(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 359 308**
A2

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: **89202220.3**

(51) Int. Cl.5: **C11D 17/00**

(22) Date of filing: **01.09.89**

(30) Priority: **16.09.88 GB 8821763**

(43) Date of publication of application:
21.03.90 Bulletin 90/12

(84) Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI NL SE

(71) Applicant: **UNILEVER NV**
Burgemeester s'Jacobplein 1 P.O. Box 760
NL-3000 DK Rotterdam(NL)
(84) **BE CH DE ES FR GR IT LI NL SE AT**

Applicant: **UNILEVER PLC**
Unilever House Blackfriars P.O. Box 68
London EC4P 4BQ(GB)
(84) **GB**

(72) Inventor: **Machin, David**
32 Brancote Road
Oxton Birkenhead, L43 6TJ(GB)
Inventor: **van de Pas, Johannes Cornelis**
Philips Willemstraat 6
NL-3136 CV Vlaardingen(NL)

(74) Representative: **Mulder, Cornelis Willem Reinier, Dr. et al**
UNILEVER N.V. Patent Division P.O. Box 137
NL-3130 AC Vlaardingen(NL)

(54) **Liquid detergents.**

(57) A concentrated structured aqueous liquid detergent composition comprising detergent active material and an aqueous medium Containing dissolved electrolyte material, characterised by at least any two of the following features:-

(i) the electrolyte material comprises a relatively insoluble electrolyte and a co-electrolyte which promotes the solubility of said relatively insoluble electrolyte;

(ii) the surfactant material comprises a stabilising surfactant which has a salting-out resistance (as hereinbefore defined) of at least 4.0; and

(iii) the viscosity of the composition is no greater than 2.5 Pas at a shear rate of $21s^{-1}$ by virtue of

a) the composition being internally structured and a portion of the surfactant material being contained in an non-network-forming phase; and/or the composition comprising a viscosity-reducing polymer; or

b) the composition is externally structured and contains sufficient hydrotrope to inhibit the surfactant material from forming sufficient of an internal structure to be capable of suspending solid particles in the absence of the external structure; provided that when the composition is formulated with feature (ii) and feature (iii) a) and contains a non-network-forming phase, then the composition also comprises a viscosity reducing polymer and/or is characterised by feature (i).

EP 0 359 308 A2

LIQUID DETERGENTS

The present invention is concerned with structured liquid detergent concentrates which comprise detergent active material and an aqueous medium containing dissolved electrolyte material. Such structured liquids can be 'internally structured' whereby the structure is formed by primary ingredients and/or they can be structured by secondary additives, such as certain cross-linked polyacrylates, or clays, which can be added as 'external structurants' to a composition.

Both forms of structuring are very well known in the art. External structuring is usually used for the purpose of suspending solid particles. Internal structuring is usually used to suspend particles and/or to endow properties such as consumer preferred flow properties and/or turbid appearance. The most common suspended particulate solids are detergency builders and abrasive particles. Examples of internally structured liquids without suspended solids are given in US patent 4 244 840 whilst examples where solid particles are suspended are disclosed in specifications EP-A-160 342; EP-A-38 101; EP-A-104 452 and also in the aforementioned US 4 244 840.

Some of the different kinds of internal surfactant structuring which are possible are described in the reference H.A.Barnes, 'Detergents', Ch.2. in K.Walters (Ed), 'Rheometry: Industrial Applications', J.Wiley & Sons, Letchworth 1980.In general, the degree of ordering of such systems increases with increasing surfactant and/or electrolyte concentrations. At very low concentrations, the surfactant can exist as a molecular solution, or as a solution of spherical micelles, both of these being isotropic. With the addition of further surfactant and/or electrolyte, structured (anisotropic) systems can form. They are referred to respectively, by various terms such as rod-micelles, planar lamellar structures, lamellar droplets and liquid crystalline phases. Often, different workers have used different terminology to refer to the structures which are really the same. The presence of a surfactant structuring system in a liquid may be detected by means known to those skilled in the art for example, optical techniques, various rheometrical measurements, x-ray or neutron diffraction, and sometimes, electron microscopy.

One common type of internal surfactant structure is sometimes referred to as a dispersion of lamellar droplets (lamellar dispersion) These droplets consist of an onion-like configuration of concentric bilayers of surfactant molecules, between which is trapped water or electrolyte solution (aqueous phase). Systems in which such droplets are close-packed provide a very desirable combination of physical stability and solid-suspending properties with useful flow properties.

When formulating internally structured liquids of the lamellar dispersion kind, there are limits to the types and amounts of ingredients compatible with having a stable, pourable product. The viscosity and stability of the product depend on the volume fraction of the liquid which is occupied by the droplets. Generally speaking, the higher is the volume fraction of the dispersed lamellar phase (droplets), the better is the stability. However, higher volume fractions also lead to increased viscosity which in the limit can result in an unpourable product. This results in a compromise being reached. When the volume fraction is around 0.6, or higher, the droplets are just touching (spacefilling). This allows reasonable stability with an acceptable viscosity (say no more than 2.5 Pas, preferably no more than 1 Pas at a shear rate of 21s-1)-.This volume fraction also endows useful solid suspending properties. Conductivity measurements are known to provide a useful way of measuring the volume fraction, when compared with the conductivity of the continuous phase.

Figure 1 shows a plot of viscosity against lamel]ar phase volume fraction for a typical composition of known kind:-

	wt%
Surfactants*	20
Na formate	5 or 7.5
Na citrate 2aq	10
Borax	3.5
Tinopal CBS-X	0.1
Perfume	0.15
Water	balance

* NaDoBS/LES/$C_{12-13}E_{6.5}$

See example 1 for definition of surfactant terminology.

It will be seen that there is a window bounded by a lower volume fraction of 0.7 corresponding to the onset of instability and an upper volume fraction of 0.83 or 0.9 corresponding to a viscosity of 1 Pas or 2.5 Pas respectively. This is only one such plot and in many cases the lower volume fraction boundary can be 0.6 or slightly lower.

When solids are suspended in such a system, they also tend to increase the viscosity of the system. Figure 2 shows this effect for increasing amounts of suspended Zeolite A4, an insoluble material. The composition was:-

	wt %
Na LAS	9.1
Na LES	5.0
Nonionic ($C_{12\text{-}15}E_3$)	3.2
Na citrate	2.8
Glycerol	8.7
Borax	7.5
NaOH	to adjust pH to 8.8
Water	balance
Zeolite A4	on top

See example 1 for definition of surfactant terminology.

If it is desired to concentrate by increasing the amount of electrolyte in the system, at some electrolyte level or another, one will inevitably encounter an amount of undissolved electrolyte which results in an unacceptably high viscosity. Whilst One could try to counter this by attempting to find a means whereby more of the electrolyte could be dissolved, if successful, that would reduce the volume fraction of the lamellar phase, e.g. by salting-out some of the surfactant. That in turn could push the composition below the lower boundary of lamellar phase fraction which corresponds to the onset of instability.

Even if one could somehow keep the surfactant contained within the lamellar droplets to maintain stability, as one tries to concentrate the system by increasing surfactant level, the volume fraction of the lamellar phase will increase correspondingly and hence will raise the viscosity towards and beyond the limit of pourability. This increase will be exacerbated in the presence of high levels of dissolved electrolyte as referred to in the preceding paragraph.

