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(54) Title: STRUCTURED CLEANING COMPOSITIONS

(57) Abstract: Stable, pourable, homogeneous, abrasive compositions which comprise particulate, solid salt suspended in a satu-
rated aqueous solution of said salt and sufficient surfactant to form, in conjunction with said solution, a stable, pourable, solid-sup-
porting structured surfactant system can be used as cleaning compositions for hard surfaces, especially as manual dishwashing
detergents or scouring liquids.

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STRUCTURED CLEANING COMPOSITIONS

The invention relates to structured cleaning compositions. In particular, it relates to liquid cleaning compositions, containing suspended abrasive particles, which are suitable for use as manual dishwashing and scouring liquids.

Conventional dishwashing liquids are unable to remove stubborn encrustations. One solution to this problem is to include an abrasive. Incorporation of abrasives in dishwashing formulations gives rise to two problems. The abrasive tends to sediment out on standing, and also leaves a gritty residue in the bowl and on the washed surfaces.

Attempts to solve the problem of dispersing solids in water have generally involved either using viscosifiers such as gums or other polymeric thickeners to raise the viscosity of the liquid medium, or else forming colloidal dispersions.

Increasing the viscosity of the liquid medium retards, but does not prevent, sedimentation, and at the same time it makes the composition harder to pour. It cannot provide a stable suspension.

For example, EP 0193375 describes dispersing fine particles of sodium carbonate in a viscous, liquid detergent base, relying on the high viscosity of the medium, and the small particle size of the carbonate to retard sedimentation. However the small particle size gives insufficient abrasive action for an effective pan scourer.

The main alternative to the use of viscosifiers for suspending particles has involved the preparation of colloidal systems. Colloidal dispersions contain particles of about 1 micron or smaller, which are prevented from sedimenting by Brownian motion. Such systems are obviously incapable of dispersing relatively coarse particles such as abrasives.

An alternative to the above methods of suspension would be the use of a structured suspending system. Structured suspending systems depend on the rheological properties of the suspending medium to immobilise the particles, irrespective of size. This requires the suspending medium to exhibit a yield point which is higher than the sedimenting or creaming force exerted by the suspended particles, but low enough to enable the medium to flow under externally imposed stresses, such as pouring and stirring, like a normal liquid. The structure

reforms sufficiently rapidly to prevent sedimentation once the agitation caused by the external stress has ceased.

The only structured systems sufficiently effective to have found widespread application have been based on aqueous surfactant mesophases. Their use has been confined to suspending water-insoluble, or sparingly soluble, solids. Their use for suspending very water-soluble solids, such as common salt, has not hitherto been envisaged.

The term "structured system", as used herein, means a pourable composition comprising water, surfactant, any structurants which may be required to impart suspending properties to the surfactant, and optionally other dissolved matter, which together form a mesophase, or a dispersion of a mesophase in a continuous aqueous medium, and which has the ability to immobilise non-colloidal, water-insoluble particles while the system is at rest, thereby forming a stable, pourable suspension.

Three main types of structured system have been employed in practice, all involving an L_α -phase, in which bilayers of surfactant are arranged with the hydrophobic part of the molecule on the interior and the hydrophilic part on the exterior of the bilayer (or vice versa). The bilayers lie side by side, e.g. in a parallel or concentric configuration, sometimes separated by aqueous layers. L_α -phases (also known as G-phases) can usually be identified by their characteristic textures under the polarising microscope and/or by x-ray diffraction, which is often able to detect evidence of lamellar symmetry. Such evidence may comprise first, second and sometimes third order peaks with a d-spacing ($2\pi/Q$, where Q is the momentum transfer vector) in a simple integral ratio 1 : 2 : 3. Other types of symmetry give different ratios, usually non-integral. The d-spacing of the first peak in the series corresponds to the repeat spacing of the bilayer system.

Most surfactants form an L_α -phase either at ambient or at some higher temperature when mixed with water in certain specific proportions. However such conventional L_α -phases do not usually function as structured suspending systems. Useful quantities of solid render them un-pourable and smaller amounts tend to sediment.

The main types of structured system used in practice are based on dispersed lamellar, spherulitic and expanded lamellar phases.

Dispersed lamellar phases are two phase systems, in which the surfactant bilayers are

arranged as parallel plates to form domains of L_α -phase, which are interspersed with an aqueous phase to form an opaque gel-like system. They are described in EP 086 614.

