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(54) Title: DETERGENT COMPOSITION IN THE FORM OF A SUSPENSION

(57) **Abstract**: The invention provides a detergent suspension comprising 70-99.5 wt.% of a fluid phase and 0.5-30 wt.% of suspended particles having a diameter of at least 0.1 mm, said detergent suspension comprising: 8-30 wt.% of water; 20-75 wt.% of glycerol; 8-40 wt.% of builder; and 0.01-1 wt.% of structuring biopolymer selected from xanthan gum, locust bean gum, guar gum, gum Arabic, gellan gum, carrageenan, carboxymethyl cellulose, microcrystalline cellulose, microfibrinous cellulose and combinations thereof; wherein the combination of water and glycerol represents at least 40 wt.% of the detergent suspension and wherein water and glycerol are present in a weight ratio of water to glycerol of less than 2:3. The detergent suspension according to the invention has a very low water activity, is very stable and easy to manufacture.



DETERGENT COMPOSITION IN THE FORM OF A SUSPENSION

TECHNICAL FIELD OF THE INVENTION

5 The present invention relates to a detergent composition in the form of a suspension. More particularly, the invention relates to a detergent composition comprising a fluid phase and suspended particles, wherein the fluid phase comprises water, glycerol, builder and structuring biopolymer, wherein the combination of water and glycerol represents at least 40 wt.% of the detergent suspension and wherein water and
10 glycerol are present in a weight ratio of water to glycerol of less than 2:3.

The detergent suspension of the present invention can be provided in the form of pourable viscous product or a semi-solid gel.

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. Also surfactants are used to provide shiny and dry dishes at the end of the wash. 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
25 tea, coffee, red wine, and various fruit and vegetable products, by oxidizing or reducing the components that make up these stains. Typical oxidizing bleaching agents for use in detergent formulations are chlorine- and peroxygen-based compounds, such as hypochlorite and percarbonate bleach, respectively.

30 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 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 commercial detergent products.

- 5 Generally, aminocarboxylate chelants are present in detergent formulations in the form of their (fully deprotonated) sodium salts. Aqueous solutions of aminocarboxylate salts are alkaline.

- 10 Liquid detergent formulations have been developed as these products offer the advantage 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
- 15 undissolved in the liquid product matrix. These undissolved components, here referred to as particles, 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
- 20 the lifecycle of the product. This objective, however, is very difficult to achieve as suspensions demix over time because suspended particles are subject to sedimentation and creaming/floating phenomena.

- 25 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.

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

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

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

DE-A 10 2014 212643 relates to liquid ADW detergent compositions comprising a liquid and a solid enzyme formulation. Example 1 describes a liquid ADW detergent containing glycerol, water, builder and solid enzyme.

10

SUMMARY OF THE INVENTION

The present inventors have developed a detergent suspension that has a very low water activity despite a considerable water content, that is very stable and that is easy
15 to manufacture.

The detergent suspension of the present invention comprises 70-99.5 wt.% of a fluid phase and 0.5-30 wt.% of suspended particles having a diameter of at least 0.1 mm, said detergent suspension comprising:

- 20
- 8-30 wt.% of water;
 - 20-75 wt.% of glycerol;
 - 8-40 wt.% of builder; and
 - 0.01-1 wt.% of structuring biopolymer selected from xanthan gum, locust bean gum, guar gum, gum Arabic, gellan gum, carrageenan, carboxymethyl cellulose,
25 microcrystalline cellulose, microfibrinous cellulose and combinations thereof;

wherein the combination of water and glycerol represents at least 40 wt.% of the detergent suspension and wherein water and glycerol are present in a weight ratio of water to glycerol of less than 2:3.