We have now found that higher concentrations than have been possible hitherto without compromising stability and/or pourability if the composition is formulated with at least any two of the following features (i) (ii) and (iii):-

(i) the electrolyte material comprises a relatively insoluble electrolyte and a co-electrolyte which promotes the solubility of said relatively insoluble electrolyte;

(ii) the surfactant material comprises a stabilising surfactant which has a salting-out resistance (as hereinbefore defined) of at least 4.0; and

(iii) the viscosity of the composition is no greater than 2.5 Pas at a shear rate of $21s^{-1}$ by virtue of

a) the composition being internally structured and a portion of the surfactant material being contained in an non-network-forming phase; and/or the composition comprising a viscosity-reducing polymer; or

b) the composition is externally structured and contains sufficient hydrotrope to inhibit the surfactant material from forming sufficient of an internal structure to be capable of suspending solid particles in the absence of the external structure; provided that when the composition is formulated with feature (ii) and feature (iii) a) and contains a non-network-forming phase, then the composition also comprises a viscosity reducing polymer and/or is characterised by feature (i).

Compositions containing a non-network forming phase supported in an internally or externally structured suspending system are disclosed in our unpublished UK patent application no. EP 328 176. Those compositions may comprise surfactant material having an SOR of 4.0 or greater.

As used herein, the term "electrolyte" means any inorganic or organic salt which is capable of ionising in aqueous solution. The electrolyte may be dissolved in the compositions of the present invention and/or it may be present as suspended solid particles. In the great majority of cases where solid particles are suspended by an internal structure form. Usually, the electrolyte will have another function, most often as a detergency builder, although it is possible to use electrolytes having no other role than to bring about internal structuring. Whether the composition is only internally structured and/or it contains an external structuring system, according to the particular ingredients and sometimes, the order of mixing, it is possible to have the same electrolyte in solution and as suspended solids. Either or both of the dissolved and suspended electrolyte material may be a single electrolyte or a mixture of different electrolytes and in any event, can be the same or different from one another. Commonly, the electrolyte material in suspension will be the same as that in solution, being an excess of same beyond the solubility limit. It is also possible to suspend particulate solids which are functional ingredients but which are insoluble in water and therefore not electrolytes, for example insoluble abrasives such as calcite, or aluminosilicate builders. In respect of feature (i) recited hereinbefore, a typical definition of a relatively insoluble electrolyte is that in the absence of a solubilising electrolyte, the relatively insoluble electrolyte in the product is for more than 20% present in undissolved form at ambient tempereature. A solubilising electrolyte is any electrolyte which decreases the amount of undissolved relatively insoluble electrolyte at room temperature, preferably the decrease of the amount of undissolved electrolyte at a weight ratio of solubilising electrolyte to relatively insoluble electrolyte of 1:4 at ambient temperature is more than 5%, preferably more than 10% based on the relatively insoluble electrolyte. An example of a relatively insoluble electrolyte and a solubilising electrolyte therefor is a sodium salt such as sodium tripolyphosphate, in combination with a water-soluble potassium and/or ammonium salt to promote solubility of the latter. A large number of such potassium and/or ammonium salts are suitable for this purpose, for example carbonates, bicarbonates, sesquicarbonates condensed phosphates, orthophosphates, pyrophosphates, etc. Non-functional salts of simple anions like sulphate and chloride may also be used. The potassium and/or ammonium salts of many organic anions are also suitable, such as alkyl carboxylates and anions corresponding to many organic detergency builders.

Preferably, sufficient of the solubilising electrolyte is present to ensure that substantially all of the relatively insoluble electrolyte is dissolved. The solubilising electrolyte material and/or the relatively insoluble electrolyte material may independently be single electrolytes or electrolyte mixtures. Typical weight ratios of solubilising electrolyte material to relatively insoluble electrolyte material are from 0.05:1 to 1:1, preferably from 0.1:1 to 0.5:1.

In respect of feature (ii) of the invention as hereinbefore defined, one needs to select a suitable stabilising surfactant. One might be identified by dissolving a candidate surfactant in water and testing its tolerance to progressively increasing amounts of added electrolyte. Unfortunately, we have found that this is not always an accurate predictor. The reason could be due to the fact that an aqueous solution of surfactant will be a molecular solution or a solution of spherical micelles.

This is quite different to the arrangement of the surfactant molecules in structured liquids. Thus, as electrolyte is progressively added to molecular or spherical micelle solutions of surfactant, the behaviour of the surfactant will not always mimic that in the structured systems.

Fortunately, the applicants have also now found that unexpectedly, especially suitable surfactants (hereinafter called 'stabilising surfactants') can be identified using a test of the general kind referred to above, provided that it is framed in a suitable manner, provided that one defines an appropriate threshold for deciding whether a particular surfactant passes the test and provided one also ensures that the composition containing the stabilising surfactant gives a certain result upon centrifugation. This provides the advantage that the surfactants may be screened for use in novel structured detergent liquids.

The test herein prescribed for electrolyte tolerance is termed the measurement of salting-out resistance. For this test, 200ml is prepared of a 5% by weight aqueous solution of the surfactant in question. Trisodium nitrilotriacetate (NTA) is added at room temperature (ca 25 °C) until phase separation, as observed by the onset of cloudiness, occurs. The amount of NTA added at this point, as expressed in gram equivalents added to 1 litre of the surfactant solution (1 mol of NTA = 3 equivalents) is the salting-out resistance of the surfactant. Where convenient, the abbreviation SOR will be used for salting-out resistance.

The stabilising surfactants for use in the present invention must have an SOR (as hereinbefore defined) of at least 4.0, preferably at least 5.0 or 5.25. Examples of such surfactants with SOR values in the range 4.0 to 6.0 are polyalkoxylated alkyl carboxylates described for use in structured liquid detergents in European Patent Specification EP-A-178,006, although not every single such surfactant disclosed in that document meets the minimum SOR requirement of 4.0. Other surfactants of the latter chemical type but having SOR values up to about 5.2 are described as components of unstructured liquid detergents in UK Patent Specification GB 1 225 218.

It is still more preferred to use a stabilising surfactant with an SOR of at least 6.0, most preferably at least 6.4. Especially preferred are those stabilising surfactants having an SOR of at least 9.0.

It is usually preferred that the stabilising surfactant should have an average alkyl chain length greater than 8 carbon atoms. Some preferred classes of stabilising surfactants are :-
alkyl amine oxides;

alkyl polyalkoxylated carboxylates;
alkyl polyalkoxylated phosphates;
alkyl polyalkoxylated sulphosuccinates;
dialkyl diphenyloxide disulphonates; and
alkyl polysaccharides (sometimes called alkyl polyglucosides or polyglycosides);
selected as those which have a salting out resistance of at least 4.0.

A wide variety of such stabilising surfactants is known in the art, for example the alkyl polysaccharides described in European patent specification nos. EP-A-70 074; 70 075; 70 076; 70 077; 75 994; 75 995; 75 996 and 92 355. The use of these materials is especially preferred for environmental reasons.

