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(54) Improvements to hard surface cleaners

(57) The invention relates to improvements to hard surface cleaners, and in particular to hard surface cleaners containing suspended particles. The invention provides a stable, structured, liquid, hard surface cleaning composition comprising a continuous aqueous phase, a dispersed lamellar phase and 1-80%wt on product of a dispersed, suspended particulate phase, said product comprising at least 2 and not more than 20%wt on aqueous phase of surfactant, said surfactant comprising primary alcohol sulphate (i) and ethoxylated nonionic surfactant (ii) wherein the ratio of (i):(ii) falls in the range 5:1 to 0.45:1, said composition further comprising not more than 20%wt dissolved electrolyte CHARACTERISED IN THAT, said electrolyte has a monovalent anion, said electrolyte is present in weight excess over the total surfactant present, said particulate phase comprises calcium carbonate, dolomite, sodium hydrogen carbonate, potassium sulphate, alumina, hydrated alumina, feldspar, talc or silica and in that the ethoxylated nonionic surfactant (ii) has more than 5 and less than or equal to 10 moles of ethoxylation per mole of surfactant.

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Description

Technical Field:

The present invention relates to improvements to hard surface cleaners, and in particular to hard surface cleaners containing suspended particles.

Background to the Invention:

Hard surface cleaners containing abrasive particles are well known. Typical compositions comprise one or more surfactants in solution and a plurality of abrasive particles dispersed therein. In this art it is generally considered necessary to ensure that the abrasive particles remain in suspension in the composition in order that the composition need not be vigorously shaken before use and sedimentation or even cementing of precipitated particles is prevented.

In one sub-class of compositions, one or more surfactant components act as a suspending agent, usually in combination with a dissolved electrolyte. The presence of the electrolyte causes the surfactant component(s) to thicken by the establishment of a lamellar phase.

In another sub-class of compositions, an additional non-surfactant suspending agent, such as a clay or polymer is present.

Related compositions are known which comprise non-abrasive particles such as hygiene agents, i.e. water-insoluble or sparingly soluble bleaching agents and the present invention includes such compositions within its scope.

In such suspending systems, the viscosity of the product generally varies with the shear applied. This property is usually referred to as 'shear thinning'. The viscosity achieved under various rates of shear is important in determining the product properties.

At low or zero shear, it is desirable that products should exhibit relatively high viscosity for storage stability of the suspension without sedimentation of the particles over a reasonable shelf life. At moderate shear, it is desirable that products should flow in order that they can be controllably dosed. At high shear it is desirable that the viscosity should be sufficiently low to facilitate cleaning operations using the product.

Surfactants employed as suspending agents in liquid abrasive cleaners have included, alkyl benzene sulphonates, alcohol ethoxylates, alkyl amido ethoxylates, fatty acid soaps and secondary alkyl sulphonates. Combinations of these surfactants, together with electrolytes are used to form the suspending systems in a number of commercial products.

As mentioned above, suspending surfactant system must be both pourable and have a high yield stress, i.e. it must be dosable and must be capable of suspending macroscopic particles. The fine structure of such systems generally consists of generally spherical structures ranging from about 0.05 to about 10 microns in diameter. These structures are believed to comprise alternating bilayers of surfactant molecules spaced apart by thin layers of aqueous electrolyte solution, i.e. lamellar phase. However, the suspending system is not the only structure which surfactants can form in the presence of water. The above-mentioned surfactants can also form structured aqueous liquids which are viscous but are not capable of suspending particles. In addition, compositions of surfactant and water may separate into two or more mixed phases with different physical properties.

It is particularly desirable, in liquid abrasive cleaners which employ surfactants as the suspending system, that the suspending system is stable over the range of temperatures encountered in use and sufficiently suspending to maintain the abrasive particles in suspension for the shelf life of the product. It is also desirable that the interactions of other components in the composition with the suspending surfactants, do not modify the rheology of the overall composition to an extent that the desired shear-thinning property is lost.

Some surfactant combinations form suspending systems more readily than others. Mixtures of alkyl benzene sulphonates with alcohol ethoxylates and, optionally, small amounts of fatty soaps comprise the suspending surfactant system used in a number of successful commercial products. A variety of electrolytes can be used with such systems, including alkali metal carbonates, citrates, halides (particularly chlorides) phosphates, sulphates, ammonium salts and acetates. Amongst the anions, the multivalent anions are preferred for reasons of cost and due to the additional benefits which these components bring: such as alkalinity from carbonate and builder activity from citrate.

Surfactant/electrolyte suspending systems can have a relatively narrow formulation window within which consumer-preferred viscosities must be achieved, depending on the type of surfactant present.

A problem with surfactant-containing suspending systems is that some of the surfactants which most readily form suspending systems, and are therefore commonly in use, are not as desirable for environmental reasons as other surfactant systems.

In particular, primary alcohol sulphate (hereinafter referred to as PAS) is an environmentally preferable surfactant, due to its ease of biodegradability and the fact that it can be obtained from natural, sustainable and hence renewable sources. It has not proved possible to form stable suspending systems comprising significant levels of PAS and relatively low levels of other surfactants. In addition it is difficult to form stable suspending systems comprising PAS and multivalent anions such as carbonate, citrate and sulphate.

Non-suspending systems comprising 1-1.2% PAS, 0.1-1.5% of a mixed non-ionic system and low molecular weight non-thickening polymer are disclosed in GB 2160887 (Bristol-Myers: 1984).

Non-suspending surfactant systems, comprising relatively high levels of PAS in combination with ether-sulphates and semi-polar non-ionic detergents (such as amine oxides, phosphine oxides and sulphoxides) are disclosed in GB 1524441 (P&G: 1976).

Complex surfactant systems comprising a plurality of components including well under 30% on total surfactant of PAS are taught in EP 0181212 (P&G: 1984) and EP 0039110 (P&G: 1980).

EP 0107946 (P&G, 1983, see Example II) discloses an unstructured dishwashing composition in which PAS is the most predominant single surfactant species present but never exceeds 50% of the total surfactant system.

EP 0125711 (Unilever, 1983) discloses almost electrolyte-free, structured liquid compositions comprising polymer, ethoxylated alcohol surfactants and PAS in a ratio such that the PAS is never in excess of one third of the total surfactant present.

Of the two known commercial products comprising PAS and a particulate abrasive, one is notoriously unstable and phase-separates, in the worst cases, after a few hours of storage into a thick clay-like mass of particles and a 'cream' of surfactant separated by a clear liquid layer.

The other product is believed to have comprised 50% of a calcite abrasive in a PAS/nonionic/sodium acetate surfactant system. In the latter case, the high level of abrasive led to difficulties in rinsing. In general, it is more difficult to suspend lower levels of abrasive due to to reduced particle-particle interactions. However, lower levels of abrasive are desirable in that compositions with low levels of abrasive are more easily rinsed.

As mentioned above, it is known to use polymers as a part of the suspending system. Known polymers include polysaccharides, e.g. sodium carboxymethyl cellulose and other chemically modified cellulose materials, xanthan gum and other non-flocculating structuring agents such as Biopolymer PS87 referred to in US Patent No. 4 329 448.

Polymers of acrylic acid cross-linked with a poly-functional agent, for example members of the CARBOPOL (RTM: Goodrich) family, are also be used as structuring agents in suspending systems. The amount of such structuring agents can be as little as 0.001% but is more typically at least 0.01% by weight of the composition. Commercial products typically contain around 0.1-0.4%wt of the cross-linked acrylic acid polymer.