30 The inventors have found that in order to obtain a stable suspension it is important to balance the relative concentrations of the ingredients. The concentrations of especially water, glycerol and builder should be chosen so as to achieve a water activity at 20°C that does not exceed 0.7. Both glycerol and builders are hygroscopic ingredients that

are capable of reducing the water activity of water containing compositions. The inventors have also discovered that phase separation and sedimentation can be minimized very effectively in detergent compositions containing water, glycerol, builder, suspended particles and other detergent ingredients by incorporating structuring
5 biopolymer in the formulation.

The detergent composition of the present invention can be prepared in the form of a pourable (viscous) suspension or in the form of a semi-solid gel. In both cases a stable suspension can be prepared. The detergent suspensions of the present invention
10 further offer the advantage that a wide range of detergent ingredients can be incorporated therein in either dispersed or dissolved form.

DETAILED DESCRIPTION OF THE INVENTION

15 A first aspect of the present invention relates to a detergent suspension comprising 70-99.5 wt.% of a fluid phase and 0.5-30 wt.% of suspended particles having a diameter of at least 0.1 mm, said detergent suspension comprising:

- 8-30 wt.% of water;
- 20-75 wt.% of glycerol;
- 20 • 8-40 wt.% of builder; and
- 0.01-1 wt.% of structuring biopolymer selected from xanthan gum, locust bean gum, guar gum, gum Arabic, gellan gum, carrageenan, carboxymethyl cellulose, microcrystalline cellulose, microfibrinous cellulose and combinations thereof;

wherein the combination of water and glycerol represents at least 40 wt.% of the
25 detergent suspension and wherein water and glycerol are present in a weight ratio of water to glycerol of less than 2:3.

The term "builder" as used herein, unless indicated otherwise, refers to a particulate matter in liquid or solid form used to soften the water by removing calcium and
30 magnesium ions from the wash liquor.

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

The terms "citrate", "carbonate", "phosphate" as used herein encompass both the protonated acids and the corresponding salts of these acids. Thus, the term "citrate" includes both citric acid and salts thereof.

- 5 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.

- 10 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 subjected to shear stress.

- 15 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.

- 20 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.

- 25 The detergent suspension of the present invention preferably comprises 75-99.2 wt.% of a fluid phase and 0.8-25 wt.% of suspended, particles having a diameter of at least 0.1 mm. Most preferably, the detergent suspension comprises 80-99 wt.% of a fluid phase and 1-20 wt.% of suspended, particles having a diameter in the range of at least 0.1 mm.

- 30 The combination of glycerol, water and builder typically represent at least 55 wt.%, more preferably at least 60 wt.% and most preferably 65-92 wt.% of the detergent suspension.

The detergent suspension typically has a water activity of less than 0.7 at 20°C, More preferably, the suspension has a water activity in the range of 0.2 to 0.6 at 20°C. Even more preferably, the water activity of the detergent suspension at 20°C is in the range of 0.3 to 0.5, most preferably of 0.35 to 0.45.

5

Water activity is a thermodynamic property that is defined as the ratio of the vapour pressure of water in a particular material to the vapor pressure of pure water at the same temperature. If the water activity is 1 it means that the vapour pressure of the water in the material is equal to that of water. In this case all water molecules are free
10 water molecules. If part of the water molecules is bound, the water activity will be lower than 1. Thus, the water activity is a measure of the amount of water available for hydration of other chemicals.

Water and glycerol

15 The combination of glycerol and water typically represent at least 45 wt.%, more preferably at least 48 wt.% and most preferably 50-80 wt.% of the detergent suspension.

According to a particularly preferred embodiment, the detergent suspension contains
20 water and glycerol in a weight ratio of water to glycerol of less than 1:2, preferably of less than 3:10.

Preferably, the detergent suspension contains 10-25 wt.%, more preferably 12-23 wt.% and most preferably 13-22 wt.% water..

25

In another preferred embodiment the detergent suspension contains 25-65 wt.%, more preferably 30-60 wt.% and most preferably 32-55 wt.% of glycerol.

Builders

30 In a preferred embodiment the detergent suspension contains 10-35 wt.% of builder. Even more preferably, the detergent suspension contains 11-30 wt.%, most preferably 12-25 wt.% of builder.