Spherulitic phases comprise well-defined spheroidal bodies, usually referred to in the art as spherulites, in which surfactant bilayers are arranged as concentric shells. The spherulites usually have a diameter in the range 0.1 to 15 microns and are dispersed in an aqueous phase in the manner of a classical emulsion, but interacting to form a structured system. Spherulitic systems are described in more detail in EP 151 884.

Many structured systems are intermediate between dispersed lamellar and spherulitic, involving both types of structure. Usually systems having a more spherulitic character are preferred because they tend to have lower viscosity. A variant on the spherulitic system comprises prolate or rod shaped bodies sometimes referred to as batonnettes. These are normally too viscous to be of practical interest.

Both of the foregoing systems comprise two phases. Their stability depends on the presence of sufficient dispersed phase to pack the system so that the interaction between the spherulites or other dispersed mesophase domains prevents separation. If the amount of dispersed phase is insufficient, e.g. because there is not enough surfactant or because the surfactant is too soluble in the aqueous phase to form sufficient of a mesophase, the system will undergo separation and cannot be used to suspend solids. Such unstable systems are not "structured" for the purpose of this specification.

A third type of structured system comprises an expanded L_α -phase. It differs from the other two types of structured system in being essentially a single phase, and from conventional L_α -phase in having a wider d-spacing. Conventional L_α -phases, which typically contain 60 to 75% by weight surfactant, have a d-spacing of about 4 to 7 nanometers. Attempts to suspend solids in such phases result in stiff pastes which are either non-pourable, unstable or both. Expanded L_α -phases with d-spacing greater than 8 nanometres, e.g. 10 to 15 nm, form when electrolyte is added to aqueous surfactants at concentrations just below those required to form a normal L_α -phase, particularly to surfactants in the H-phase.

The H-phase comprises surfactant molecules arranged to form cylindrical rods of indefinite length. It exhibits hexagonal symmetry and a distinctive texture under the polarising microscope. Typical H-phases have so high a viscosity that they appear to be curdy solids. H-phases near the lower concentration limit (the L_1 /H-phase boundary) may be pourable but have a very high viscosity and often a mucous-like appearance. Such systems tend to form expanded

L_{α} -phases particularly readily on addition of sufficient electrolyte.

Expanded L_{α} -phases are described in more detail in EP 530 708. In the absence of suspended matter they are generally translucent, unlike dispersed lamellar or spherulitic phases, which are normally opaque. They are optically anisotropic and have shear-dependent viscosity. In this they differ from L_1 -phases, which are micellar solutions or microemulsions. L_1 -phases are clear, optically isotropic and are usually substantially Newtonian. They are unstructured and cannot suspend solids.

Some L_1 -phases exhibit small angle x-ray diffraction spectra which show evidence of hexagonal symmetry and/or exhibit shear dependent viscosity. Such phases usually have concentrations near the L_1 /H-phase boundary and may form expanded L_{α} -phases on addition of electrolyte. However, in the absence of any such addition of electrolyte they lack the yield point required to provide suspending properties, and are not, therefore, "structured systems" for the purpose of this specification.

Expanded L_{α} -phases of the above type are usually less robust than spherulitic systems. They are liable to become unstable at low temperatures. Moreover they frequently exhibit a relatively low yield stress, which may limit the maximum size of particle that can be stably suspended.

Most structured surfactants require the presence of a structurant, as well as surfactant and water in order to form structured systems capable of suspending solids. The term "structurant" is used herein to describe any non-surfactant capable, when dissolved in water, of interacting with surfactant to form or enhance (e.g. increase the yield point of) a structured system. It is typically a surfactant-desolubiliser, e.g. an electrolyte.

It has now been found that stable, pourable, homogeneous, abrasive dishwashing compositions can be obtained by suspending solid particles of common salt in a saturated aqueous solution of said salt, and adding sufficient surfactant to form, in conjunction with said solution, a stable, pourable, solid-supporting structured surfactant system. The saturated salt solution acts as a structurant, interacting with the surfactant to form a suspending system. The excess salt acts as an abrasive when the liquid is applied in the undiluted form, but readily dissolves in water on rinsing.