It is also known to employ at least partially esterified resins such as an at least partially esterified adduct of rosin and an unsaturated dicarboxylic acid or anhydride, or an at least partially esterified derivatives of co-polymerisation products of mono-unsaturated aliphatic, cycloaliphatic or aromatic monomers having no carboxy groups and unsaturated dicarboxylic acids or anhydrides thereof as deposition agents.

Typical examples of suitable copolymers of the latter type are copolymers of ethylene, styrene and vinylmethylether with maleic acid, fumaric acid, itaconic acid, citraconic acid and the like and the anhydrides thereof including the styrene/maleic anhydride copolymers.

It will be appreciated that, polymers are of use where the surfactant system structures poorly at low shear, i.e. where storage stability is poor. However polymers have the disadvantage of also increasing the viscosity at high shear and therefore increasing the effort required in cleaning operations using the product.

In order to achieve particular viscosities under specific shear conditions, is desirable that products should derive their structural and rheological properties both from a polymeric structuring agent and from surfactant-electrolyte interactions. Known products have therefore comprised a surfactant such as alkyl benzene sulphonate, a co-surfactant such as an alcohol ethoxylate, an electrolyte and a polymer.

Brief Description of the Invention:

We have now devised a stable, particle suspending, structured liquid composition comprising PAS as a substantial proportion of the surfactant an electrolyte and, optionally a polymeric structuring agent. In the context of the present invention 'stable' should be taken to mean stable under the condition specified below.

It is believed that the formulations described herein provide products which are stable under the range of commonly encountered storage temperatures, exhibit acceptable cleaning properties and rheology and comprise relatively higher proportions of the more preferable surfactants having regard to biodegradation properties than previously known compositions.

Detailed Description of the Invention:

According to the present invention there is provided a stable, structured, liquid composition comprising a continuous aqueous phase, a dispersed lamellar phase and 1-80%wt on product of a dispersed, suspended, particulate phase, said product comprising 2-25%wt on product of surfactant, said surfactant comprising primary alcohol sulphate (i) and alkoxylated nonionic surfactant (ii) wherein the ratio (i)/(ii) falls in the range 20 to 0.40 said composition further comprising 1-20% dissolved electrolyte on product.

Polymers:

High molecular weight hydrophillic polymer is an optional ingredient of compositions according to the present invention.

In those embodiments of the present invention which are hard surface cleaners, it is particularly preferable that such a polymer is present. Typically compositions will comprise 0.01-2% of a hydrophillic polymer having a average molecular weight in excess of 500,000 Dalton.

Without wishing to be bound by any theory of operation, it is believed that the polymer is of sufficiently high molecular weight to remain in the continuous phase when hydrated and that the affinity of the polymer for water, causes a partial repartitioning of water from the lamellar phase of the product into the continuous phase of the product, increasing the effective concentration of surfactant and electrolyte in the lamellar phase and improving the structuring properties of that phase.

Preferred types of polymer include poly-carboxylates, polysaccharides and mixtures thereof, including co-polymers within or between these classes or co-polymers with styrenes and so forth.

Preferred amongst the poly-carboxylates are the crosslinked poly-acrylates, crosslinked poly-methacrylates, and mixtures thereof. Crosslinked, poly-acrylates are the most preferred polymers. These materials are available from a variety of commercial sources as illustrated hereafter by way of example.

Preferred amongst the poly-saccharides are xanthan and guar gums, cellulose ethers, and mixtures thereof.

Preferred levels of polymer are 0.05-1% on product, more preferably 0.1-0.5wt% with levels of around 0.1-0.3 being particularly preferred for the cross-linked poly-acrylate, so as to achieve the desired viscosity.

In general, the levels of polymer present should be such that the viscosity, as measured at 25 Celsius, at a shear rate of 21 sec^{-1} falls in the range 300-2500 mPas. It is particularly preferred that the viscosity at this shear rate should fall into the range 600-1800 mPas. Such viscosities facilitate easy dosing.

The viscosity at lower rates of shear, i.e below 10^{-3} sec^{-1} should be sufficiently high to provide for storage stability of the product in that significant particle sedimentation should be avoided.

The viscosity at higher rates of shear, i.e above 100 sec^{-1} should be sufficiently low provide for ergonomic use of the product and avoid excessive effort being required in use.

In compositions according to the present invention in which the particles are chemically reactive, suspended, hygiene agents rather than chemically inert abrasives, polymer is not an essential component but where present a polymer should be selected which is chemically stable in the presence of the hygiene agent.

Surfactant System:

Primary alcohol sulphates and alkoxylated nonionic surfactants are essential ingredients of the compositions according to the present invention.

Preferably, the ratio of primary alcohol sulphate (i) to the one or more nonionic surfactants (ii), expressed as (i)/(ii) in weight% falls in the range 5-0.45. More preferably the ratio falls into the range 2-0.6. Even more preferably the ratio falls is 1.5-0.75 and is most preferably around 1.

As mentioned above, primary alcohol sulphate (hereinafter referred to as PAS) is an environmentally desirable surfactant, due to its ease of biodegradability and the fact that it can be obtained from renewable sources.

The preferred primary alcohol sulphate comprises a mixture of materials of the general formulation:

$$ROSO_3X$$

wherein R is a C_8 to C_{18} (mean chain length) primary alkyl group and X is a solubilising cation. Suitable cations include sodium, magnesium, potassium, ammonium and mixtures thereof.

C8-18 (mean chain length) PAS is preferred due to its detergent and structuring properties. Above mean alkyl chain lengths of C18, the material tends to become too insoluble for use, whereas below mean chain lengths of C8 the material tends to become too soluble for use. C10-C16 (mean chain length) PAS is particularly preferred as materials with this chain length average have optimal detergent properties and are readily available.

The preferred alkoxylated non-ionic surfactants are selected from the group comprising alkoxylated: alkyl polyglucosides, alcohols, alkyl sulphoxides, alkyl polyglycerols, fatty acid esters, amides and amines and mixtures thereof.

The most preferred nonionic surfactant is selected from the group comprising ethoxylated alcohols of the general formula:

$$R_1\text{-}(OCH_2CH_2)_m\text{-}A\text{-}OH$$

wherein R_1 is the residue of a branched, or unbranched, C_8 to C_{18} preferably primary, alcohol, A is preferably absent or is the residue of a polyol of at least two carbons and two hydroxyl groups, and the average degree of ethoxylation (i.e. the ethylene oxide chain length) m is 1-14. R1 can be a 2-hydroxy alkyl residue of the same chain length.

Where A is present it can be the residue of an alkylene glycol or a sugar. Generally, A will be absent. It should be noted that propoxy residues can replace the ethoxy residues in whole or in part.

The alcohol ethoxylates are excellent detergents, available at low cost in commercial quantities and exhibit concentration-sensitive interactions with electrolyte and PAS enabling the formation of a suspending system.

Optimum detergent properties are obtained where m is (mean for the surfactant) in the range 1-14.

Most preferred amongst the ethoxylated alcohols are those which have m less than or equal to 10. These shorter chain ethoxylated alcohols have better biodegradability than the longer chain ethoxylated alcohols, and it becomes progressively more difficult to form a suspending system with the longer ethoxylate chain ethoxylated alcohols.

In preferred embodiments of the invention the overall surfactant system consists of: 2-10% primary alcohol sulphate (i) and 2-10% ethoxylated alcohol (ii) in a weight ratio of (i)/(ii) which falls in the range 2.0-0.6 , and, 0.1-2% of a fatty acid soap having a mean of C10-C18 carbon atoms.

Electrolyte:

Electrolyte is an essential component of compositions according to the present invention.

For the longer chain ethoxylated alcohols, wherein m (the average degree of ethoxylation) is greater than 5, i.e. generally 5-10, monovalent anion electrolyte needs to be present in weight excess over the total surfactant present in the composition: whereas either monovalent or divalent anions can be used as the electrolyte with the shorter chain ethoxylates (i.e where m is less than or equal to 5).