Traditionally phosphorous based builders, such as phosphates have been used as builders, but due to environmental pressures alternative builders have been developed. These include organic builders such as citrate and aminocarboxylate chelants as well as inorganic builders such as carbonates, in particular sodium carbonate.

5

In a preferred embodiment the detergent suspension comprises a builder wherein the builder is selected from aminocarboxylate chelant, citrate, carbonate, phosphate and combinations thereof. More preferably, the builder comprises aminocarboxylate chelant. Aminocarboxylate chelants are extremely hygroscopic and in combination with glycerol aminocarboxylate chelants are very effective in reducing the water activity of the water-containing detergent suspension of the present invention.

10

In another preferred embodiment the detergent suspension comprises a builder wherein the builder is selected from citrate, carbonate, and combinations thereof.

15 Aminocarboxylate chelants are preferably 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 diethoxysuccinic acid (AES), aspartic acid-N, -diacetic acid (ASDA),
20 hydroxyethylethylenediaminetetraacetic 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),
25 ethylenediaminedimaleic acid and (EDDMAL), dipicolinic acid, and their salts.

In a preferred embodiment the detergent suspension contains a builder, wherein the builder is an aminocarboxylate chelant selected from GLDA, MGDA, IDS and combinations thereof, GLDA being particularly preferred.

30

According to a particularly preferred embodiment, the detergent suspension contains citrate in a concentration of at least 0.1 wt.%, more preferably of 0.2-20 wt.%, most preferably of 0.25-5 wt.% citric acid equivalent.

Structuring biopolymer

The detergent suspension of the present invention contains 0.01-1 wt.% of 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 prepare a highly stable suspension. Preferably, the suspension contains at least 0.05 wt.%, more preferably at least 0.08 wt.% and most preferably at least 0.1 wt.% of structuring biopolymer

Expressed differently, the suspension preferably contains at least 0.15% 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.

Preferably, the structuring biopolymer that is employed in accordance with the present invention is selected from xanthan gum, guar gum, carboxymethyl cellulose, microfibrinous cellulose and combinations thereof. Most preferably, the structuring biopolymer is xanthan gum.

In accordance with a particularly advantageous embodiment, the detergent suspension of the present invention contains 0.03-0.5 wt.%, more preferably 0.05-0.3 wt.% of xanthan gum.

Expressed differently, the detergent suspension typically contains 0.2-5% xanthan gum by weight of water. Even more preferably, the detergent suspension contains 0.3-3%, most preferably 0.4-2% xanthan gum by weight of water.

Fluid phase

The fluid phase of the detergent suspension of the present invention largely consists of glycerol, water and builder. Also the structuring biopolymer is contained in the fluid phase of the suspension.

The fluid phase may additionally contain liquid and non-liquid components in dissolved or non-dissolved form. Only dissolved components and non-dissolved components that

are present as particles/droplets having a diameter of less than 100 μm are considered as part of the fluid phase.

5 The fluid phase can suitably contain other detergent ingredients besides the liquid component, aminocarboxylate chelant. Examples of such ingredients include surfactants, anti-scaling agents, glass corrosion inhibitors, anti-tarnishing agents, perfumes, dyes and combinations thereof.

Particles

10 The particles suspended in the detergent suspension of the present invention preferably contain detergent ingredients selected from bleaching agents, bleaching activators, water-soluble salts, carbohydrates, enzymes and combinations thereof. The particles in the detergent suspension preferably contain at least 50 wt.% of solid component selected from bleaching agent, bleach activator, water-soluble salt,
15 carbohydrate, enzymes and combinations thereof.

According to one preferred embodiment, the particles contain bleaching agent. According to another preferred embodiment, the particles contain active enzyme.

20 The suspension contains particles that, during the lifetime of the product, do not dissolve in the continuous fluid phase.