The selection of a stabilising surfactant as described above allows greater flexibility in the incorporation of large amounts of salts, especially soluble salts (i.e. electrolytes) and improved possibilities for the incorporation of polymer builders, which can also act to bring about a desirable viscosity reduction in the product. The incorporation of higher levels of surfactants is advantageous for fatty soil removal. In particular, where the stabilising surfactant is nonionic in character, the ensuing incorporation of high levels of nonionic rather than anionic surfactant is advantageous for the stability of any enzymes present, these in general being more sensitive to anionics than to nonionics. In general, the applicants have observed a trend that the higher the measured SOR, the lower is the concentration of surfactant necessary to achieve a given advantage.

When present, the stabilising surfactant may constitute all or part of the detergent active material in the composition. The only restriction on the total amount of detergent active and electrolyte is that together they must result in formation of a structuring system. Thus, within the ambit of this aspect of the present invention, a very wide variation in surfactant types and levels is possible. The selection of surfactant types and their proportions, in order to obtain a stable liquid with the required structure will, in the light of the present teaching, now be fully within the capability of those skilled in the art. However, it can be mentioned that an important sub-class of useful compositions is those where the detergent active material comprises one or more conventional or 'primary' surfactants, together with one or more stabilising surfactants. Typical blends useful for fabric washing compositions include those where the primary surfactant(s) comprise nonionic and/or a non-alkoxylated anionic and/or an alkoxylated anionic surfactant.

Generally, it is very desirable that the compositions should have a rheology and a minimum stability, compatible with most commercial and retail requirements. For this reason, we generally prefer the compositions of the present invention to yield no more than 2% by volume phase separation upon storage at 25°C for 21 days from the time of preparation and to have a viscosity of no greater than 2.5 Pas, preferably 1.5 Pas, most preferably 1 Pas and especially 850 mPas, these viscosities being measured at a shear rate of 21 s^{-1}.

In the case of blends of primary and stabilising surfactants, the precise proportions of each component which will result in such stability and viscosity will depend on the type(s) and amount(s) of the electrolytes, as is these case with conventional structured liquids.

However, in such systems, the stabilising surfactant not only enables formulation of stable compositions over a wider spectrum of primary/stabilising surfactant ratios but also over a wider range of electrolyte concentrations, and most importantly, at higher electrolyte concentrations. This is illustrated in Figure 3 which shows the range of stable formulations for three systems of 10% by weight surfactant blends comprising nonionic and anionic (sodium dodecyl benzene sulphonate), the ratios between them being varied and likewise, the electrolyte concentration. The three diagrams A, B, C show the effect of increasing the SOR of the stabilising surfactant. The precise SOR values for the nonionics indicated can be found hereinbelow in Example 1. In Figure 3, only diagram C represents the situation on using a stabilising surfactant which fulfils feature (ii) of the present invention. It will be appreciated that similar effects occur in systems comprising three or more surfactants.

The feature (iii) specified hereinbefore in the definition of the present invention requires a sub-feature (a), wherein the composition is internally structured and has certain other limitations, and/or a sub-feature (b) wherein the composition is externally structured and either there is no internal structure or any internal structure present is incapable on its own of suspending solid particles (whether or not the composition actually contains such particles).

Thus, it will be appreciated that the presence of external structurants and an internal structure are not mutually exclusive. That may be explained as follows. One may envisage a model system containing an internal structure. If one wishes to incorporate more surfactant, to concentrate in the manner of the present invention, to avoid increasing viscosity, according to subfeature (b), one may add sufficient hydrotrope such that the additional surfactant, and optionally some or all of the existing surfactant is present as a micellar solution. The partial or total destruction of the internal structure thereby destroys the solid suspending capabilities of the system (even though solids may not be present). It is then necessary to include external structurant to restore the latter property. The requirement is that the total of the volume fraction occupied by the internal structure (if any) and the "volume fraction" of the external structurant must not be large enough to raise the viscosity above 2.5 Pas at a shear rate of 21 s^{-1}.

The first variant of sub-feature (a) is to ensure that when the composition is internally structured, a portion of the surfactant material is contained in a non-network forming phase. In particular this portion of the surfactant material may be distributed and suspended in the composition as discrete units of one or more non-network-forming phases each selected from

(A) solid particles containing detergent active material;

(B) lyotropic liquid crystals containing detergent active material; and

(C) liquid droplets containing detergent active material.

Preferably, the total of the non-network-phase(s) has a higher concentration by weight of surfactant material than the aqueous solution which, other than suspended non-surfactant solids and any internal structuring phases and any external structuring materials, forms the remainder of the composition.

For a composition according to the present invention which exhibits feature (iii), sub-feature (a), first variant, it is preferred that it satisfy one of the following conditions:-

(i) it has a viscosity at the shear rate 21 s^{-1} which is substantially less than the viscosity of a corresponding reference composition which is physically stable for 1 hour and contains in all respects the same components but in which the detergent active material(s) is/are entirely in said aqueous solution or in said aqueous solution and an internally structuring lamellar phase if the latter is present,

(ii) such a corresponding composition cannot be made.

Similarly, we prefer a detergent composition according to the invention having feature (iii) (a), first variant, to contain at least two detergent active materials and which satisfies the condition that, in respect of each detergent active material, notional gradual replacement of that material by the other detergent active materials (where there are two in total) or by the other detergent active materials in the ratio in which they are present in the composition (where there are more than two) leads from a region of physical stability to a region of higher viscosity or physical instability. The term "notional replacement" here means that in practice, comparative compositions of different proportions of components are made up, in order to perform this test. Note that, according to this test, the preferred composition of the invention is in a region of stability; slightly differing compositions may be in the same region of stability.

It is particularly convenient to use one or more non-alkoxylated anionic surfactants to at least predominantly form non-network-forming phases of types (B) or (C). Examples of these are non-alkoxylated water-soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Typical examples comprise sodium and potassium alkyl sulphates, especially those obtained by sulphating higher (C_8-C_{18}) alcohols produced for example from tallow or coconut oil, sodium and potassium alkyl (C_9-C_{20}) benzene sulphonates, particularly sodium linear secondary alkyl (C_{10}-C_{15}) benzene sulphonates; the reaction products of fatty acids such as coconut fatty acids esterified with isethionic acid and neutralised with sodium hydroxide; sodium and potassium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by reacting alpha-olefins (C_8-C_{20}) with sodium bisulphite and those derived from reacting paraffins with SO_2 and Cl_2 and then hydrolysing with a base to produce a random sulphonate; and olefin sulphonates, which term is used to describe the material made by reacting olefins, particularly C_{10}-C_{20} alpha-olefins, with SO_3 and then neutralising and hydrolysing the reaction product. Very common such non-alkoxylated anionic detergent compounds are sodium (C_{11}-C_{15}) alkyl benzene sulphonates and sodium (C_{16}-C_{18}) alkyl sulphates.

Such non-alkoxylated anionic surfactants may also be used in those compositions of the present invention which do not contain any non-network-forming phases.

When such non-alkoxylated anionic surfactants are present as non-network-forming phases(s), the composition preferably also contains one or more of :

alkoxylated anionic surfactants
alkoxylated nonionic surfactants
mono-and di-alkanolamides
amine oxides
betaines
sulphobetaines
sugar ethers

which further material at least partly forms an internal structure of the lamellar phase kind, together with the remainder said non-alkoxylated anionic surfactant.

However, surfactants of the kinds referred to in this paragraph may also be used in many other compositions according to the present invention.