Consequently, preferred embodiments of the present invention comprise:

a) 2-25%wt surfactant on aqueous phase, said surfactant comprising primary alcohol sulphate (i) and one or more ethoxylated alcohols (ii) of the general formula:

$$R_1\text{-}(OCH_2CH_2)_m\text{-}OH$$

wherein R_1 is straight or branched, C_8 to C_{18} alkyl and the average degree of ethoxylation m is 5-10,

b) a weight-excess of electrolyte on aqueous phase as compared with (a), said electrolyte comprising a salt in which the anion is monovalent, and,

c) 0.01-2% of a hydrophillic polymer having a average molecular weight in excess of 500,000 Dalton.

Preferably, the monovalent anions are selected from the group comprising chlorides, bromides, iodides, acetates, bicarbonates, and mixtures thereof having regard to the chemical nature of the particulate phase such that where the particulate phase is chemically reactive, the electrolyte is selected to be inert towards the particulate phase.

The preferred ratio's of the surfactants are as described above.

As mentioned above, we have determined that, when the ethoxylated alcohols have m less than or equal to 5, it is possible to formulate stable products in which the electrolyte solution comprises either multivalent or monovalent anions. In those compositions in which the ethoxylated alcohols have m greater than or equal to 5, it is not possible to formulate products in which the electrolyte solution comprises significant levels of multivalent anions.

Consequently, preferred embodiments of the present invention comprise:

a) 2-25%wt surfactant on aqueous phase, said surfactant comprising primary alcohol sulphate (i) and one or more ethoxylated alcohols (ii) of the general formula:

$$R_1\text{-}(OCH_2CH_2)_m\text{-}OH$$

wherein R_1 is straight or branched, C_8 to C_{18} alkyl and the average degree of ethoxylation m is 1-5,

b) 1-20%wt electrolyte on aqueous phase, and,

c) 0.01-2% of a hydrophillic polymer having a average molecular weight in excess of 500,000 Dalton.

Preferably, said electrolyte comprises 25-100mole% multivalent anions on total anions.

Preferably, the multivalent anions are selected from the group comprising, carbonates, citrates, sulphates and mixtures thereof. Carbonates alone, or mixtures comprising carbonates are particularly preferred.

The presence of multivalent anions is preferred due to the benefits of alkalinity (with carbonates) and builder activity (with both carbonates and citrates).

Preferred levels of electrolyte fall in the range 1-10%, more preferably 2-8%. It is particularly preferred that the anions of the electrolyte comprise at least 50mole% carbonate.

Particulate Phase:

A dispersed, suspended particulate phase is an essential ingredient of compositions according to the present invention.

Preferably, the dispersed suspended particulate phase comprises a particulate abrasive which is either insoluble in the aqueous phase or present in such excess that the solubility of the abrasive in the aqueous phase is exceeded and consequently solid abrasive exists in the composition.

Preferred abrasives for use in general purpose compositions have a Moh hardness below 6 although higher hardness abrasives can be employed for specialist applications.

Suitable abrasives can be selected from, particulate zeolites, calcites, silicas, silicates, carbonates, aluminas, bicarbonates, borates, sulphates, and, polymeric materials such as polyethylene.

Preferred average (weight average) particle sizes for the abrasive fall in the range 0.5-200 microns, with values of around 10-100 microns being preferred. In this range an acceptable compromise between good cleaning behaviour and low substrate damage is achieved.

Preferred levels of abrasive range from 5-70wt% on product, preferably in the range 20-40wt%, most preferably around 35wt%. Such levels of abrasive give effective cleaning and good rinsing.

The most preferred abrasives are calcium carbonate (as calcite), mixtures of calcium and magnesium carbonates (as dolomite), sodium hydrogen carbonate, potassium sulphate, zeolite, alumina, hydrated alumina, feldspar, talc and silica. Calcite and dolomite are particularly preferred due to their low cost, hardness and colour.

Preferably, where the suspended particulate phase is calcite at 50%wt on product the electrolyte is other than acetate.

As mentioned above it is progressively more difficult to formulate compositions with more dense as opposed to less dense particles, consequently, the particles used in embodiments of the present invention preferably have a density lower than 2.7 gm/cm^3: this excludes unmodified calcite. Where calcite is used it should be used at levels below 50% on product in order to improve rinsing performance. The suspending systems of the present invention are capable of suspending calcite at relatively low levels, i.e. 20-40%wt, at which levels particle-particle interactions are reduced as compared with higher levels of calcite.

Without wishing to be restricted by theory, is believed that there is an interaction between the calcite and polymer, in the continuous phase, which leads to the formation of a complex structure comprising both polymer and calcite. It is believed that this structure has an effective density lower than that of calcite (s.g. 2.7-2.9) and consequently the calcite is less difficult to suspend in systems according to the present invention.

In the alternative, the particulate phase can comprise a hygiene agent, preferably a solid organic peracid. Examples of such hygiene agents include diperoxy-dodecanedioic acid (DPDA) and e-N-N-phthaloyl-amino-peroxy-caproic acid (PAP). Alternative, insoluble hygiene agents include triclosan (2,4,4'-trichloro-2'-hydroxy diphenyl ether) and insoluble derivatives thereof. These may be present in combination with or to the exclusion of the abrasive particles.

Solvents:

In addition to the abovementioned components compositions according to the present invention can comprise a solvent. Solvents are an optional component and are not essential to the practice of the present invention.

Preferred solvents are selected from: propylene glycol mono n-butyl ether, dipropylene glycol mono n-butyl ether, propylene glycol mono t-butyl ether, dipropylene glycol mono t-butyl ether, diethylene glycol hexyl ether, ethyl acetate, methanol, ethanol, isopropyl alcohol, ethylene glycol monobutyl ether, diethylene glycol monobutyl ether, n-methyl pyrollidone and mixtures thereof.

The preferred solvents are propylene glycol mono n-butyl ether, dipropylene glycol mono n-butyl ether, ethanol, isopropyl alcohol, diethylene glycol monobutyl ether and mixtures thereof.

Minors:

The compositions of the invention can further comprise other non-essential components selected from the group comprising: perfumes, colours, whitening agents (such as titanium dioxide) and dyes, hygiene agents, foam-control agents, preservatives and mixtures of one or more thereof.

Preferably the foam control agents comprise calcium sensitive soaps. Particularly preferred soaps are the C10-C18 saturated or unsaturated fatty acids and salts thereof. Preferred levels of soap range from 0.1-2% of a fatty acid soap having C10-C18 carbon atoms. It is particularly preferred that the ratio of soap to total active should fall into the range: 1:5-1:20.

As will be elaborated upon hereafter, while not necessary, the presence of fatty acid soap is required for preferred process aspects of the present invention.

Having regard to the various constraints and preferred features required to obtain optimum performance, particularly preferred embodiments of the present invention provide a stable, liquid composition comprising a continuous aqueous phase and a dispersed, suspended particulate phase, wherein the particles comprise calcite, dolomite, bicarbonate and mixtures thereof, and the aqueous phase comprises:

a) 2-10% primary alcohol sulphate comprising a mixture of materials of the general formulation:

$$ROSO_3X$$

wherein R is a C_{10} to C_{16} primary alkyl group and X is a solubilising cation selected from the group comprising sodium, magnesium, potassium, ammonium and mixtures thereof,

b) 2-10% ethoxylated alcohols of the general formula

$$R_1\text{-}(OCH_2CH_2)_m\text{-}OH$$

wherein R_1 is straight or branched, C_8 to C_{18} alkyl and the average degree of ethoxylation m is 1-5, wherein the ratio of a:b falls in the range 1:2 to 2:1,

c) 1-10%wt electrolyte on aqueous phase, said electrolyte comprising 25-100mole% multivalent anions selected from the group comprising carbonates, citrates, sulphates and mixtures thereof on total anions,

d) 0.1-2% of a fatty acid soap having C10-C18 carbon atoms, and,

e) 0.1-0.5% of a hydrophillic, crosslinked polymer having a average molecular weight in excess of 500,000 Dalton.