In a preferred embodiment the suspension contains at least 0.5 wt.% of suspended particles having a diameter of at least 0.2 μm .
25

Rheology

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

30 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 present detergent suspension 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 detergent suspension 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 detergent suspension is lower than G' , but at an ω in the range of 0.05-50 rad/s G'' surpasses G' .

Both the storage modulus (G') and the loss modulus (G'') of the detergent suspension 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%.
- 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.

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 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 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.

In contrast, if the material is a purely viscous fluid, the stress in the sample is
 5 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
 10 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
 15 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
 20 scale at which it is deformed. At the lowest accessible frequencies the detergent suspension 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.

25 In accordance with a particularly advantageous embodiment of the present invention the detergent suspension 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:

- 30
- $G''(\omega) > G'(\omega)$ 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.

The detergent suspension 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 detergent suspension 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.

- 5 In accordance with another advantageous embodiment of the invention the detergent suspension is non-pourable semi-solid gelled suspension.

Surfactants

The present detergent suspension preferably contains one or more surfactants.

- 10 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.%, preferably 1-20 wt.%, more preferably 1.3-10 wt.% of one or more surfactants. In a preferred embodiment, the surfactants are selected from
- 15 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 mixture of two or more non-ionic surfactants. Examples of nonionic
- 20 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
- 25 groups include hydroxy, carboxy, mercapto, amino or amido 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
- 30 alkanolamides. 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-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-
5 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. 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
10 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 composition that is not only chemically but also physically very stable can be produced if the nonionic surfactant employed is solid at
15 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.

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
20 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.

25 *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 suspension in a concentration of 0.5 to 8%, more
30 preferably of 0.8 to 6% by 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 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.
- 5
- 10 Preferably, the one or more active enzymes contained in the present composition are selected from protease, amylase, cellulase, peroxidase, mannanase, pectate lyase and lipase. Most preferably, the active enzyme is selected from protease, amylase and combinations thereof.
- 15 The composition of the present invention typically contains at least 10 mg/kg, more preferably 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.
- 25 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 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.
- 30

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 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™, 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 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™ 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 °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.

30

Bleach

The present detergent suspension preferably contains at least 0.3 wt.%, more preferably 1-15 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 combinations thereof. More preferably, the bleaching agent is a
5 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 include alkyl peroxy acids and aryl peroxyacids such as peroxybenzoic
10 acid and ring substituted peroxybenzoic acids (e.g. peroxy- α -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 aryldiperoxy acids, such as 1,12 di-peroxy-dodecanedioic acid (DPDA), 1,9 diperoxyazelaic acid,
15 diperoxybrassylic acid, diperoxysebacic acid and diperoxy-isophthalic acid, and 2 decyldiperoxybutane 1,4 dioic acid.

The detergent suspension of the present invention preferably contains bleaching agent in the form of particles. More preferably, the composition contains 0.3-15 wt.%, more
20 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
25 coating advantageously comprises a coating agent selected from alkali sulphate, alkali carbonate or alkali chloride and combinations thereof.

The detergent suspension may contain one or more bleach activators such as peroxyacid bleach precursors. Peroxyacid bleach precursors are well known in the art.
30 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.

5 *Dispersing polymers*

The detergent suspension 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.

- 10 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
- 15 the glass and spots formed when the water subsequently evaporates.

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-
- 20 hydroxy-2 phenyl ethyl diphosphonate, ethylene diphosphonate, hydroxy 1,1 - hexylidene, vinylidene 1,1 -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
- 25 from an allyloxybenzenesulfonic acid monomer, a methallyl sulfonic acid monomer, a copolymerizable nonionic monomer and a 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
- 30 methallyl ether such as Alcosperse™ 240 supplied (AkzoNobel). Also suitable is a terpolymer containing polyacrylate with 2-acrylamido-2 methylpropane sulphonic acid 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. Sokolan™ PA 25 from BASF or Acusol™ 425 from Dow.

- 5 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 Sokalan™ CP42, Sokalan™ CP50 from BASF or Alcoguard™ 4160 from AkzoNobel may also be used.