Examples of alkoxylated anionic surfactants include sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty monoglyceride sulphates and sulphonates; sodium and potassium salts of sulphuric acid esters of higher (C_8-C_{18}) fatty alcohol-alkylene oxide, particularly ethylene oxide, reaction products.

Examples of alkoxylated nonionic surfactants include the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Specific nonionic detergent compounds are alkyl (C_6-C_{18}) primary or secondary linear or branched alcohols with ethylene oxide, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylenediamine. Other so-called nonionic detergent compounds include long chain tertiary amine oxides, long chain tertiary phospine oxides and dialkyl sulphoxides.

Conventional methods of making up detergent formulations can be used to produce compositions of the invention which contain non-network-forming phases of type (A) or (B). In principle, where a phase of the latter type is present, that phase can be added in the form of particles before or after "structuring" of the liquid phases. However, it has been found more convenient to form such phases <u>in situ</u>.

According to the invention in another aspect therefore, there is provided a method of forming a structured aqueous detergent composition in which the non-network-forming phase (A) and/or the non-network-forming phase (B) is/are present, the method comprising the steps:

(I) preparing an aqueous solution of a first detergent active component;

(II) after step (I), adding electrolyte to the aqueous solution so produced in order to cause said first component to form said non-network-forming phase(s) (A) and/or (B); and thereafter forming an internal structuring phase by at least one of the following steps:

(III) after step (II) dissolving in the solution a second detergent active component more soluble in the continuous aqueous phase than said first component,

(IV) after step (II) and step (III) are performed, adding further electrolyte to the solution. Preferably all of steps (I), (II), (III) and (IV) are performed. Part of said second component may be included in the aqueous solution of step (I).

Compared with adding the non-network forming phase as particles, this method has the advantages that problems of stirring-in the particles are avoided and that a problem of achieving partial solution of the particles (which is needed if the material of the particles is to form an internal structuring phase is avoided. The method here proposed also allows use of a wide variety of raw materials.

In the case where step (IV) is performed in the above method, said electrolyte added in step (II) may have a monovalent anion while said electrolyte added in step has a polyvalent anion.

Part of the final water content of the composition formed may be added after the addition of all detergent active material and all electrolyte. This technique is of general application. Therefore, the invention further provides a method of preparing a composition of the invention as described above where in the internal structuring phase and the non-network-phase (A) and/or (B) are present, in which method part of the final water content of the composition formed, is added after the addition of all detergent active material and all electrolyte. In this method, the formation of the non-network-forming phase can be achieved by the high concentration of the detergent active materials and electrolyte, prior to the final addition of water.

This part of the final water content added after the addition of all detergent active material and all electrolyte may be from 5 to 30% by weight of the total amount of water incorporated in the composition other than water added in association with other components.

When it is desired to formulate a composition according to the present invention, containing a non-network-forming phase of type (C), i.e. dispersed droplets of surfactant, these preferably comprise surfactant of the alkoxylated anionic type, for example from 1% to 20% preferably from 2% to 10% by weight of the total composition. In that case, the internal structuring phase should preferably comprise a surfactant system containing non-alkoxylated anionic surfactant or a mixed non-alkoxylated anionic/nonionic surfactant system.

It should also be noted that when formulating to create a non-network-forming phase of type (A) or (B), the order of addition of electrolyte can be important. Electrolytes with polyvalent anions such as sodium sulphate, citrate, carbonate, or phosphates such as tripolyphosphate are more effective for initiating formulation of an internal structuring phase but are poor at forming non-network-forming phases. Other electrolytes with monovalent anions such as sodium chloride, magnesium chloride or sodium bicarbonate are more effective for producing non-network-forming phases but so poor at initiating formation of internal structuring phases that if used alone, there may be insufficient structuring phase to stably disperse the non-networkforming phase(s), together with any solids which may be present. Thus, it is preferred in this aspect of the present invention, to use a mixture of electrolytes, at least one from each category.

Turning now to compositions of the present inventions which exhibit feature (iii) (a), second variant, these comprise a viscosity-reducing polymer. This polymer may be selected from those viscosity reducing polymers which are only partly soluble in the composition and those which are substantially totally soluble. Mixtures may also be used, comprising one or more from both categories or a plurality from within only one category. For a polymer to fulfil the requirement of viscosity reducing, it must be capable of producing a measurable reduction in viscosity when used at a concentration at which it will not render the product unstable.

Many of the partly soluble viscosity reducing polymers can bring about a viscosity reduction (due to the polymer which is dissolved) whilst incorporating a sufficiently high amount to achieve a secondary benefit, especially building, because the part which is not dissolved permits incorporation of sufficient material whilst not causing the instability that would occur if substantially all were dissolved.

Examples of partly dissolved polymers include many of the polymer and co-polymer salts already known as detergency builders. For example, may be used (including building and non-building polymers) polyethylene glycols, polyacrylates, polymaleates, polysugars, polysugarsulphonates and co-polymers incorporating any of these. Preferably, the partly dissolved polymer comprises a co-polymer which includes an alkali metal salt of a polyacrylic, polymethacrylic or maleic acid or anhydride. Preferably, compositions with these co-polymers have a pH of above 8.0. In general, the amount of partly dissolved viscosity reducing polymer can vary widely according to the formulation of the rest of the composition. However, typical amounts are from 0.5 to 4.5% by weight.

Any viscosity reducing polymer which is of the kind which is substantially totally soluble in the aqueous phase must have an electrolyte resistance of more than 5 grams sodium nitrilotriacetate in 100ml of a 5% by weight aqueous solution of the polymer, said second polymer also having a vapour pressure in 20% aqueous solution, equal to or less than the vapour pressure of a reference 2% by weight or greater aqueous solution of polyethelene glycol having an average molecular weight of 6000; said second polymer having a molecular weight of at least 1000.

The incorporation of the soluble polymer permits formulation with higher concentrations at the same viscosity (relative to compositions without the soluble polymer) or at fixed concentration, with lower viscosity whilst maintaining stability. The soluble polymer can also reduce upward viscosity drift, even when it also brings about a viscosity reduction.

It is especially preferred to incorporate the soluble polymer with a partly dissolved polymer which has a large insoluble component. This is because although the building capacity of the partly dissolved polymer will be good (since relatively high quantities can be stably incorporated), the viscosity reduction will be optimum (since little will be dissolved). Thus, the soluble polymer can usefully function to reduce the viscosity further, to an ideal level.

The soluble polymer can, for example, be incorporated at from 0.05 to 20% by weight, although usefully, from 0.1 to 2.5% by weight of the total composition is sufficient, and especially from 0.2 to 1.5% by weight. Often, levels above these can cause instability. A large number of different polymers may be used as such a soluble polymer, provided the electrolyte resistance and vapour pressure requirements are met. The former is measured as the amount of trisodium nitrilotriacetate (NaNTA) solution necessary to reach the cloud point Of 100ml of a 5% solution of the polymer in water at 25 °C, with the system adjusted to neutral pH, i.e. about 7. This is preferably effected using sodium hydroxide. Most preferably, the electrolyte resistance is 10g NaNTA, especially 15g. The latter indicates a vapour pressure of a 20% aqueous solution of said polymer, having a vapour pressure equal to or lower than the vapour pressure of a 2% aqueous solution of polyethyleneglycol with a molecular weight of 6,000, preferably equal to or lower than that of a 10% aqueous solution of said polyethyleneglycol, and particularly preferably equal to or lower than that of an 18% aqueous solution of said polyethyleneglycol.

