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## (54) Liquid cleaning compositions.

(57) A liquid detergent composition comprises a nonionic surfactant, suspended sodium tripolyphosphate and a surfactant desolubilising electrolyte of the formula:- NaX, where X is OH-, or the anion of a monobasic acid, in an amount sufficient to provide a stable homogenous non-sedimenting spherulitic detergent composition.

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**Description**

# LIQUID CLEANING COMPOSITIONS

The present invention relates to liquid cleaning compositions of the spherulitic type containing sodium tripolyphosphate builder and a non-ionic surfactant.

U.S.P. 4,618,446 describes the preparation of liquid detergents comprising an aqueous liquid medium which contains a surfactant and an electrolyte with which the surfactant interacts to form spherulites. The latter can pack together to support suspended solid particles, e.g. builders such as sodium tripolyphosphate.

Typically, the surfactant used to form the spherulites is an anionic mixture such as a mixture of sodium $C_{8-14}$ alkyl benzene sulphonate with an alkyl polyethyleneoxy ether sulphate or a olefin or paraffin sulphonate or else a mixture of anionic surfactant with minor amounts of an an alkanolamide or amine oxide. The electrolyte is usually dissolved builder, especially sodium tripolyphosphate, an( sometimes also sodium carbonate and/or sodium silicate.

For some types of washing, e.g. heavy oil stains or synthetic fibre, it is desirable to include in the formulation a relatively high level of ethoxylated non-ionic surfactant. Unfortunately it has been found that the inclusion of even small amounts of non-ionic alkoxylates in built liquid detergents of the spherulitic type tends to cause loss of stability and of homogeneity of the product, giving a curdled appearance on standing.

Our copending UK Patent application no. 8813132.1 describes the use of low HLB (e.g. less than 10) non-ionic surfactant systems to avoid promblems of instability or curdling in spherulitic liquid detergents. However detergents normally have an HLB of 12 to 15 and there remains a need for spherulitic liquid detergents containing non-ionic surfactants which are not limited to low HLB surfactants.

We have now discovered that the instability of non-ionic surfactants is due to the presence of certain polyvalent anions such as tripolyphosphate, carbonate, silicate or borate. In the absence of such anions it is possible to formulate stable spherulitic liquids containing high HLB non-ionic surfactants provided that, if the amount of surfactant is not sufficient to form spherulitic compositions spontaneously, sufficient electrolyte is present. This however presents problems if a builder is required. The most cost effective detergent builder is sodium tripolyphosphate, with causes particularly severe problems of curdling of non-ionic detergent surfactants. It is possible to replace sodium tripolyphosphate by certain other builders e.g. zeolite, or citrate but the performance is substantially inferior. Other alternatives such as carbonate, silicate and pyrophosphate cause similar problems of curdling the surfactant, as well as being less cost effective.

We have found that the adverse effect of sodium tripolyphosphate on non-ionic detergents is substantially reduced or eliminated if a sufficient amount of a salt, preferably a sodium salt, of a monobasic acid is present. We believe that this phenomenon is due to the effect of monobasic sodium salts reducing the solubility and/or the degree of dissociation of the tripolyphosphate anions resulting in the amount of polyvalent anion in solution being reduced below the critical level at which instability of non-ionic sufactants is usually observed. In this way relatively high levels of non-ionic alkoxylates up to 100% of the total surfactant may be included in sodium tripolyphosphate built liquid detergents of the spherulitic type if the composition additionally contains sodium hydroxide or a surfactant desolubilising sodium salt of a monobasic acid.

Our invention provides a liquid detergent composition comprising a non-ionic surfactant, suspended sodium tripolyphosphate and a surfactant desolubilising electrolyte of the formula NaX, where X is $OH^-$, or the anion of a monobasic non-surfactant acid, in an amount sufficient to provide a stable homogeneous non-sedimenting detergent composition.

The non-ionic surfactant is preferably an alkoxylate. "Alkoxylates", whenever the context permits herein, are preferably ethoxylates or less preferably propoxylates or mixed ethoxylate propoxylate copolymers. For example the alkoxylate may typically be an alkoxylated $C_{8-18}$ natural or synthetic alcohol or an alkoxylated fatty acid, $C_{6-18}$ alkyl phenol, or glycerol or sorbitan ester, preferably with an HLB of from 10 to 18, e.g. 12 to 15.