The invention, therefore, provides a stable, pourable, homogeneous composition comprising particulate, solid salt suspended in a saturated aqueous solution of said salt, and sufficient surfactant to form, in conjunction with said solution, a stable, pourable, solid-supporting structured surfactant system.

In the following discussion of the invention, unless stated to the contrary, the disclosure of alternative values for the upper or lower limit of the permitted range of a parameter, coupled with an indication that one of said values is more highly preferred than the other, is to be construed as an implied statement that each intermediate value of said parameter, lying between the more preferred and the less preferred of said alternatives, is itself preferred to said less preferred value and also to each value lying between said less preferred value and said intermediate value.

"Salt", as used herein, refers to an alkali metal and/or alkaline earth metal halide composition, which may comprise sodium, potassium, magnesium and/or calcium chloride, but will usually, in practice, consist at least predominantly of sodium chloride. The salt may contain minor amounts of the impurities commonly present in naturally occurring salt, such as other halides (e.g. bromide and/or iodide) and other anions (e.g. carbonate and/or sulphate). The cationic component consists essentially of alkali metal and/or alkaline earth metal, e.g. more than 90%, preferably more than 95%, most preferably more than 99% by weight, based on the total weight of cations. Preferably at least 40% of the cations by weight are alkali metal. We particularly prefer that at least 50%, more preferably at least 75%, most preferably at least 90% by weight of the cationic component of the salt should be alkali metal. We prefer that the alkali metal consist essentially of sodium and potassium, and that any alkaline earth metal consist essentially of calcium and magnesium. We further prefer that at least 50%, more preferably at least 70%, most preferably at least 90% by weight of the alkali metal is sodium. We prefer that at least 70%, more preferably at least 80%, most preferably at least 90% by weight of the anionic component is halide, of which preferably at least 75%, more preferably at least 80%, most preferably at least 90% by weight is chloride.

Salt is highly soluble, i.e. more than 30% by weight at 25°C. It is highly desirable that the solubility does not vary by a large amount over the normal range of storage temperatures, to avoid unacceptable crystal growth, and destabilisation of the surfactant structure. A variation of less than 10% between 0 and 40°C is preferred.

Sodium chloride meets these requirements particularly well. It is also cheap, natural and a

highly effective hypoallergenic biocide. We have found that cleaning compositions based on saturated brine are self-preserving. Sea salt or rock salt (halite) are very suitable.

Saturated brine is a very aggressive medium for surfactants and the choice of structuring surfactant is therefore rather restricted. Generally only surfactants with a high HLB or solubility product are suitable. The HLB is preferably greater than 12, more preferably greater than 15, even more preferably greater than 20, most preferably greater than 30. Relatively few surfactants meet these criteria, but one that does is alkyl ether sulphate, which is, fortuitously, one of the preferred surfactants for use in dishwashing formulations. Alkyl ether sulphates having more than one, and more preferably more than two, ethyleneoxy groups are preferred.

The alkyl ether sulphate is preferably the product obtained by:

- (1) ethoxylating a natural fatty or synthetic alcohol having an average of more than 8, preferably more than 10, more preferably more than 12, but less than 30, preferably less than 25, more preferably less than 20, most preferably less than 15 carbon atoms with an average of at least 1, preferably at least 2, more preferably more than 3, but less than 60, preferably less than 50, more preferably less than 25, even more preferably less than 15, more preferably still less than 10, most preferably less than 5 ethyleneoxy groups;
- (2) optionally stripping any unreacted alcohol;
- (3) reacting the ethoxylated product with a sulphating agent; and
- (4) neutralising the resulting alkyl ether sulphuric acid with a base.

The base is typically an alkali metal and/or alkaline earth metal hydroxide or carbonate, usually sodium. However, for Dead Sea salt, with its high magnesium content, a mixed sodium/-magnesium ether sulphate may be preferred. Alternatively the base may comprise an amine, especially an ethanolamine.

Alternative surfactants which may be used include high HLB non-ionic surfactants, such as alcohol or fatty acid ethoxylates with more than 3, preferably more than 5, most preferably more than 10 ethoxy groups. Especially preferred are those with bent chain hydrocarbon groups such as oleyl or isostearyl groups. Non-ionic surfactants may require the presence of a deflocculant, such as an alkyl polyglycoside, in order to be stable. Other surfactants, which may be employed according to the invention, include alkyl ether carboxylates and high HLB amphoteric and zwitterionic surfactants and amine oxides.