Suitable external structurants include water-swellable polymers and/or inorganic colloids, or filamentary soap crystals or cellulose.

Typical water-swellable polymers are water-soluble polymers of acrylic acid, cross-linked with about 1% of a polyallyl ether of sucrose having an average of about 5-8 allyl groups for each sucrose molecule, and having an average molecular weight of about 1,000,000. Examples of such polymers are disclosed in our UK patent application GB 2 079 305 A.

The use of inorganic colloid materials as external structurants is described in, for example, US patents 4 005 027 and 4 438 016, whilst typical use of filamentary soap crystals and cellulose are disclosed in UK patent specification GB 1 418 671.

When a composition according to the present invention exhibits feature (iii), sub-feature (b) then optionally, it may also contain a non-network-forming phase of type (A) or (B) as hereinbefore defined.A non-network-forming phase of type (C) would be dissolved by the amounts of the hydrotrope which would be necessary to inhibit formation of an internal structure having solid suspending properties.

In the broadest sense of the present invention, the surfactant material may comprise one or more surfactants chosen from a very wide range and may include one or more of the surfactants recited hereinbefore. In general, they may be selected from anionic, cationic, nonionic, zwitterionic and amphoteric species, and (provided mutually compatible) mixtures thereof. For example, they may be chosen from any of the classes, subclasses and specific materials described in 'Surface Active Agents' Vol.I, by Schwartz & Perry, Interscience 1949 and 'Surface Active Agents' Vol.II by Schwartz, Perry & Berch (Interscience 1958), in the current edition of "McCutcheon's Emulsifiers & Detergents" published by the McCutcheon division of Manufacturing Confectioners Company or in 'Tensid-Taschenbuch', H.Stache, 2nd Edn., Carl Hanser Verlag, Munchen & Wien, 1981.

It is also possible to include, as a primary surfactant, an alkali metal soap of a mono- or di fatty acid, especially a soap of an acid having from 12 to 18 carbon atoms, for example oleic acid, ricinoleic acid, and fatty acids derived from castor oil, rapeseed oil, groundnut oil, coconut oil, palmkernel oil or mixtures thereof. The sodium or potassium soaps of these acids can be used, the potassium soaps being preferred.

The compositions which contain an internal surfactant structure preferably also contain electrolyte in an amount sufficient to promote that structuring. Preferably though, all or most will be salting-out electrolyte. Salting-out electrolyte has the meaning ascribed to in specification EP-A-79 646. Optionally, some salting-in electrolyte (as defined in the latter specification) may also be included, provided if of a kind and in an amount compatible with the other components and the composition is still in accordance with the definition of the invention claimed herein. Some or all of the electrolyte (whether salting-in or salting-out and whether suspended or in solution), or any substantially water insoluble salt (non-electrolyte) which may be present, may have detergency builder properties. In any event, it is preferred that compositions according to the present invention include detergency builder material, some or all of which may be electrolyte. The builder material is any capable of reducing the level of free calcium ions in the wash liquor and will preferably provide the composition with other beneficial properties such as the generation of an alkaline pH, the suspension of soil removed from the fabric and the dispersion of the fabric softening clay material.

Examples of phosphorus-containing inorganic detergency builders, when present, include the water-soluble salts, especially alkali metal pyrophosphates, orthophosphates, polyphosphates and phosphonates. Specific examples of inorganic phosphate builders include sodium and potassium tripolyphosphates, phosphates and hexametaphosphates.

Examples of non-phosphorus-containing inorganic detergency builders, when present, include water-soluble alkali metal carbonates, bicarbonates, silicates and crystalline and amorphous alumino silicates. Specific examples include sodium carbonate (with or without calcite seeds), potassium carbonate, sodium and potassium bicarbonates, silicates and zeolites.

Examples of organic detergency builders, when present, include the alkali metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates, polyacetyl carboxylates and polyhydroxysulphonates. Specific examples include sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediaminetetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, tartrate mono succinate, tartrate di succinate, melitic acid, benzene polycarboxylic acids and citric acid. Some of the polymeric organic builders may also function as viscosity reducing polymers as hereinbefore described.

The key aim in formulating detergent aqueous liquid concentrates is to enhance the amount of functional ingredients. Clearly, the more of these that are present, the less will be the quantity of water in the system. The concentrated structured aqueous liquid detergent compositions according to the present invention will contain no more than 80% by weight of water but preferably they will comprise only from 50% to 30%, most preferably from 45% to 35% and especially from 40% to 35% by weight of water.

Typically the total amount of electrolyte (dissolved plus non-dissolved) will be from 1% to 60%, preferably from 10% to 50%, most preferably from 20% to 45% and possibly from 30% to 40% by weight of the total composition.

The amount of suspended solid material (undissolved electrolyte and insoluble material such as calcite or aluminosilicate) is typically from 0% to 40%, preferably from 1% to 20% and most preferably from 3% to 10% by volume of the total composition. Alternatively, when expressed in terms of weight percentage of the total composition, the suspended solid material will usually be present at from 0% to 65%, preferably from 2.5% to 35% and most preferably from 5% to 15%.

The amount of dissolved electrolyte is typically from 1% to 65%, preferably from 5% to 35% and most preferably from 10% to 15% by weight of the total composition.

The total amount of surfactant material will typically be from 10% to 50%, preferably from 15% to 40% and most-preferably from 20% to 30% by weight of the total composition.

Apart from the ingredients already mentioned, a number of optional ingredients may also be present, for example lather boosters such as alkanolamides, particularly the monoethanolamides derived from palm kernel fatty acids and coconut fatty acids, fabric softeners such as clays, amines and amine oxides, lather depressants, oxygen-releasing bleaching agents such as sodium perborate and sodium percarbonate, peracid bleach precursors, chlorine-releasing bleaching agents such as tricloroisocyanuric acid, inorganic salts such as sodium sulphate, and, usually present in very minor amounts, fluorescent agents, perfumes, enzymes such as proteases and amylases, germicides and colourants.

The compositions of the present invention may be concentrated mainly in detergent active material, mainly concentrated in electrolyte and/or insoluble solids or relatively concentrated in a combination of these. The precise amounts will also depend on the intended application. Thus, for example, a typical concentrated heavy duty liquid detergent product for fabrics washing might comprise, by weight :

30% - 35% electrolyte
20% - 25% detergent actives
0% - 5% minor ingredients
50% - 35% water

A concentrated general purpose cleaner without suspended solid, may for example comprise by weight:

5% - 25% electrolyte
15% - 25% detergent actives
0% - 5% minor ingredients
80% - 45% water

A concentrated liquid abrasive cleaner, by weight might comprise :

20% - 30% electrolyte
10% - 25% detergent actives
0% - 5% minor ingredients
70% - 40% water

In a liquid abrasive cleaner composition of this type, the abrasive particles are water soluble and hence are readily rinsed away when the treated surface is washed with water. Therefore, in the product, the particles, constitute undissolved electrolyte.

The invention will now be illustrated by way of the following Examples.

