceding claims, wherein the composition contains at least 0.1% of structuring biopolymer by weight of water.
7. Detergent composition according to claim 7, wherein the structuring biopolymer is selected from xanthan gum, locust bean gum, guar gum, gum Arabic, gellan gum, carrageenan, carboxymethyl cellulose, microcrystalline cellulose, microfibrinous cellulose and combinations thereof.
8. Detergent composition according to claim 8, wherein the structuring biopolymer is xanthan gum.

9. Detergent composition according to any one of the preceding claims, wherein the composition contains citrate in a concentration of 0.1-4 wt.% citric acid equivalent.
10. Detergent composition according to any one of the preceding claims, wherein the composition has a water activity of 0.2 to 0.6 at 20°C.
11. Detergent composition according to any one of the preceding claims, wherein the composition is a thixotropic composition having a storage modulus at 20°C ($G'(\omega)$) and a loss modulus at 20°C ($G''(\omega)$), both moduli measured as a function of angular frequency (ω) on a rheometer in oscillatory mode operating at a strain of 0.1%, wherein:
- $G''(\omega) > G'(\omega)$ at angular frequencies (ω) in the range of 50 to 100 rad/s, and
 - $G''(\omega) < G'(\omega)$ at angular frequencies (ω) in the range of 0.01 to 0.05 rad/s.
12. Detergent composition according to any one of the preceding claims, wherein the composition has a storage modulus (G') at 0.2 rad/s and 20°C in the range of 1 to 100 Pa.
13. Detergent composition according to any one of the preceding claims, wherein the composition has a loss modulus (G'') at 0.2 rad/s and 20°C in the range of 1 to 100 Pa.
14. Detergent composition according to any one of the preceding claims, wherein the composition contains at least 0.3 wt.% of bleaching agent.
15. A process of preparing a detergent composition according to any one of the preceding claims, said process comprising the steps of
- combining glycerol and water to prepare a liquid mixture; and
 - adding the one or more aminocarboxylate chelants to the liquid mixture.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/054718

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D1/66 C11D3/20 C11D3/33 C11D17/00
ADD.

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

B. FIELDS SEARCHED

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

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2015/267153 A1 (BENDA KONSTANTIN [DE] ET AL) 24 September 2015 (2015-09-24) paragraphs [0002], [0003], [0007] - [0011], [0014] - [0017], [0024], [0025] - [0027], [0071], [0077], [0100], [0103], [0114] paragraphs [0126], [0128]; claim 1; examples E1, E2 ----- -/--	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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

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

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

"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2014/198547 A2 (UNILEVER NV [NL]; UNILEVER PLC [GB]; CONOPCO INC DBA UNILEVER [US]) 18 December 2014 (2014-12-18) page 1, paragraph 1-2 page 5, paragraph 1 - page 6, paragraph 2 page 11, paragraph 3 page 18, paragraph 3-4 page 26, paragraph 1 page 2, paragraph 3 -----	1-15
Y	WO 2013/092276 A1 (UNILEVER NV [NL]; UNILEVER PLC [GB]; UNILEVER HINDUSTAN [IN]; CONOPCO) 27 June 2013 (2013-06-27) cited in the application page 19; table 5 -----	6-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

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