The proportion of surfactant required will depend on the HLB. Higher HLB generally requires

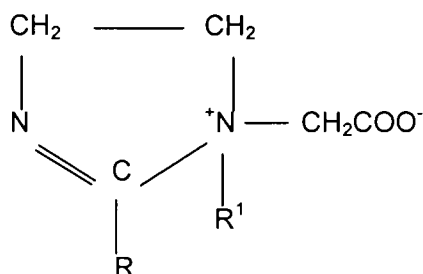
more surfactant. Preferably the amount of surfactant is greater than 2% by weight, more preferably greater than 4%, most preferably greater than 6%, but less than 25%, more preferably less than 20%, most preferably less than 15%.

The surfactant may also comprise minor amounts of other anionic surfactants, such as, for example, C₁₀₋₂₀ alkyl sulphate, e.g. C₁₂₋₁₈ alkyl sulphate, C₁₀₋₂₀ alkyl benzene sulphonate or a C₈₋₂₀ aliphatic soap, e.g. C₁₀₋₂₀ aliphatic soap. The soap may be saturated or unsaturated, straight or branched chain. Preferred examples include dodecanoates, myristates, stearates, oleates, linoleates, linolenates, behenates, erucates and palmitates and coconut and tallow soaps. The surfactant may also include other anionic surfactants, such as olefin sulphonates, paraffin sulphonates, taurides, isethionates, ether sulphonates, ether carboxylates, sarcosinates, aliphatic ester sulphonates, e.g. alkyl glyceryl sulphonates, sulphosuccinates or sulphosuccinamates.

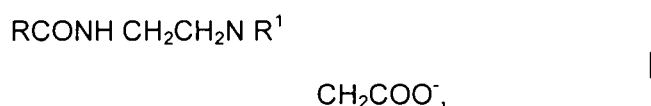
The cation of any anionic surfactant is typically sodium but may alternatively be, or comprise potassium, lithium, calcium, magnesium, ammonium, or an alkyl or hydroxyalkyl ammonium having up to 6 aliphatic carbon atoms including ethylammonium, isopropylammonium, monoethanolammonium, diethanolammonium, and triethanolammonium. Ammonium and ethanolammonium salts are generally more soluble than the sodium salts. Mixtures of the above cations may be used.

The non-ionic surfactants may typically comprise amine oxides, polyglyceryl fatty esters, fatty acid ethoxylates, fatty acid monoalkanolamides, fatty acid dialkanolamides, fatty acid alkanolamide ethoxylates, propylene glycol monoesters, fatty alcohol propoxylates, alcohol ethoxylates, alkyl phenol ethoxylates, fatty amine alkoxyates and fatty acid glyceryl ester ethoxylates. Other non-ionic compounds suitable for inclusion in compositions of the present invention include mixed ethylene oxide/ propylene oxide block copolymers, ethylene glycol monoesters, alkyl polyglycosides, alkyl sugar esters including alkyl sucrose esters and alkyl oligosaccharide esters, sorbitan esters, ethoxylated sorbitan esters, alkyl capped polyvinyl alcohol and alkyl capped polyvinyl pyrrolidone.

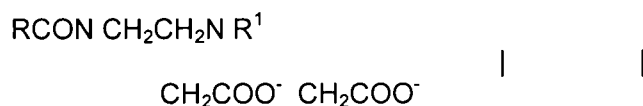
The surfactant may comprise an amphoteric or zwitterionic surfactant. The former preferably comprises so-called imidazoline betaines, which are also called amphotoacetates, and were traditionally ascribed the zwitterionic formula:



because they are obtained by treating sodium chloracetate with an imidazoline. It has been shown, however, that they are actually present, at least predominantly, as the corresponding amphoteric linear amidoamines:



which are usually obtained commercially in admixture with the dicarboxymethylated form:



R preferably has at least 8, more preferably at least 10 carbon atoms but less than 25, more preferably less than 22, even more preferably less than 20, most preferably less than 18. Typically, R represents a mixture of alkyl and alkenyl groups, obtained, for example, from coconut or palm oil, and having sizes ranging from 8 to 18 carbon atoms, with 12 predominating, or a fraction of such a feedstock, such as lauryl with at least 90% C₁₂. R¹ is preferably an alkyl or hydroxyalkyl group with 1 to 4 carbon atoms, i.e. methyl, ethyl, hydroxyethyl, propyl, isopropyl, hydroxypropyl, butyl, isobutyl or hydroxybutyl, particularly preferably hydroxyethyl.