10

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 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.%.

15

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
20 the group 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.%.

25

- 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
30 composition. Other anti-tarnishing agents that may be included in the detergent suspension 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, II, 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 suspension 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.

10 *Packaging*

The detergent suspension 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 detergent dosing to the amount of soil on the dish ware. Such a container or bottle is suitable for multiple use. In a 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, the container holds one unit of the detergent formulation and is at least partly made from water-soluble material. Examples of 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 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 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 co-monomers thereof.

5

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.

10

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 suspension.

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

15

EXAMPLES

Example 1

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

Table 1

Ingredients	Wt. %
Glycerol	47.50
Citric Acid (50%)	1.43
Dissolvine™ GL 47-S ¹	9.40
Dissolvine™ PD-S 2 ²	18.40
Demi water	7.99
Xanthan Gum	0.21
Carbonate ash light	12.10
Percarbonate ³	1.10
Lutensol™ AT80 (nonionic surfactant)	1.87

- 25 ¹ Contains appr. 48 wt.% GLDA and 45 wt.% water
² Contains appr. 85 wt.% GLDA and 9 wt.% water
³ Coated percarbonate, 98 wt.% between 0.2 mm and 1.4 mm

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, the Dissolvine™ PD-S was mixed in. Finally the remaining

5 ingredients were added to the mix under stirring. All ingredients were mixed in under vacuum to minimize formation of air bubbles.

The detergent product so obtained was a stable suspension that did not suffer from phase separation or sedimentation when stored under ambient conditions. The product

10 was quite viscous but could be poured from the bottle without any problems.

Example 2

Thixotropic machine dishwashing compositions were prepared on the basis of the recipes shown in Table 2

15

Table 2

Ingredients	Wt. %		
	1	A	B
Glycerol	47.50	47.50	30.10
Citric Acid (50%)	1.43	1.43	1.43
Dissolvine™ GL 47-S	9.40	9.40	9.40
Dissolvine™ PD-S 2	18.40	18.40	18.40
Demi water	7.99	7.99	25.39
Xanthan Gum	0.21		0.21
Carbonate ash light	12.10	12.31	12.10
Percarbonate	1.10	1.10	1.10
Lutensol™ AT80 (nonionic surfactant)	1.87	1.87	1.87

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

20

- 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;
- 25 • add Dissolvine™ PD-S 2 and continue mixing for 40 minutes;
- add Lutensol™ AT80 and carbonate, and continue mixing for 30 minutes;

- add percarbonate and continue mixing for 35 minutes.

The water activity and stability of these compositions were analyzed. The results are shown in Table 3

5

Table 3

	Composition 1	Composition A	Composition B
Water activity	0.38	0.39	0.56
Stability	Very stable	Phase separation shortly after preparation	Sedimentation during storage

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Claims

1. A detergent suspension comprising 70-99.5 wt.% of a fluid phase and 0.5-30 wt.% of suspended particles having a diameter of at least 0.1 mm, said detergent suspension comprising:
 - 8-30 wt.% of water;
 - 20-75 wt.% of glycerol;
 - 8-40 wt.% of builder; and
 - 0.01-1 wt.% of structuring biopolymer selected from xanthan gum, locust bean gum, guar gum, gum Arabic, gellan gum, carrageenan, carboxymethyl cellulose, microcrystalline cellulose, microfibrinous cellulose and combinations thereof;wherein the combination of water and glycerol represents at least 40 wt.% of the detergent suspension and wherein water and glycerol are present in a weight ratio of water to glycerol of less than 2:3.
2. Detergent suspension according to claim 1, wherein the suspended particles contain a detergent ingredient selected from bleaching agents, bleaching activators, bleaching catalysts, enzymes, surfactants, builders, dispersing polymers and combinations thereof.
3. Detergent suspension according to claim 1 or 2, wherein the water and glycerol are present in the suspension in a weight ratio of water to glycerol of less than 1:2, preferably of less than 3:10.
4. Detergent suspension according to any one of the preceding claims, wherein the builder is selected from aminocarboxylate chelant, citrate, carbonate, phosphate and combinations thereof.
5. Detergent suspension according to claim 4, wherein the builder is an aminocarboxylate chelant selected from GLDA, MGDA, IDS and combinations thereof.