Process Aspects:

Further aspects of the present invention concerns the process.

Primary alcohol sulphate (PAS) is unstable in the acid form, decomposing to the corresponding alcohol and oxides of sulphur. This difficulty does not arise with the commonly used linear alkyl benzene sulphonate (LAS) surfactants which are stable in the acid form. Consequently, PAS is commonly handled and transported as an aqueous solution of around 30%wt or 70%wt concentration, neutralised with a suitable base, such as sodium or ammonium hydroxide, to form an alkali metal salt solution, whereas LAS, as the acid, can be handled and transported in substantially anhydrous form as a viscous liquid.

PAS forms a gel phase at concentrations above 30%wt in aqueous solution, depending on the chain lengths of the PAS and degree of branching and remains in this phase until higher concentrations, of around 70% are reached, where a pumpable phase is again formed. Compositions which comprise both polymers and PAS are difficult to prepare as the production process must not at any stage form a composition in which the PAS or the polymer form a significant quantity of gel. Gels can be formed, when PAS and polymer are mixed, due to the reduction of the water activity in the PAS caused by the presence of the polymer and subsequent competition for the available water.

Moreover, certain hydrophillic, high molecular weight polymers, such as the crosslinked polyacylates should not be exposed to other than mildly alkaline conditions as such conditions will cause gelling of the polymer. In addition, these polymers cannot be dissolved at high concentrations in neutral aqueous solution.

Where abrasive components are present, initial suspension of abrasives in the absence of a suspending system requires high shear which can incorporate air into any viscous mixture which is formed during mixture of components. This air is difficult to remove.

We have now determined how aqueous compositions comprising the preferred hydrophillic high molecular weight polymers, particulate abrasives and primary alcohol sulphates can be prepared without the abovementioned difficulties.

Accordingly, a further aspect of the present invention provides a process for the preparation of a cleaning composition which comprises the steps of:

a) obtaining a mixture of 1-3%wt hydrophillic polymer having a molecular weight in excess of 500,000 and water, substantially free of electrolyte,

b) separately to (a) obtaining a premix of primary alcohol sulphate, and at least 20% water,

c) separately to (a) and (b) obtaining a suspension of particulate abrasive in an aqueous electrolyte solution.

d) combining the products of steps (a), (b) and (c) with a fatty acid and a nonionic surfactant such that the mixture at no stage comprises:

i) both the products of steps (a) and (b) in the absence of fatty acid, or,
ii) nonionic surfactant and the product of step

(a) in the absence of the products of steps
(b) or the product of step (c).

One particularly preferred process route comprises:

a) obtaining a mixture of the fatty acid and the polymer, and combining the said mixture with water,

b) combining primary alcohol sulphate surfactant with the product of step (a), and,

c) combining the product of step b) with electrolyte, abrasive and nonionic.

An alternative preferred process route comprises:

a) preparing a mixture of electrolyte, abrasive and water,
b) mixing with the product of step (a), fatty acid, primary alcohol sulphate, and nonionic surfactant, and
c) preparing a separate premix of water and the polymer and combining this premix with the product of step (b).

In order that the present invention may be further understood it will be explained hereafter with reference to examples and by reference to the accompanying figures 1-4 which are:

Figure 1: shows the lamellar regions for formulations containing either PAS or alkyl benzene sulphonate with a 6.5 EO nonionic surfactant at varying levels of electrolyte levels,

Figure 2: shows the lamellar regions for formulations containing either PAS and a nonionic surfactant at varying electrolyte levels and for varying environmental conditions,

Figure 3: shows the lamellar regions for formulations containing PAS with a 3.0 EO nonionic surfactant at varying mono-valent electrolyte levels,

Figure 4: shows the lamellar regions for formulations containing PAS with a 3.0 EO nonionic surfactant at varying di-valent electrolyte levels,

Figure 5: shows the lamellar regions for formulations containing PAS with a 6.5 EO nonionic surfactant at varying mono-valent electrolyte levels,

<u>EXAMPLES</u>:

In order to illustrate the storage stability of the products according to the present invention four sets of storage conditions were employed.

These storage conditions are intended to model the environments encountered by the product during transport and storage either prior to, or after, sale of the product. The conditions are:

1) AMBIENT: Products were stored in closed containers, without agitation, for ten days at laboratory temperature (15-25 Celsius).

2) COLD: Products were stored in closed containers, without agitation, for twelve weeks at a temperature of 4 degrees Celsius in a thermostatted cold-box.

3) FREEZE: Products were stored in closed containers, without agitation, for ten days at a temperature of -10 degrees Celsius in a thermostatted cold-box.

4) WARM: Products were stored in closed containers, without agitation, for ten days at a temperature of 37 degrees Celsius in a thermostatted oven.

5) CYCLE: Products were stored in closed containers, without agitation, during ten temperature cycles, each of a twenty-four hour duration and each consisting of eight hours at -5 degrees Celsius followed by sixteen hours at 25 degrees Celsius.

At the end of each of the above-mentioned storage tests, products were, allowed to come to room temperature, examined visually and were categorised either as 'stable', where little or no phase separation had occurred; or 'unstable' where sedimentation of the abrasive had occurred to a clearly visible extent. The sedimentation of abrasive was generally accompanied by the formation of an at least 1mm clear layer in the product.

The materials listed below are identified both by the names used in the following examples and by their tradenames:

Polymers:

PolyGel DB	[RTM ex Sigma], a cross-linked polyacrylate supplied as a powder,
Alcogum SL71	[RTM ex Alco/National Starch], an acrylic terpolymer commercial gum,
Alcosperse 602N	[RTM ex Alco/national Starch], a linked acrylate copolymer commercial gum,
National 467-100	[RTM ex National Starch], a cross-linked polymethacrylate-styrene copolymer,
National 467-45	[RTM ex National Starch], a cross-linked polymethacrylate-styrene copolymer,
Kelzan T	[RTM ex Kelco], a xanthan gum

Surfactants:

LIAL-123S	[RTM ex. DAC], a sodium salt of synthetic, partly branched, primary alcohol sulphate having an average alkyl chain length in the range C_{12}-C_{13};
Empicol-LX	[RTM ex Albright & Wilson], a sodium salt of naturally derived, linear, primary alcohol sulphate having an average alkyl chain length in the range C_{12}-C_{14};
Synperonic A3	[RTM ex. ICI], an alcohol ethoxylate, nonionic surfactant having an average ethylene oxide chain length of 3 units.
Synperonic A7	[RTM ex. ICI], an alcohol ethoxylate, nonionic surfactant having an average ethylene oxide chain length of 7.5 units.
Dobanol 23-6.5	[RTM ex. Shell], an alcohol ethoxylate surfactant having an average ethylene oxide chain length (EO) of 6.5 units.
Dobanol 91-2.5	[RTM ex. Shell], an alcohol ethoxylate surfactant having an average ethylene oxide chain length (EO) of 2.5 units.
Prifac 7901	[RTM ex. Unichema], a mixed chain-length fatty acid having a similar chain length distribution to the fatty acids obtainable from coconut oil.

Abrasive:

MM5F	Calcite [ex. Minerva].