Other non-ionic surfactants that may be present include alkanolamides, such as coconut diethanolamide or monoethanolamide, amine oxides and alkoxylated amine oxides. The non-ionic surfactant may be present in a proportion of from 10 to 100% by weight of the total surfactant, preferably 15 to 90% more preferably 20 to 70%, e.g. 25 to 40%. The total concentration of nonionic surfactant is typically from 2 to 20% by weight of the composition, preferably 3 to 15%, e.g. 3.5 to 10%.

The detergent preferably contains an anionic surfactant. The latter is preferably a sodium linear alkyl benzene sulphonate (e.g. $C_{8-14}$ alkyl) or a mixture thereof with a sodium alkyl polyoxyethylene sulphate. Other anionic surfactants which may be used include olefin sulphonates, paraffin sulphonates, alkyl sulphates and mixtures of alkyl benzene sulphonate with alkanolamides.

The anionic surfactant is preferably present in a concentration of from 3 to 25% by weight of the composition, especially 5 to 24% e.g. 6 to 20% by weight. For some markets, compositions containing a high ratio of builder to surfactant are desirable, and the anionic surfactant is typically in the range 5 to 15%, e.g. 6 to 12%. Other markets may require high total surfactant levels, e.g. 15 to 30%.

One preferred active system comprises a major proportion of anionic surfactant, preferably sodium alkyl benzene sulphonate or, most preferably a mixture of sodium alkyl benzene sulphonate and sodium alkyl polyoxyalkylene ether sulphate and a minor proportion of non-ionic surfactant comprising

an alkylethoxylate and, optionally, but preferably, a mono- or di-ethanolamide such as coconut diethanolamide. The alkylbenzene sulphonate and the ethyl polyoxyethylene sulphate may be present in a relative proportion by weight of from 10:1 to 1:2, preferably 5:1 to 1.5:1, especially 2:1 to 1:1.2, e.g. 1:1. The total of the anionic surfactant is preferably from 12 to 25%, more preferably 15 to 20%, by weight of the composition. The total proportion of nonionic is preferably from 20 to 40%, e.g. 25 to 37%, more usually 30 to 35%, by weight of the total anionic and preferably from 2 to 8%, especially 3 to 6%, e.g. 4 to 5.5%, by weight of the composition. The alkanolamide may typically be present in a proportion of from 0.5 to 5%, e.g. 0.75 to 4%, especially 0.8 to 2% by weight of the composition.

The composition preferably contains sufficient total dissolved electrolyte to provide a spherulitic structure. This can usually be identified by centrifuging off the suspended builder and examining the liquid medium by optical or electron microscopy whereupon close packed spherulites may be observed. Preferably the total electrolyte concentration is adjusted to form a substantially space filling flocculated system, e.g. one which does not form two or more separate liquid layers when centrifuged for two minutes at 20,000 G. The spherulites are believed to exhibit a concentric structure which exhibits X-ray scattering or neutron diffraction peaks indicative of a 110-140 nm repeat spacing.

The surfactant may also be present as an emulsified lamellar phase. This may appear, with some surfactant systems, as droplets resembling spherulites, but distinguishable from them both in appearance and properties at electrolyte concentrations slightly greater than those required to provide true spherulites. The emulsified, lamellar phase shows evidence of the presence of a 30-70nm repeating structural unit under neutron scattering or X-ray diffraction analysis. In some systems the emulsion separates on standing into a liquid lye layer and a lamellar liquid crystal ("G" phase) layer unless a stabiliser, e.g. a film forming polymer, such as a polyacrylate, or an emulsifying or dispersing agent, is present. In such systems we prefer that an appropriate emulsifying or dispersing agent should be used.

The surfactant may alternatively be present as an open reticular lamellar phase cocontinuous with the lye phase, as described in G.B. 2123846.