The zwitterionic surfactant is preferably a betaine, which typically has the formula R''R'₂⁺NCH₂COOH, where R' is an aliphatic group having 1 to 4 carbon atoms and R'' is an aliphatic group having from 8 to 25 carbon atoms, preferably a straight or branched chain alkyl or alkenyl group, or more preferably a group of the formula RCONR'(CH₂)_n, where R and R' have the same significance as before, and n is an integer from 2 to 4.

We prefer that R' is a methyl, carboxymethyl, ethyl, hydroxyethyl, carboxyethyl, propyl, isopropyl, hydroxypropyl, carboxypropyl, butyl, isobutyl or hydroxybutyl group.

The surfactant may comprise cationic surfactants such as fatty alkyl trimethylammonium or benzalkonium salts, amidoamines or imidazolines.

The aqueous structured systems formed by the interaction of surfactants with saturated brine include systems which may be in the form of an expanded L_α -phase, such as those described in EP 530 708. The systems of the present invention may comprise structures which preferably show d-spacings greater than 5 nm, more preferably greater than 7 nm, even more preferably greater than 8 nm, more preferably still, greater than 9 nm, most preferably greater than 10 nm. Preferably the d-spacing is less than 30 nm, more preferably less than 20 nm, most preferably less than 15 nm.

Alternatively or additionally, the suspending medium may contain spherulites, e.g. having a d-spacing of 3.5 to 5.5, preferably 4 to 5 nm. The discussion is based on the assumption that the structure is lamellar. We do not, however, intend to exclude the possibility that the system may comprise non-lamellar components.

The salt is present in total concentrations greater than saturation at ambient temperature. The composition generally comprises suspended solid salt in amounts greater than 1%, preferably greater than 3%, more preferably greater than 5%, even more preferably greater than 10%, most preferably greater than 15% by weight, based on the weight of the composition. Amounts of suspended solid greater than 30% by weight are usually undesirably viscous. We prefer that the suspended solid should be less than 25% by weight.

The suspended solid salt typically has a relatively coarse granular texture, with a mean particle size greater than 100 microns, preferably greater than 300 microns, more preferably greater than 500 microns, still more preferably greater than 550 microns, most preferably greater than 1 mm, but less than 5mm, preferably less than 3mm, most preferably less than 2mm. Preferably at least 10%, more preferably at least 30%, still more preferably at least 50%, most preferably at least 80%, by weight of the particles are greater than 200microns.

Usually the total concentration of salt is greater than 50%, preferably greater than 60%, most preferably greater than 65%, but less than 90%, preferably less than 80%, most preferably less than 75%, by weight, based on the total weight of the composition.

The product may optionally contain other common ingredients of dishwashing and scouring liquids, such as builders, essential oils, fragrances, pigments, dyes, and antiseptics. Acids and/or bases can also be added in order to obtain pH values between 4 and 11 if grease- or limescale-removing action is desired. Organic solvents, on the other hand, preferably are not

among the ingredients as they render the system unstable. It is particularly preferred that the composition be preservative-free.

The product may also contain suspended particles other than salt, especially abrasive particles and/or particles comprising active ingredients.

The structured surfactant may suspend other abrasive particles to achieve an additional scouring action. Abrasive particles which can be used within the scope of this invention preferably have no sharp edges or tips in order to protect the surfaces to be scrubbed; preferably they are spherical or ellipsoidal, which additionally gives the product an aesthetically pleasing appearance. These additional abrasive particles are preferably water insoluble.

The additional abrasives are preferably selected from the group consisting of polymers, hard waxes, natural materials, ceramic particles, inorganic substances and mixtures thereof. In a preferred embodiment, the abrasives used are polymer particles. In this context, the polymer is preferably selected from the group consisting of polyethylene, polypropylene, polystyrene, polyethylene terephthalate, polyester, polycarbonate, polyvinyl chloride, polyvinyl acetate, polymethyl methacrylate and copolymers and mixtures thereof; polystyrene spheres are particularly preferred.