Minors:

CL318A	Perfume (ex. Quest International), a commercially available oily fragrance with a citrus odour.
Lindalia	Perfume (RTM ex. Firmenich), a commercially available fragrance with a flowery odour.
Proxel	Preservative (RTM ex. ICI).

Products were prepared by the following processes:

Process 1:

a) A premix was prepared of the fatty acid (soap) and the polymer, under moderate shear, using a Janke and Kunkel mixer with a star-shaped blade at a temperature of 50 Celsius.

b) The premix of (a) is dispersed in approximately one third of the water at 50 Celsius using a Janke and Kunkel mixer with a standard impeller.

c) The primary alcohol sulphate surfactant is added to the product of (b), as a paste of 70% active, preheated to a temperature of 37 Celsius. The non-ionic surfactant is either added at this point, after preheating to 35-45 Celsius or added as mentioned at (d) below.

d) The balance of the water is placed in a vessel at a temperature of 37 Celsius, followed by the electrolytes which are dissolved by stirring. The calcite is added with continuous stirring followed by the premix of (c). The non-ionic is added at this stage if not added at (c).

e) Preservative and volatile minors such as perfume, are added to the mix with stirring until a homogeneous dispersion is achieved.

Process 2:

a) A premix was prepared of the fatty acid, approximately one third of the water and the primary alcohol sulphate surfactant as a paste of 70% active at 37 Celsius using a Janke and Kunkel mixer with a standard impeller. The non-ionic surfactant is either added at this point, after preheating to 35-40 Celsius or added as mentioned at (b) below,

b) The balance of the water is placed in a vessel at 37 Celsius followed by the electrolytes which are dissolved by stirring. The calcite is added with continuous stirring and the resulting product mixed with the premix of (a). The non-ionic is added at this stage if not added at (a),

c) A separate premix of the polymer in 2% aqueous solution is prepared, under moderate shear, using a Janke and Kunkel mixer with a standard impeller at ambient temperature,

d) The premix of (c) is added to the product of step (b),

e) Preservative and volatile minors such as perfume, are added to the mix with stirring until a homogeneous dispersion is achieved.

Process 3:

a) A premix was prepared of the fatty acid (soap) and the polymer, under moderate shear, using a Janke and Kunkel mixer with a star-shaped blade at a temperature of 50 Celsius,

b) The premix of (a) is dispersed in approximately one third of the water at 50 Celsius using a Janke and Kunkel mixer with a standard impeller,

c) The balance of the water is placed in a vessel at 37 Celsius followed by the electrolytes which are dissolved by stirring. The calcite is added with continuous stirring using a Janke and Kunkel mixer with a standard impeller. To the mixture thus obtained, the primary alcohol sulphate surfactant as a solution of 27% active was added,

d) The product of step (b) was combined with the product of step (c), and the nonionic added after preheating to 35-40 Celsius, and,

e) Preservative and volatile minors such as perfume, are added to the mix with stirring until a homogeneous dispersion is achieved.

Process 4:

a) A premix of the polymer in 2% aqueous solution is prepared, under moderate shear, using a Janke and Kunkel mixer with a standard impeller at ambient temperature,

b) The balance of the water is placed in a vessel at 37 Celsius followed by the electrolytes which are dissolved by stirring. The calcite is added with continuous stirring using a Janke and Kunkel mixer with a standard impeller. To the mixture thus obtained, the primary alcohol sulphate surfactant as a solution of 27% active was added, followed by nonionic added after preheating to 35-40 Celsius and optional fatty acid,

c) The product of step (a) was combined with the product of step (b), and,

d) Preservative and volatile minors such as perfume, are added to the mix with stirring until a homogeneous dispersion is achieved.

Examples 1-7:

TABLE 1 below shows the storage stability of compositions according to the present invention and comparative examples which were either unstable or had unacceptable viscosity characteristics. These examples illustrate the importance of polymer.

TABLE 1

EXAMPLE	1	2	3	4	5	6	7
PolyGel DB	0.15	-	0.20	-	0.20	-	0.20
Lial-123S	3.25	3.22	3.22	3.57	3.57	2.86	2.86
Synperonic A3	3.25	3.22	3.22	2.86	2.86	3.22	3.22
Prifac 7901	0.65	0.71	0.71	0.71	0.71	1.07	1.07
Na_2CO_3	2.60	3.25	3.25	3.25	3.25	3.25	3.25
$NaHCO_3$	0.65	-	-	-	-	-	-
Calcite	35.0	35.0	35.0	35.0	35.0	35.0	35.0
Lindalia	0.21	0.21	0.21	0.21	0.21	0.21	0.21
Proxel	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Water	------------------to 100%-------------						
Process:	3	4	4	4	4	4	4
Viscosity:	1840	380	2210	Unst	1730	Unst	1900

Viscosity was measured at 21 sec^{-1}, at 25 Celsius using a Haake RV2 as supplied, with the MV cup provided with the MV2 bob. Results are given in mPas.

Comparative examples 4 and 6 showed unstable, many-phase behaviour and consequently the viscosity of these products was not measured.

Example 2 illustrates that while a stable product can be made without polymer the viscosity of the product under the shear conditions specified is undesirably low.

Examples 1,3, 5, and 7 are embodiments of the invention. The products of examples 1-3, 5 and 7 were all stable under storage conditions 1 and 3-5 as described above.

Examples 8-15:

TABLE 2 provides examples showing that other polymers can be employed at various levels.

TABLE 2

EXAMPLE	8	9	10	11	12	13	14	15
PolyGel DB	0.12	-	-	-	-	-	-	-
N-467-45	-	0.30	0.20	-	-	-	-	-
N-467-100	-	-	-	0.30	-	-	-	-
Alcogum	-	-	-	-	0.20	0.10	-	-
Kelzan-T	-	-	-	-	-	-	0.10	0.30
Lial-123S	3.25	3.25	3.25	3.25	3.22	3.22	3.25	3.25
Synperonic A3	3.25	3.25	3.25	3.25	3.22	3.22	3.25	3.25
Prifac 7901	0.65	-	-	-	-	-	0.65	0.65
ratio PAS/NI	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Na_2CO_3	2.60	3.25	3.25	3.25	3.25	3.25	3.25	3.25
$NaHCO_3$	0.65	-	-	-	-	-	-	-
Calcite	35.0	35.0	35.0	35.0	35.0	35.0	35.0	35.0
Lindalia	0.21	0.21	0.21	0.21	0.21	0.21	0.21	0.21
Proxel	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Water	----------------to 100%------------------							
Process:	1	4	4	4	4	4	4	4
Viscosity:	1200	1340	890	583	2000	1360	800	1460

Viscosity was measured at 21 sec^{-1}, at 25 Celsius using a Haake RV2 as supplied, with the MV cup provided with the MV2 bob. Results are given in mPas.

All products were found to be stable under conditions 1 and 3-5 as described above.

Examples 8-15 illustrate that stable compositions according to the present invention can be prepared with acceptable viscosity using alternative polymers.

Examples 16-18:

Table 3 shows the effect of modification of the surfactant system.

TABLE 3

EXAMPLE	16	17	18
PolyGel DB	0.12	0.12	0.12
Lial-123S	3.25	3.25	3.25
Dobanol-6.5	3.25	-	-
Dobanol91-2.5	-	3.25	-
Synperonic A7	-	-	3.25
Prifac 7901	0.65	0.65	0.65
ratio PAS/NI	1.00	1.00	1.00
Na_2CO_3	2.60	2.60	2.60
$NaHCO_3$	0.65	0.65	0.65
Calcite	35.0	35.0	35.0
Lindalia	0.21	0.21	0.21
Proxel	0.03	0.03	0.03
Water	----to 100%-----		
Process:	1	1	1
Viscosity:	Unst	1400	Unst

Viscosity was measured at 21 sec^{-1}, at 25 Celsius using a Haake RV2 as supplied, with the MV cup provided with the MV2 bob. Results are given in mPas.