The total quantity of electrolyte required will depend upon the nature and concentration of surfactant present. The electrolyte comprises dissolved sodium tripolyphosphate and may additionally comprise any builder which is a surfactant-desolubilising, ionisable salt of a monovalent acid or base such as sodium or potasssium nitrilotriacetate, or phosphonate. It is, however, essential to include in the electrolyte, at least a substantial proportion of at least one compound NaX. The latter may for example be sodium hydroxide, a sodium halide such as sodium chloride, sodium fluoride, sodium bromide or sodium iodide, sodium nitrate or a surfactant desolubilising sodium salt of a monobasic organic acid, such as sodium formate, sodium acetate or sodium trichloracetate. Preferably the compound NaX is present in a concentration of at least 0.5%, typically more than 1%, most preferably more than 1.25% by weight. The compound NaX may constitute the whole of the dissolved electrolyte, other than sodium tripolyphosphate, or preferbaly at least a major part of the total dissolved elecrolyte. Sodium hydroxide used to neutralise any sulphonic or alkyl sulphuric acid present so as to form surfactant in situ does not contribute to the electrolyte content, since it is not present as a non-surfactant electrolyte in the composition.

Depending upon what other electrolytes are present the compound NaX may be present in concentrations up to 10 or even 15% by weight of the composition. We do not exclude the possibility of using higher concentrations, although they will normally be precluded by considerations such as cost, adverse effects on washing performance or on the stability of the spherulitic system or by solubility limitations. usually the compound NaX will be present in total concentration of from 0.75 to 5% by weight of the composition, especially 1 to 3%. Two or more compounds NaX may be present, for instance we have found mixtures of sodium hydroxide and sodium chloride particularly useful.

Polyvalent anions are preferably absent or present in concentrations below the minimum at which they cause instability. For instance carbonate, pyrophosphate, orthophosphate, metaphosphate, sulphate and other polyvalent anions are preferably avoided, or maintained at concentrations below 6% preferably below 5%, more preferably below 4% e.g. below 2% especially below 1%, more especially below 0.5%, of the weight of the composition. Sodium silicate has also been found undesirable because of its adverse affect on the physical properties of the system when substantial levels of non-ionic surfactant are present. While we do not exclude the possibility of including sodium silicate, we prefer that it is absent, or maintained within the above limits.

Salts which are chemically unstable in the composition are also preferably absent unless they have been protected against decomposition or premature reaction, e.g. by a suitable form of encapsulation or by the inclusion of chemical stabilisers. Such salts include perborates, chlorates, hypochlorites, perchlorates and persulphates.

The compositions of our invention contain sodium tripolyphosphate in excess of its solubility in the aqueous medium, the excess being present as suspended solid particles. The tripolyphosphate may typically be present in a total proportion between about 10 and about 35% by weight of the composition, e.g. 12 to 30%, preferably 15 to 25% by weight.

The compositions of our invention may contain any of the usual additives and minor ingredients that are compatible with the formulation, e.g. soil suspending agents such as sodium carboxymethyl cellulose, optical brightening agents, perfumes, dyes, fabric softeners, clays such as bentonite, foaming agents, antifoams enzymes and bleaches.

While it is possible to include in our compositions

solvents such as ethanol, ethyleneglycol, isopropanol, propyleneglycol or glycerol or hydrotropes such as sodium benzene sulphonate, sodium xylene sulphonate or sodium toluene sulphonate, we have found in general that they do not improve the washing performance of the composition, add to its cost and make it more difficult to obtain a stable spherulitic composition. We therefore prefer that they be absent.

The invention is illustrated by the following examples:

| | Example A | Example B | Example C |
|---|---|---|---|
| Sodium Linear $C_{12-14}$ alkyl benzene sulphonate | 9.06 | 8.96 | 9.7 |
| Sodium $C_{12-14}$ alkyl 5 mole poly-oxyethylene sulphate | 7.05 | 8.96 | - |
| $C_{12-15}$ synthetic alkyl 7 mole ethoxylate | 5.03 | 4.01 | 4.8 |
| Cocount diethanol-amide | - | 0.98 | - |
| Sodium tripoly-phosphate | 20.14 | 18.0 | 19.4 |
| Potassium carbonate | 2.01 | 2.5 | - |
| Sodium chloride | 1.15 | 0.5 | - |
| Sodium hydroxide | - | 1.02 | 4.0 |
| Optical brightener | 0.1 | 0.1 | 0.1 |
| Sodium carboxy-methyl cellulose | 0.1 | 0.2 | 0.1 |
| Perfume | 0.3 | 0.3 | 0.3 |
| % Solids | 45.3 | 45.5 | 38.4 |

Examples A, B and C were made up by stirring together the specified ingredients, the balance in each case being water. The compositions were pourable, homogenous and stable, showing no sign of sedimentation after three months at laboratory ambient temperature, and gave good performance in washing tests.