6. Detergent suspension according to any one of the preceding claims, wherein the structuring biopolymer is xanthan gum.
7. Detergent suspension according to any one of the preceding claims, wherein the suspension has a water activity at 20°C of not more than 0.70.
8. Detergent suspension according to any one of the preceding claims, wherein the suspension contains 25-65 wt.% glycerol.
9. Detergent suspension according to any one of the preceding claims, wherein the suspension contains 10-30 wt.% of builder.
10. Detergent suspension according to any one of the preceding claims, wherein the suspension contains 0.2-5% structuring biopolymer by weight of water.
11. Detergent suspension according to any one of the preceding claims, wherein the suspension contains 0.5-30 wt.% surfactant.
12. Detergent suspension according to any one of the preceding claims, wherein the suspension contains citrate in a concentration of at least 0.1 wt.% citric acid equivalent.
13. Detergent suspension according to any one of the preceding claims, wherein the suspension is a pourable thixotropic suspension 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.
14. Detergent suspension according to claims, wherein the suspension is a pourable suspension having a storage modulus (G') at 0.2 rad/s and 20°C in the range of 1 to 100 Pa.

15. Detergent suspension according to any one of the preceding claims, wherein the suspension is a pourable suspension having a loss modulus (G'') at 0.2 rad/s and 20°C in the range of 1 to 100 Pa.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/054726

A. CLASSIFICATION OF SUBJECT MATTER INV. C11D3/20 C11D3/22 C11D17/00 C11D3/06 C11D3/10 C11D3/33 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 <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category*</th> <th style="width: 70%;">Citation of document, with indication, where appropriate, of the relevant passages</th> <th style="width: 20%;">Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>DE 10 2014 212643 A1 (HENKEL AG & CO KGAA [DE]) 31 December 2015 (2015-12-31) paragraphs [0001], [0004], [0007], [0013], [0070], [0076], [0080], [0086] - [0093]; example 1 -----</td> <td style="text-align: center; vertical-align: top;">1-15</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>US 2015/184115 A1 (MEIER FRANK [DE] ET AL) 2 July 2015 (2015-07-02) paragraphs [0006] - [0007] -----</td> <td style="text-align: center; vertical-align: top;">1-15</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>US 2015/267153 A1 (BENDA KONSTANTIN [DE] ET AL) 24 September 2015 (2015-09-24) examples -----</td> <td style="text-align: center; vertical-align: top;">1-15</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	A	DE 10 2014 212643 A1 (HENKEL AG & CO KGAA [DE]) 31 December 2015 (2015-12-31) paragraphs [0001], [0004], [0007], [0013], [0070], [0076], [0080], [0086] - [0093]; example 1 -----	1-15	A	US 2015/184115 A1 (MEIER FRANK [DE] ET AL) 2 July 2015 (2015-07-02) paragraphs [0006] - [0007] -----	1-15	A	US 2015/267153 A1 (BENDA KONSTANTIN [DE] ET AL) 24 September 2015 (2015-09-24) examples -----	1-15
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A	DE 10 2014 212643 A1 (HENKEL AG & CO KGAA [DE]) 31 December 2015 (2015-12-31) paragraphs [0001], [0004], [0007], [0013], [0070], [0076], [0080], [0086] - [0093]; example 1 -----	1-15												
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A	US 2015/267153 A1 (BENDA KONSTANTIN [DE] ET AL) 24 September 2015 (2015-09-24) examples -----	1-15												
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Date of the actual completion of the international search 16 May 2017	Date of mailing of the international search report 24/05/2017													
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Marttin, Emmeline													

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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