Comparative Examples 16 and 18 illustrate that in the presence of electrolyte based on divalent anions (carbonate), compositions wherein the ethoxylate has a ethoxy chain length of greater than 5 are unstable.

Example 17 illustrates that an embodiment of the present invention formulated with a non-ionic having a shorter ethoxy chain is stable in comparison with the Examples 16 and 18. This sample was stable when stored as described above.

EXAMPLES 19-23:

Examples 19-23 illustrate the results of a plurality of experiments relating to lamellar phase of a range of compositions based on PAS, nonionics and electrolytes, in the absence of minors. The results of examples 19-21 are shown in the accompanying figures 1-5. The process routes used to obtain the compositions of examples 19-23 were selected from processes 1-4 as mentioned above or were minor modifications thereupon.

In order to determine whether a relatively stable lamellar phase was present, liquid samples of the compositions were examined after at least three days storage at the specified temperatures. A small sample was placed between glass slides and examined using polarised light, transmission microscopy. The presence of a lamellar phase was indicated by a characteristic 'Maltese cross' pattern generally believed to be caused by the presence of a lamellar phase dispersion.

Figure 1: (Example 19a) shows the stable lamellar regions for formulations containing either PAS (Empicol LX) or alkyl benzene sulphonate together with a 6.5 EO nonionic surfactant (Dobanol 23 6.5 EO) at a constant total surfactant level of 10%wt and at varying electrolyte levels.

In this example the electrolyte was sodium chloride and stability was assessed at 25 Celsius. From figure 1, it can be seen that, the existence of a lamellar phase depends on both the selection of the correct electrolyte level and the correct ratio of surfactants. With the alkyl benzene sulphonate/non-ionic surfactant systems of the prior art (Region A), lamellar-phase formulations can be made over a relatively wide formulation range. With the primary alkyl sulphate/non-ionic surfactant system employed in the compositions of the present invention, the range of electrolyte levels and surfactant ratios which enable the formation of a lamellar phase (Region B) is markedly smaller. When the electrolyte was changed from NaCl to sodium carbonate, supplying a divalent cation (Example 19b), no lamellar phase region could be found (see also examples 16 and 18).

Figure 2: (Example 20) shows the stable lamellar regions for formulations containing both sodium PAS (Empicol LX) and a 6.5 EO nonionic surfactant (Dobanol 23 6.5 EO) at varying ratios to a constant total surfactant level of 10%, at varying levels of electrolyte (sodium chloride) and under varying environmental conditions. These conditions are 1,2 and 4 as discussed above and the limits of the boxes marked 1, 2 and 4 indicate the limits of stability under the specified conditions. It can be seen that for general stability under a practical range of storage conditions over a temperature range of 4-37 Celsius, the preferred range of electrolyte levels and surfactant ratios is particularly narrow (Region C). Outside of this region not all of the formulations produce the lamellar phase and the formulations would consequently not be capable of suspending particles under certain conditions of storage.

Figure 3: (Example 21) shows the stable lamellar regions at 25 Celsius for formulations containing PAS (Empicol LX) with a 3.0 EO nonionic surfactant (Synperonic A3) at a total surfactant level of 10% and at varying electrolyte (NaCl) levels. It can be seen that for these short-chain ethoxylates in combination with PAS the ranges over which a lamellar phase (Region D) can be formed in the presence of a monovalent cation electrolyte (sodium chloride) are much larger than with the corresponding higher EO compositions.

Figure 4: (Example 22) shows the stable lamellar regions at 25 Celsius for formulations containing PAS (Empicol LX) with a 3.0 EO nonionic surfactant (Synperonic A3) at a constant surfactant level of 10%wt on product and at varying divalent cation electrolyte (sodium carbonate) levels. The region over which a lamellar phase can be formed (Region E) is indicated. It is noted that with the same electrolyte and higher levels of ethoxylation in the surfactant (compare Examples 16, 18 and 19b) no lamellar region could be found, although, in this instance, with the 3.0 EO surfactant and carbonate a small region exists in the phase diagram wherein a lamellar phase could be found. This region is much smaller than the corresponding region with the mono-valent anion (compare with Example 21).

Figure 5: (Example 23) shows the stable lamellar regions at 25 Celsius for formulations containing various ratios of PAS (Empicol LX) with a 6.5 EO nonionic surfactant (Dobanol 23-6.5) at a total surfactant level of 10% and at varying mono-valent cation electrolyte levels. In this instance, as compared with Example 19a, the cation is ammonium as opposed to sodium. It is to be noted that relatively high levels of electrolyte are required to form a lamellar phase. High levels of electrolyte are discouraged for reasons of residue deposition and corrosiveness.

EXAMPLES 24-26:

TABLE 4 below shows the storage stability of compositions according to the present invention and comparative examples which were unstable. None of these compositions comprise polymer.

All compositions were prepared by mixing the components as listed, under shear, at room temperature.

In examples whose number is not suffixed by a letter (i.e. examples 24, 25 and 26), the formulations were stable in all four of the storage regimes described above. In examples whose number is suffixed by letter, the compositions were unstable under one or more of the storage conditions. Ratios of PAS to nonionic for the formulations are given in the table. None of the compositions were stable if electrolyte was omitted.

TABLE 4

% COMPONENT	24	24A	24B	24C	25	25A	26
Calcite	35.0	35.0	35.0	35.0	35.0	35.0	35.0
Empicol LX (PAS)	3.58	1.30	3.58	3.58	-	-	4.55
Lial 123S (PAS)	-	-	-	-	4.23	4.23	-
Dobanol 23-6.5 (NI)	2.28	4.56	2.28	2.28	-	4.88	-
Synperonic A3 (NI)	-	-	-	-	4.88	-	7.80
Prifac 7901	0.65	0.65	0.65	0.65	0.65	0.65	0.65
NaCl	9.75	9.75	5.0	-	-	-	-
Na_2CO_3	-	-	-	9.75	3.25	3.25	3.25
CL318A	-	-	-	-	0.65	0.65	0.65
Water							
Ratio PAS/NI	1.57	0.29	1.57	1.57	0.87	0.87	0.58
Stability	stable	unstable	unstable	unstable	stable	unstable	stable

Claims

From the table it can be seen that for compositions to be stable under all storage conditions, it is necessary for electrolyte to be present and for the PAS to nonionic ratio to not be too low (example 24 compared with 24A).

The choice of electrolyte which can be used is somewhat dependent on the nature of the nonionic surfactant. When longer ethylene oxide chain, nonionic, surfactants such as Dobanol 23-6.5EO are used, it is particularly preferable that the electrolyte contains a monovalent anionic species such as a halide, preferably chloride. Examples 24 and 24C illustrate this point: the formulation was unstable when the divalent carbonate was employed instead of the monovalent chloride.

Furthermore, for the longer chain ethoxylated alcohols, wherein m is greater than 5, the electrolyte very preferably needs to be present in weight excess over the total surfactant present in the composition (compare example 25 with example 25B)

However, when short chain, non-ionic ethylene oxide chain surfactant are used (such as Synperonic A3: 3EO, as in example 25 and example 26) it is possible to formulate stable products with electrolyte salts comprising multivalent anionic species such as carbonates (compare example 25 with example 25A), irrespective of the type of PAS (compare example 25 and example 26). The level of electrolyte need not exceed the total surfactant level when shorter chain ethylene oxide non-ionics are used.