Example 1: Salting-out Resistance of Surfactants

Active detergent	Salting-out Resistance: Amount of NTA to get phase separation at room temperature of a 5% w/w surfactant solution	
	grams NTA added to 200 ml surfactant solution	grams equivalent added to 1 litre surfactant solution
Ethoxylated fatty alcohol, $C_{12-15}E_7$	18.5-22	1.0-1.2
Alkyl ether sulphate, LE_3S	59	3.2
" " " LE_3S	74	4.0
" " " LE_3S	59	3.2
" " " LE_3S	48	2.6
Alkyl ether carboxylate, $LE_{2.5}C$	59	3.2
" " " $LE_{4.5}C$	94	5.1
" " " LE_6C	98	5.3
" " " LE_8C	106	5.8
" " " $LE_{10}C$	106	5.8
Alkyl ether phosphate, $C_{12-15}EP$	118	6.4
" " " $C_{1-15}E_{10}P$	140	7.6
Alkyl ether sulphosuccinate, $LE_{2.2}SC$ di sodium salt	> ca 180*	> ca 9.5*
Alkyl dimethyl amine oxide, LAO	116	6.3
Di C_{10} diphenyloxide disulphonate = Dowfax 3B2 ex Dow	170	9.2
Alkyl polyglucoside, C_{8-10} G_{2-6} Triton CG-110	> ca 180*	> ca 9.5*
Alkyl polyglucoside Triton BG-10	> ca 180*	> ca 9.5*

Active detergent	Salting-out Resistance: Amount of NTA to get phase separation at room temperature of a 5% w/w surfactant solution	
	grams added to 200 ml surfactant solution	NTA grams equivalent added to 1 litre surfactant solution
Alkyl polyglucoside, $C_{9-11}G1$	97	5.3
" " " $C_{9-11}G_3$	> ca 180*	> ca 9.5*
" " " $C_{12-13}G_3$	> ca 180*	> ca 9.5*

C_x x = alkyl chain length
L = Lauryl
S = Sulphate
E = Ethylene oxide chain length
Cy = Carboxylate
P = Phosphate
G = Glucoside units
* = saturated with NTA.

Other raw material definitions used herein

NaDOBS - Sodium dodecyl benzene sulphonate
PEG - Polyethylene glycol (mW 2,000)
Dextran - Polysacharide (mW 17K)
STP - Sodium tripolyphosphate
TKPP - Tetrapotassium pyrophosphate

Example 2

Surfactant molecules ranked in order of their Salting-out Resistance.

Active detergent		SOR g.equiv NTA/litre
Ethoxylated fatty alcohol, $C_{12-15}E_7$		10 - 1.2
Alkyl ether sulphate,	LE_8S	2.6
" " "	LE_3S	3.2
" " "	LE_6S	3.2
Alkyl ether carboxylate,	$LE_{2.5}C$	3.2
Alkyl ether sulphate,	LE_5S	4.0
Alkyl ether carboxylate,	$LE_{4.5}C$	5.1
" " "	LE_6C	5.3
Alkyl poly glucoside,	$C_{9-11}G_1$	5.3
Alkyl ether carboxylate,	LE_8C	5.8
" " "	$LE_{10}C$	5.8
Alkyl dimethyl amineoxide,	LAO	6.3
Alkyl ether phosphate,	$C_{12-25}E_5P$	6.4
" " "	$C_{12-15}E_{10}P$	7.6

Active detergent		SOR g.equiv NTA/litre
Di-C_{10} diphenyloxide disulphonate		9.2
Alkyl ether sulphosuccinate,	$LE_{2.2}SC$	> 9.5
Alkyl poly glucoside,	$C_{8-10}G_{2-6}$	
" (Triton BG-10)		> 9.5
Alkyl poly glucoside,	$C_{9-11}G_3$	> 9.5
" " "	$C_{12-13}G_3$	> 9.5

Example 3: Compositions										
	Composition (%w/w)									
Component	A_1	A_2	A_3	A_4	B_1	B_2	B_3	C_1	C_2	C_3
Na DOBS	10.35	10.35	10.35	10.35	11.0	11.16	11.0	15.10	15.53	15.10
K coconut soap	1.65	1.65	1.65	1.65	1.75	1.77	1.75	2.40	2.47	2.40
$C_{12-13}G_3$ (ii)	-	1.5	1.5	1.5	-	0.94	1.5	-	1.0	1.5
$C_{12-15}E_7$	3.0	1.5	1.5	1.5	2.25	1.12	0.75	2.5	1.0	1.0
STP	24	24	24	24	24	24	24	24	24	24
} (i)										
TKPP	6	6	6	6	6	6	6	6	6	6
Glycerol	5	5	5	5	5	5	5	5	5	5
Sodium pentaborate	2	2	2	2	2	2	2	2	2	2
Perfume	1	1	1	1	1	1	1	1	1	1
PEG	-	-	2.0	-	-	-	-	-	-	-
} iii (a)(ii)										
Dextran	-	-	-	0.5	-	0.5	0.5	-	0.5	0.5
Water	up to 100				up to 100			up to 100		
Stability	unstable	stable	stable	stable	unstable	stable	stable	unstable	stable	stable
Viscosity	-	2120	1440	1220	-	680	1000	-	870	1250

Example 4						
	Composition % wt					
	D_1	D_2	E_1	E_2	F_1	F_2
NaDOBS	16.4		16.4		16.4	
$C_{12-15}E_7$	6.6		--		--	
LE_3S	--		6.6		--	
C_{12-13} G_3	--		--		6.6	
Sodium citrate	10.0		10.0		10.0	
Sokalan CP5	0	0.3	0	0.5	0	0.5
Water	up to 100					
Stability Viscosity (mPas at 21 s-1)	Stable 1340	unstable	stable 1120	unstable	stable 1270	stable 410

Example 5				
Component	Composition (wt %)			
	G1	G2	G3	G4
NaDOBS	28	28	28	28
$C_{12\text{-}15}$ E_7	12	4	4	4
$LE_{10}C$, Na-salt	-	8	8	8
Sodium citrate	10	10	10	10
Ethanol	-	-	5.5	5.5
Carbopol 941*	-	-	-	0.55
Foam depressor	0.28	0.28	0.28	0.28
Water	60	60	60	60
Stability	Unstable	Stable	Unstable	Stable
Viscosity (mPas at 21 s^{-1})	440	7500	330	620

* Carbopol is a structuring polymer and is a high molecular weight polyacrylate which is only slightly crosslinked, delivered by B.F. Goodrich.

Note that by replacing part of the 7EO-nonionic, of formulation G1, by a surfactant which has a higher salting-out resistance, a stable composition (G2) can be obtained which has, however, such a high viscosity that it is not pourable (gel-like). The pourability can be improved by partial breakdown of the internal structure by adding ethanol (G3) followed by externally structuring the composition by a structuring polymer. This yields a stable and pourable composition (G4) according to our invention.