A further preferred embodiment comprises abrasives which are obtained from natural materials. In the context of the invention, these include, for example, comminuted shells of hazelnuts, almonds, brazil nuts, walnuts, coconuts and further nuts, and also shells of the stones of various types of fruit, for example apricots, peaches, plums, etc., but also optionally comminuted kernels of grapes and various soft fruits such as strawberries, raspberries, blackberries, etc. Under some circumstances, comminuted roots or pieces of bark may also serve as abrasives. In the course of production of such abrasives obtained from natural materials, it is of particular importance that the formation of sharp-edged particles which under some circumstances attack the surface is prevented.

In addition to the abrasives mentioned, it is also possible to use hard waxes, ceramic particles, glass beads and inorganic substances as scouring particles in the context of the invention. The usable inorganic compounds include, for example, alkali metal carbonates, alkali metal bicarbonates and alkali metal sulphates, alkali metal borates, alkali metal phosphates, silicon dioxide, crystalline or amorphous alkali metal silicates and sheet silicates, finely crystalline sodium aluminum silicates, aluminum oxides and calcium carbonate.

In the context of the present invention, the additional abrasives used may be particles having a

diameter of from 0.05 to 4 mm. They preferably have a diameter of from 0.3 to 1.5 mm. When the shape of the particles deviates from the spherical form, the particle diameter is averaged over the three spatial directions. The composition according to the invention may comprise up to 10% by weight of additional abrasives, preferably up to 5% by weight, especially 0.3 to 2% by weight.

The structured cleaning composition may also suspend particles comprising active ingredients. It is preferred that these particles are microcapsules, which consist of an active ingredient in the core and a protective shell. The shell may be composed from any material which can dissolve, be perforated or become friable under mechanical stress, upon dilution, due to a change in pH or chemical or electrical potential when the composition is used in a cleaning operation. The active ingredients may be any kind of active substance which can serve as cleaning and/or surface treatment and/or skincare agent in hard surface cleaning compositions, especially manual dishwashing and/or scouring compositions. Examples of such active substances are bleaching agents, enzymes, essential oils and skin care agents such as emollients, vitamins or plant extracts.

The composition according to the invention can be used as a manual dishwashing detergent. Thus, a manual dishwashing method using the inventive composition is also encompassed by this invention. Likewise, a method of scouring hard surfaces using the inventive composition also falls under the scope of the invention, as the inventive composition can also be put to use as a scouring liquid.

Hard surfaces, for the purpose of this specification, are all common household surfaces with the exception of carpets, upholstery and other textile surfaces, especially kitchen and bathroom floors, worktops, porcelain, tiles and other surfaces. Thus, glass, ceramics, metal, porcelain, wood, stone, plastics, laminated floors, tiles and similar surfaces can be considered hard surfaces falling within the boundaries of this specification.

The invention will be illustrated by the following examples, in which all proportions are % by weight, with the balance being water, unless stated to the contrary.

EXAMPLE 1

Sodium C ₁₂₋₁₄ alkyl 3 mole ethoxylate	12
C ₁₂₋₁₄ alkyl amine oxide	8
Sodium chloride	26
Fragrance	0.3

The above composition was a stable, spherulitic, structured surfactant system containing about 7% solid salt in suspension. The composition provided a satisfactory scouring action on encrusted pans, but was fully soluble on dilution with water, leaving no residue. No separation was visible after 1 month's storage at laboratory ambient temperature.

EXAMPLE 2

Sodium C ₁₂₋₁₄ alkyl 3 mole ethoxy sulphate	11.4
C ₁₂₋₁₄ alkyl amine oxide	7.6
Sodium chloride	30.3
Perfume	0.47
Dye	0.002

The above composition was a stable, structured surfactant system containing about 12.7% solid salt in suspension. The composition provided a satisfactory scouring action on encrusted pans, but was fully soluble on dilution with water, leaving no residue. No separation was visible after 1 month's storage at laboratory ambient temperature. The formulation was self-preserving.

The small angle X-ray scattering plot of the product featured a sharp peak at 10.2nm with a smaller peak at 4.5 nm. The ratio between these features does not correspond to a specific symmetry. It suggests a spherulitic phase having a d-spacing of 10.2. Electron microscopy confirms the presence of spherulites having a diameter in the range 0.4 to 4 µm.