1. A stable, structured, liquid composition comprising a continuous aqueous phase, a dispersed lamellar phase and 1-80%wt on product of a dispersed, suspended particulate phase, said product comprising 2-25%wt on product of surfactant, said surfactant comprising primary alcohol sulphate (i) and alkoxylated nonionic surfactant (ii) wherein the ratio of (i)/(ii) falls in the range 20 to 0.4, said composition further comprising 1-20% dissolved electrolyte on product.

2. Composition according to claim 1 wherein the ratio of (i)/(ii) is 5-0.45.

3. Composition according to claim 2 wherein the ratio of (i)/(ii) is 2-0.6.

4. Composition according to claim 3 wherein the ratio of (i)/(ii) is 1.5-0.75.

5. Composition according to claim 1 wherein the primary alcohol sulphate comprises a mixture of materials of the general formula:

$$ROSO_3X$$

   wherein R is a C_8 to C_{18} primary alkyl group and X is a solubilising cation.

6. Composition according to claim 1 wherein the preferred nonionic surfactant is selected from the group comprising ethoxylated alcohols of the general formula:

$$R\text{-}(OCH_2CH_2)_m\text{-}OH$$

   wherein R is straight or branched, C_8 to C_{18} alkyl and the average degree of ethoxylation m is 1-14.

7. Composition according to claim 6 wherein m is 1-10.

8. Composition according to claim 7 wherein m is 5-10,

9. Composition according to claim 8, wherein the electrolyte has a monovalent anion and is present in weight excess over the total surfactant present in the composition.

10. Composition according to claim 9 wherein the monovalent anion is selected from the group comprising chloride, bromide, iodide, acetate, bicarbonate, and mixtures thereof.

11. Composition according to claim 1 wherein the electrolyte comprises 25-100mole% multivalent anions on total anions.

12. Composition according to claim 11 wherein the multivalent anion is selected from the group comprising, carbonate,

citrate, sulphate and mixtures thereof.

13. Composition according to claim 1 wherein the dispersed suspended particulate phase comprises an abrasive having a mean particle size in the range 0.5-200 microns.

14. Composition according to claim 1 wherein the dispersed suspended particulate phase is present at a level of 20-40% and comprises one or more components selected from the group comprising zeolites, calcites, silicates, carbonates, aluminas, bicarbonates, borates, sulphates, and, polymeric materials.

15. Composition according to claim 1 wherein particulate phase comprises one or more substance selected from calcite, bicarbonate and mixtures thereof, said composition comprising:

a) 2-15% primary alcohol sulphate comprising a mixture of materials of the general formula:

$$ROSO_3X$$

wherein R is a C_8 to C_{18} primary alkyl group and X is a solubilising cation selected from the group comprising sodium, magnesium, potassium, ammonium and mixtures thereof,

b) 2-15% ethoxylated alcohols of the general formula

$$R_1\text{-}(OCH_2CH_2)_m\text{-}OH$$

wherein R_1 is straight or branched, C_8 to C_{18} alkyl and the average degree of ethoxylation m is between 1 and 5, and wherein the ratio of a:b falls in the range 1:2 to 2:1, and,

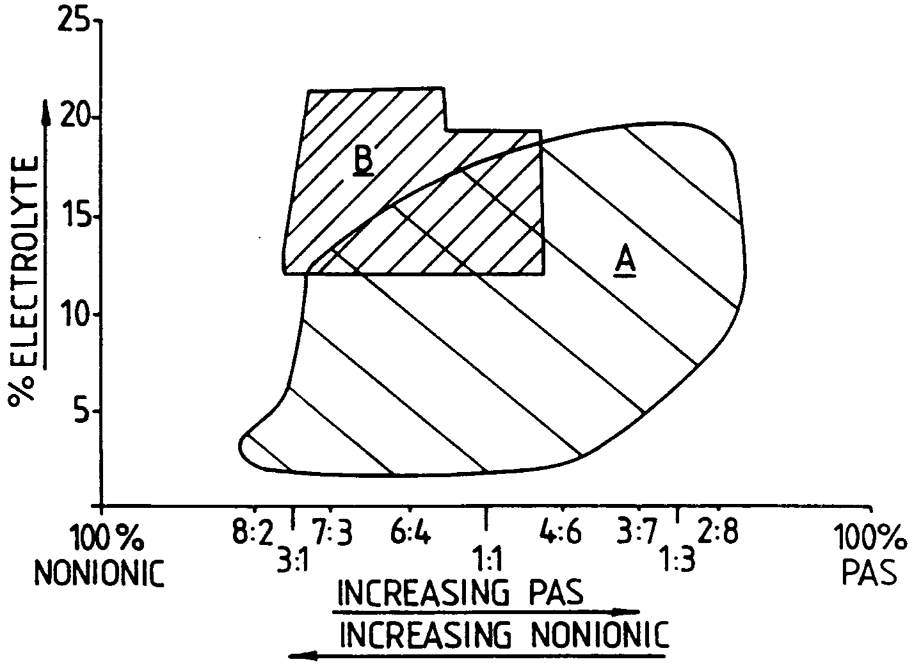
c) 1-20%wt electrolyte on aqueous phase, said electrolyte comprising 25-100mole% multivalent anions selected from the group comprising carbonates, citrates, sulphates and mixtures thereof on total anions.

16. Composition according to claim 1 which is stable when stored without agitation, for twelve weeks at a temperature of 4 degrees Celsius in a thermostatted cold-box, and, for twelve weeks at a temperature of 37 degrees Celsius in a thermostatted oven, and, during ten temperature cycles, each of a twenty-four hour duration and each consisting of eight hours at -5 degrees Celsius followed by sixteen hours at 25 degrees Celsius.

17. Composition according to claim 1 further comprising 0.01-2% of a hydrophillic polymer having a average molecular weight in excess of 500,000 Dalton.

18. Composition according to claim 17 wherein the polymer is selected from the group comprising crosslinked polyacrylates, crosslinked poly-methacrylates, and mixtures thereof.

Fig.1.


25
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B
A
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7:3
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4:6
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1:3
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100% PAS
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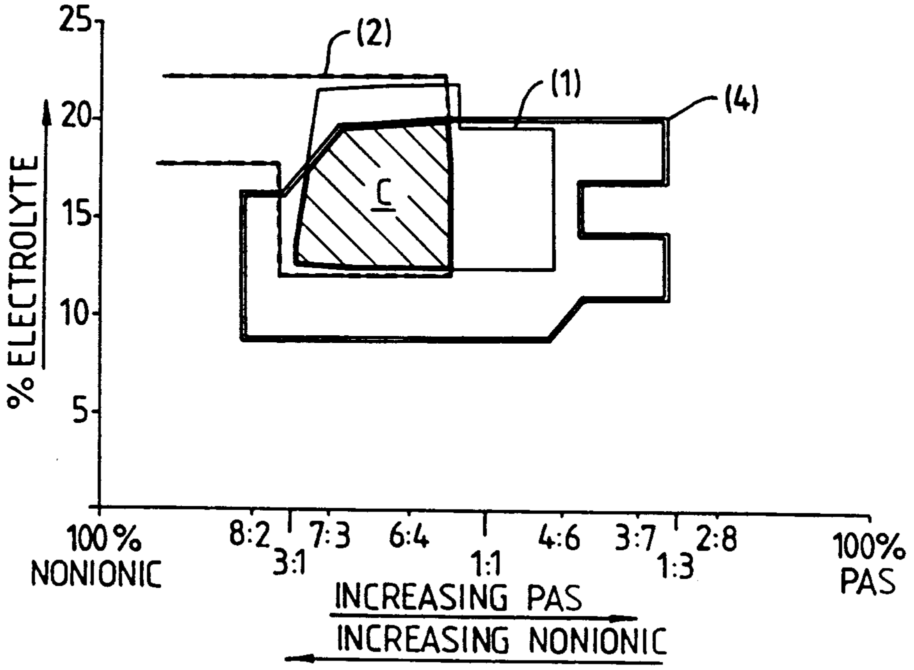
INCREASING NONIONIC

Fig.2.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100% PAS
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INCREASING NONIONIC

Fig. 3.