Claims

1. A concentrated structured aqueous liquid detergent composition comprising detergent active material and an aqueous medium containing dissolved electrolyte material, characterised by at least any two of the following features:-
(i) the electrolyte material comprises a relatively insoluble electrolyte and a co-electrolyte which promotes the solubility of said relatively insoluble electrolyte;
(ii) the surfactant material comprises a stabilising surfactant which has a salting-out resistance (as hereinbefore defined) of at least 4.0; and
(iii) the viscosity of the composition is no greater than 2.5 Pas at a shear rate of $21s^{-1}$ by virtue of:
a) the composition being internally structured and a portion of the surfactant material being contained in an non-network-forming phase; and/or the composition comprising a viscosity-reducing polymer; or
b) the composition is externally structured and contains sufficient hydrotrope to inhibit the surfactant material from forming sufficient of an internal structure to be capable of suspending solid particles in the absence of the external structure;
provided that when the composition is formulated with feature (ii) and feature (iii) a) and contains a non-network-forming phase, then the composition also comprises a viscosity reducing polymer and/or is characterised by feature (i).

2. A composition according to claim 1, characterised by each of features (i), (ii) and (iii).

3. A composition according to either preceding claim, which exhibits feature (i), wherein the relatively insoluble electrolyte is a sodium salt and the solubilising electrolyte is a water-soluble potassium and/or ammonium salt.

4. A composition according to any preceding claim, which exhibits feature (ii). wherein the salting-out resistance of the stabilising surfactant is at least 9.0.

5. A composition according to any preceding claim, which exhibits feature (iii), is internally structured, and wherein a portion of the surfactant material is contained in at least one non-network forming phase selected from

(A) solid particles containing detergent active material;
(B) lyotropic liquid crystals containing detergent active material; and
(C) liquid droplets containing detergent active material.

6. A composition according to any preceding claim, which exhibits feature (iii), is internally structured

and comprises a viscosity reducing polymer which is only partly soluble in the composition.

7. A composition according to any preceding claim, which exhibits feature (iii), is internally structured and comprises a viscosity reducing polymer which is substantially totally soluble in the composition.

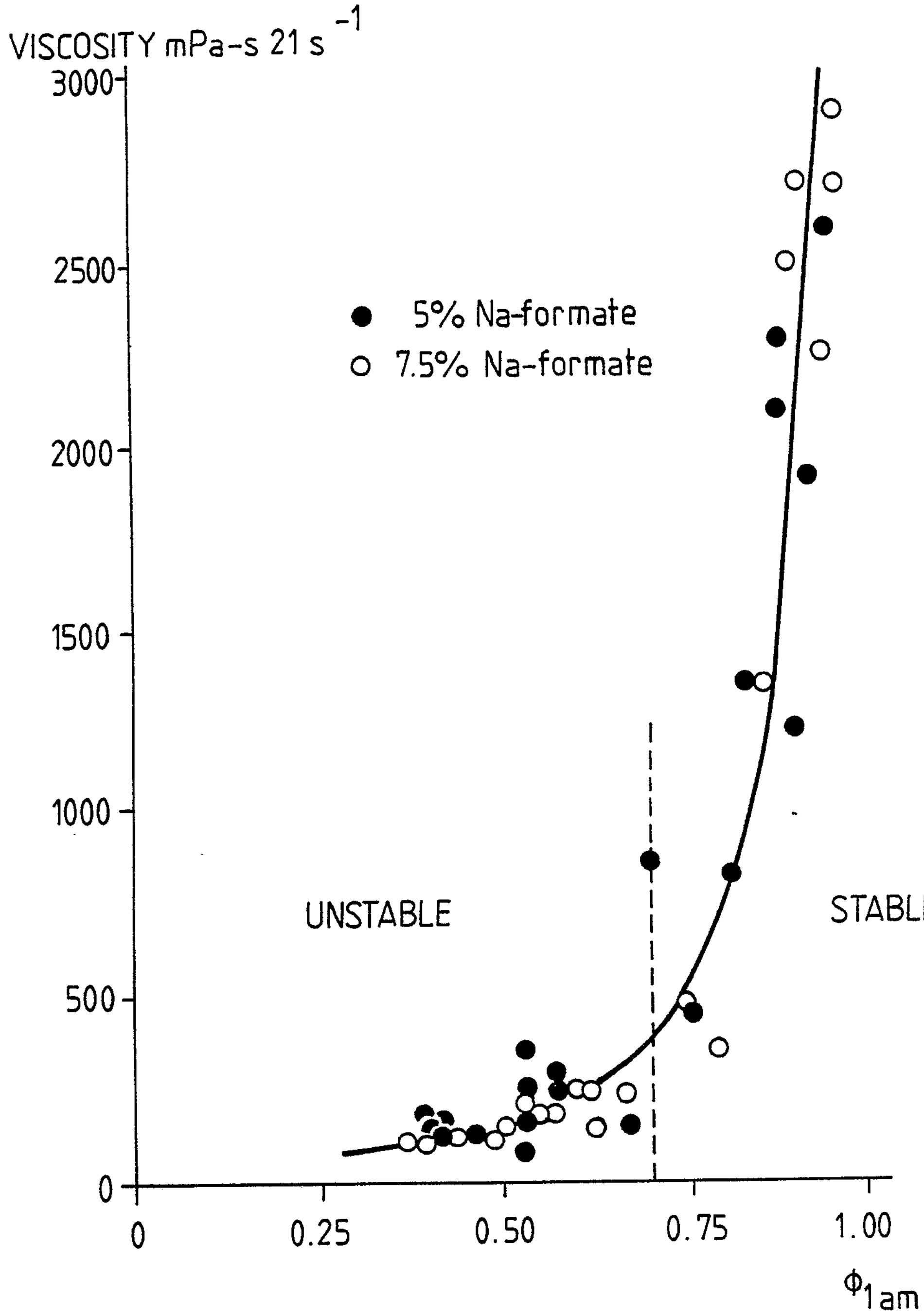
8. A composition according to any of claims 1-4, which exhibits feature (iii) and is structured by one or more external structurants selected from water-swellable polymers, inorganic colloids, filamentary soap crystals and cellulose.

9. A heavy duty liquid detergent being a composition according to any of claims 1-8 and which comprises:-
from 30% to 35% by weight of electrolyte;
from 20% to 25% by weight of detergent actives;
from 0% to 5% by weight of minor ingredients; and
from 50% to 35% by weight of water.

10. A concentrated general purpose cleaner being a composition according to any of claims 1-8 and which comprises:-
from 5% to 25% by weight of electrolyte;
from 15% to 25% by weight of detergent actives;
from 0% to 5% by weight of minor ingredients; and
from 80% to 45% by weight of water.

11. A liquid abrasive cleaner being a composition according to any of claims 1-8 and comprising:-
from 20% by 30% by weight of electrolyte;
from 10% to 25% by weight of detergent actives;
from 0% to 5% by weight of minor ingredients; and
from 70% to 40% by weight of water.

Fig.1.



RELATION BETWEEN THE VISCOSITY AND THE VOLUME FRACTION LAMELLAR PHASE Φ_{1am}

Fig.2.