CLAIMS

1. Stable, pourable, homogeneous, abrasive composition comprising particulate, solid salt suspended in a saturated aqueous solution of said salt, characterized in that said composition comprises sufficient surfactant to form, in conjunction with said solution, a stable, pourable, solid-supporting structured surfactant system.
2. Composition according to claim 1, characterized in that said salt is preferably selected from alkali metal and/or alkaline earth metal halides, more preferably from sodium, potassium, magnesium and/or calcium chloride, most preferably sodium chloride.
3. Composition according to one of the preceding claims, characterized in that more than 90% of the cations in said salt, preferably more than 95%, most preferably more than 99% by weight, based on the total weight of cations, are alkali metal and/or alkaline earth metal cations.
4. Composition according to one of the preceding claims, characterized in that at least 40% by weight of the cations are alkali metal, preferably at least 50%, more preferably at least 75%, most preferably at least 90% by weight.
5. Composition according to one of the preceding claims, characterized in that at least 50%, more preferably at least 70%, most preferably at least 90% by weight of the alkali metal is sodium.
6. Composition according to one of the preceding claims, characterized in that at least 70%, more preferably at least 80%, most preferably at least 90% by weight of the anionic component is halide.
7. Composition according to claim 6, characterized in that at least 75%, more preferably at least 80%, most preferably at least 90 % by weight of the halide is chloride.
8. Composition according to one of the preceding claims, characterized in that the surfactant has an HLB of greater than 12, more preferably greater than 15, even more preferably greater than 20, most preferably greater than 30.
9. Composition according to one of the preceding claims, characterized in that the surfactant is selected from anionic surfactants, non-ionic surfactants, amphoteric and zwitterionic surfactants and mixtures.
10. Composition according to one of the preceding claims, characterized in that the surfactant is preferably selected from the group comprising alkyl ether sulphates, alcohol or fatty acid ethoxylates with more than three ethoxy groups, alkyl ether carboxylates, high HLB amphoteric and zwitterionic surfactants, amine oxides, and mixtures.
11. Composition according to one of the preceding claims, characterized in that the amount of surfactant is preferably greater than 2% by weight, more preferably greater

- than 4%, most preferably greater than 6%, and less than 25%, more preferably less than 20%, most preferably less than 15%.
12. Composition according to one of the preceding claims, characterized in that it comprises suspended solid salt in amounts greater than 1%, preferably greater than 3%, more preferably greater than 15% by weight, and preferably less than 25% by weight, based on the weight of the composition.
 13. Composition according to one of the preceding claims, characterized in that the suspended solid salt has a mean particle size greater than 100 microns, preferably greater than 300 microns, more preferably greater than 500 microns, still more preferably greater than 550 microns, most preferably greater than 1 mm, but less than 5mm, preferably less than 3mm, most preferably less than 2mm.
 14. Composition according to one of the preceding claims, characterized in that preferably at least 10%, more preferably at least 30%, still more preferably at least 50%, most preferably at least 80% by weight of the suspended particles are greater than 200microns.
 15. Composition according to one of the preceding claims, characterized in that it additionally comprises other common ingredients of dishwashing and scouring liquids, especially builders, acids, bases, essential oils, fragrances, pigments, dyes and/or antiseptics.
 16. Use of a composition according to one of the preceding claims as a manual dishwashing detergent.
 17. Use of a composition according to any one of claims 1-15 as a scouring liquid.
 18. Manual dishwashing method using a composition according to any one of claims 1-15.
 19. Method of scouring hard surfaces using a composition according to any one of claims 1-15.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2007/000535

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C11D17/00 C11D3/02

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 practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 151 884 A2 (ALBRIGHT & WILSON [GB]) 21 August 1985 (1985-08-21) page 16, lines 21-25 page 27, lines 21-25 page 30, lines 9-13 page 33, lines 1-7 page 44, columns 25-34 claims; examples	1-19
X	WO 94/05757 A (UNILEVER PLC [GB]; UNILEVER NV [NL]) 17 March 1994 (1994-03-17) page 14, lines 24-28; claims; figures; examples	1-19
X	US 5 633 223 A (VASUDEVAN TIRUCHERAI V [US] ET AL) 27 May 1997 (1997-05-27) column 4, lines 36-64; claims	1-15, 17

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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

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

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

Z document member of the same patent family

Date of the actual completion of the international search

19 April 2007

Date of mailing of the international search report

04/05/2007

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2007/000535

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