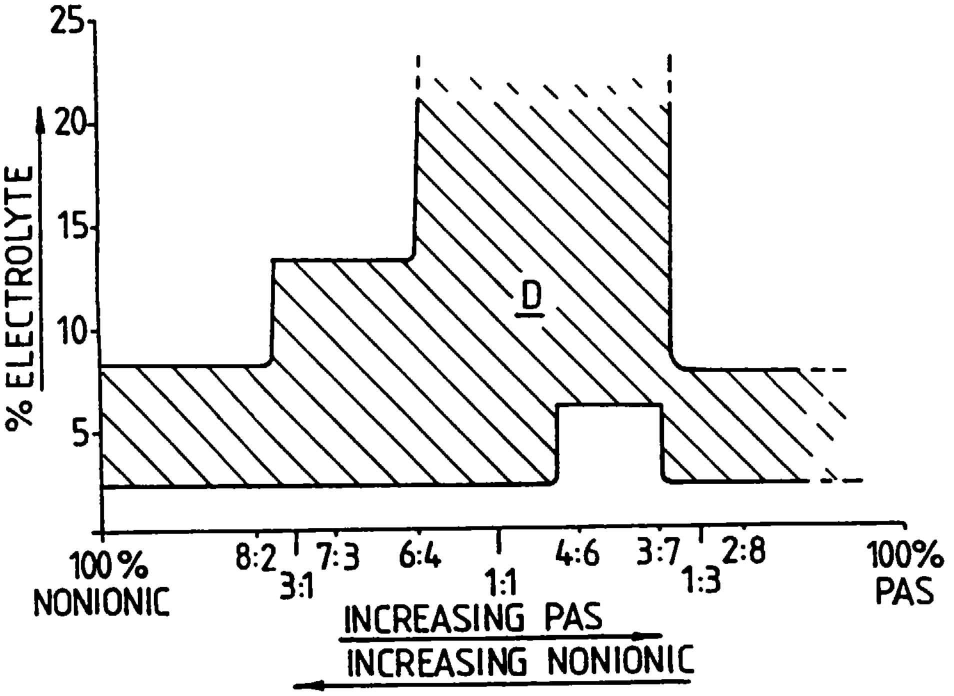
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Fig. 4.

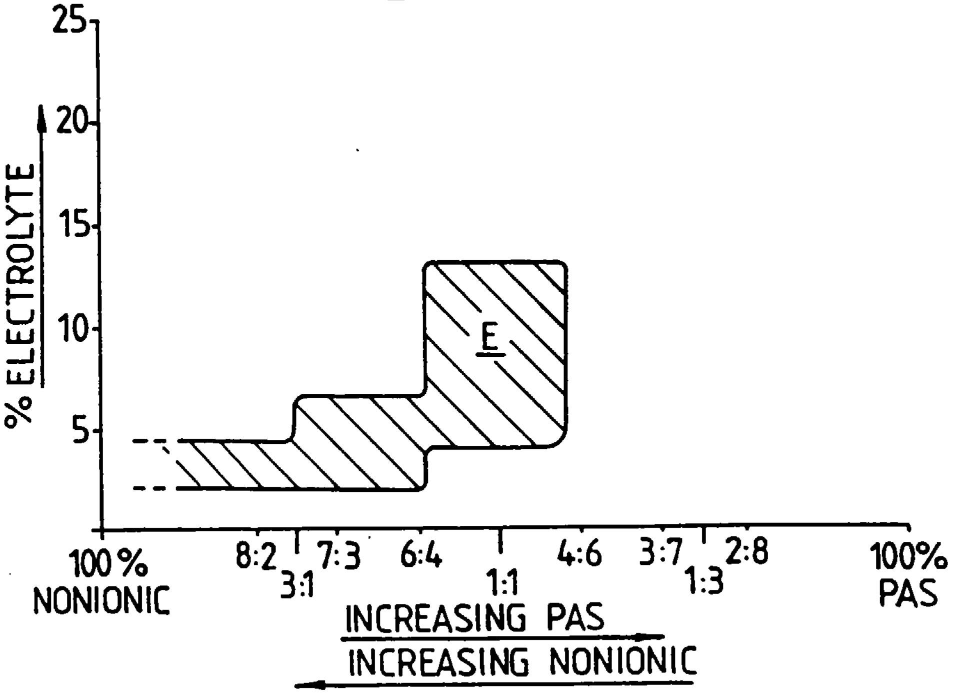
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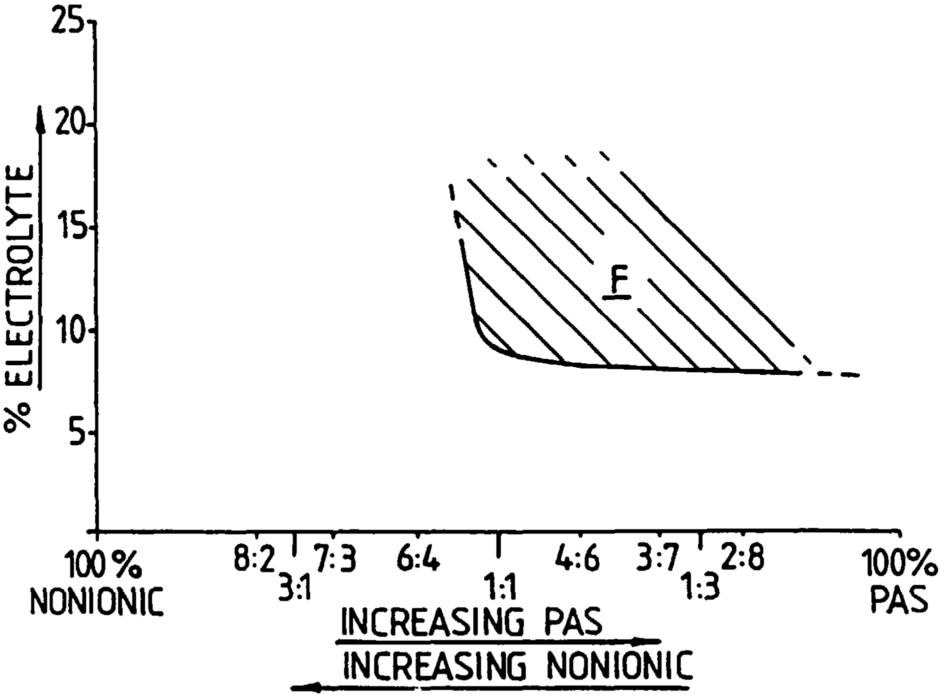
Fig.5.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INCREASING PAS
INCREASING NONIONIC

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 11 6919.8

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.6)
A	GB 2160887 A (BRISTOL-MYERS COMPANY), 2 January 1986 (02.01.86) --	1-18	C11D 1/83 C11D 17/00
A	GB 2108996 A (UNILEVER PLC), 25 May 1983 (25.05.83) --	1-18	
A	EP 0362916 A2 (UNILEVER NV), 11 April 1990 (11.04.90) --	1-18	
P,A	EP 0544492 A1 (UNILEVER PLC ET AL), 2 June 1993 (02.06.93) -----	1-18	
			TECHNICAL FIELDS SEARCHED (Int. Cl.6)
			C11D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
STOCKHOLM	29 October 1997	DAGMAR JÄRVMAN

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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