**Examples D-F**

Automatic diswashing liquids have the following formulae:

| | Example D | Example E | Example F |
|---|---|---|---|
| LF403 | 6.98 | 13.5 | 13.5 |
| NP9 | 3.48 | 6.8 | 6.8 |
| NaCl | 2.03 | 2.2 | 2.2 |
| $K_2CO_3$ | 6.10 | - | - |
| S.T.P. | 20.35 | 22.1 | 22.1 |
| Polyelec-trolyte | - | - | 2.0 |
| Perfume | - | - | 0.2 |
| Water | Balance | Balance | Balance |

(LF 403 is an ethoxylated and propoxylated $C_{18-15}$ alcohol NP9 is nonyl phenyl 9 mole ethoxylate. STP is sodium tripolyphosphate).

In each case the composition was a brilliant white, opaque pourable fluid which gave good performance with low foaming in automatic dishwasher tests.

For comparison, when the above formulations were prepared in the absence of NaCl the compositions had a curdled appearance resembling cottage cheese.

**Claims**

**1.** A liquid detergent composition comprising a non-ionic surfactant, suspended sodium tripolyphosphate and a surfactant desolubilsing electrolyte of the formula NaX where X is OH or the anion of monobasic non-surfactant acid, in an amount sufficient to provide a stable homogeneous, non-sedimenting detergent composition.

**2.** A composition according to claim 1 wherein said non-ionic surfactant comprises an alkoxylate.

**3.** A composition according to claim 2 wherein a said alkoxylate is an ethoxylated $C_{8-18}$ natural or synthetic alcohol, fatty acid, alkyl phenol or sobitan or glycerol ester.

**4.** A composition according to any foregoing claim wherein said non-ionic surfactant comprises an alkanolamide, amine oxide or alkoxylated amine oxide.

**5.** A composition according to any foregoing claim additionally comprising an anionic surfactant.

**6.** A composition according to claim 5 wherein the anionic surfactant comprises sodium alkyl benzene sulphonate, or a mixture thereof with a sodium alkyl polyethyleneoxy sulphate.

**7.** A composition according to any foregoing claim wherein the nonionic surfactant is present in a proportion of from 15 to 100% of the total surfactant.

**8.** A composition according to any foregoing

claim wherein the nonionic surfactant is present in a proportion of 2 to 20% by weight of the composition.

**9.** A composition according to any of claims 5 to 8 wherein the nonionic surfactant is present in a proportion of from 3 to 25% by weight of the composition.

**10.** A composition according to any foregoing claim containing sufficient dissolved electrolyte to form a spherulitic structure which does not form two or more separate liquid layers when centrifuged for two minutes at 20,000 G.

**11.** A composition according to claim 10 which exhibits an X-ray diffraction and/or neutron scattering peak corresponding to a repeat distance of 110 to 140 nm.

**12.** A composition according to any of claims 1 to 9 comprising sufficient dissolved electrolyte to form a lamellar phase emulsified in a liquid lye phase.

**13.** A composition according to claim 12 which exhibits an X-ray diffraction and/or neutron scattering peak corresponding to a repeat spacing of 30 to 70 nm.

**14.** A composition according to either of claims 12 and 13 containing sufficient of a polymeric film forming, emulsifying or dispersing agent to maintain said lamellar phase emulsified in said lye phase.

**15.** A composition according to any foregoing claim wherein said electrolyte comprises, sodium hydroxide, a sodium halide, sodium nitrate or a surfactant desolubilising salt of a monobasic organic acid.

**16.** A composition according to claim 15 wherein said electrolyte comprises sodium chloride.

**17.** A composition according to claim 15 wherein said electrolyte comprises sodium formate, sodium acetate or sodium trichloracetate.

**18.** A composition according to any foregoing claim containing from 0.5 to 15% by weight of said electrolyte NaX.

**19.** A composition according to claim 18 containing at least 1% by weight of said electrolyte NaX.

**20.** A composition according to any foregoing claim containing from 1 to 3% by weight of said electrolyte NaX.

**21.** A composition according to any foregoing claim which is substantially free from dissolved polyvalent anions.