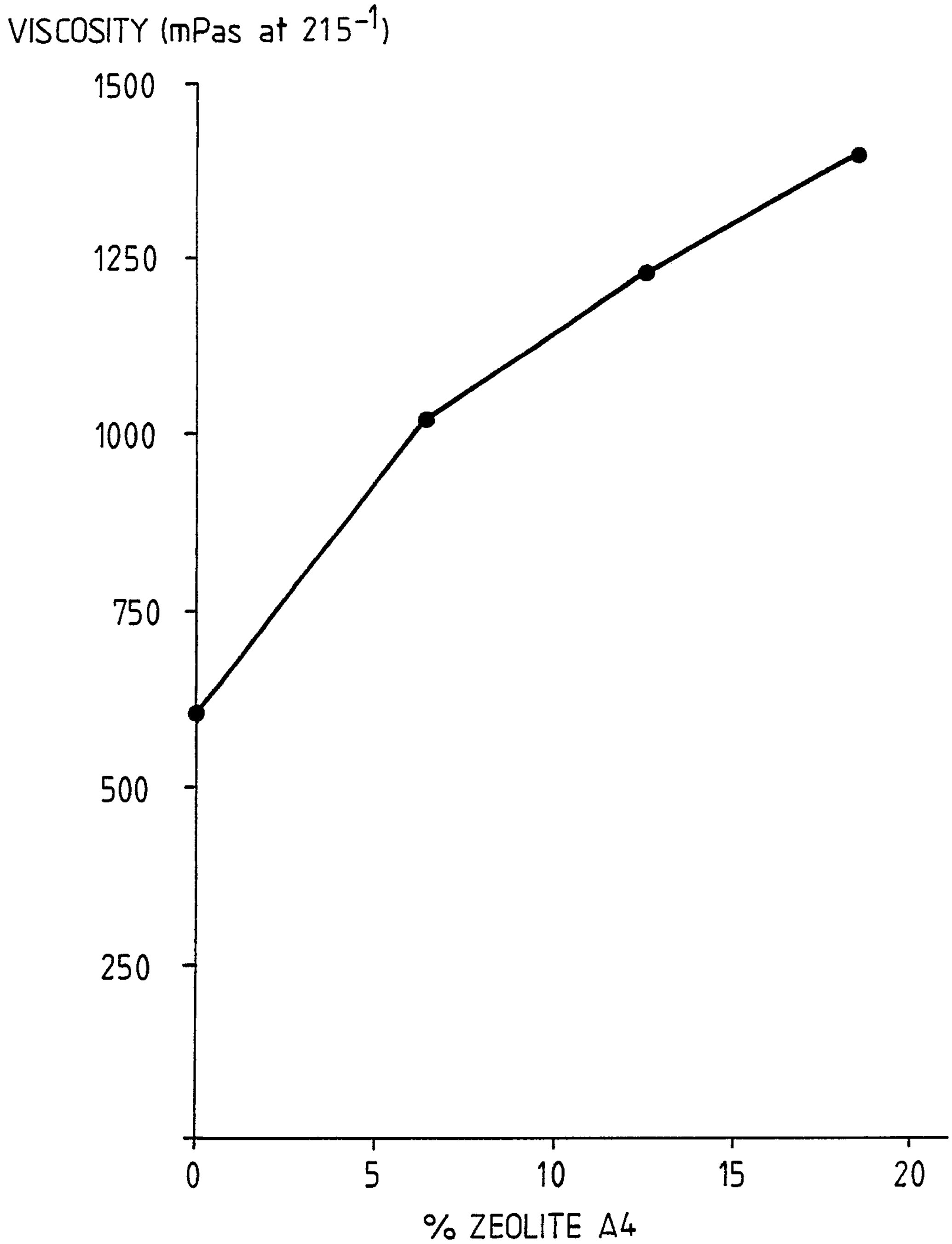
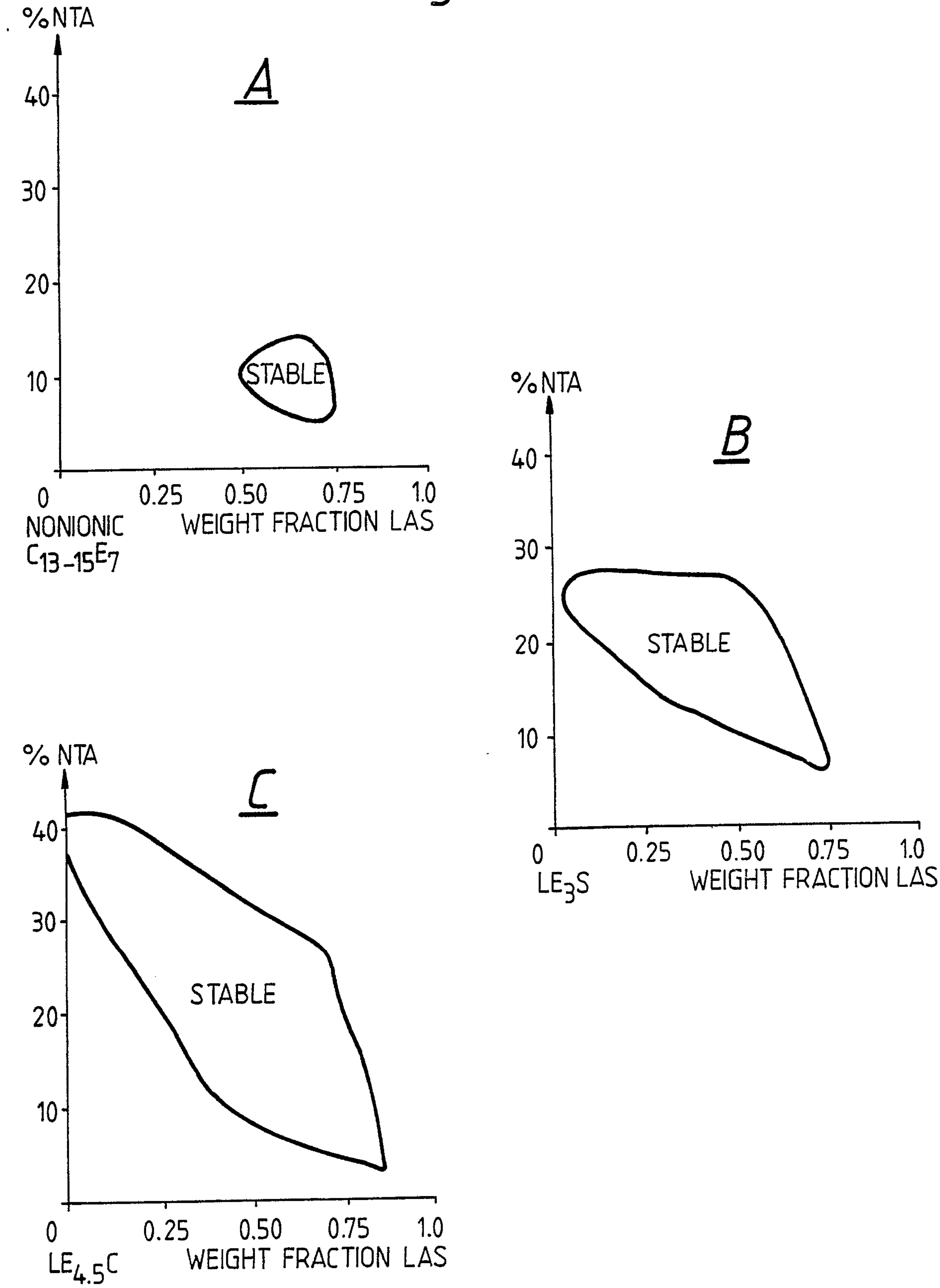

VISCOSITY (mPas at 215⁻¹)
1500
1250
1000
750
500
250
0
5
10
15
20
% ZEOLITE A4

Fig.3.


A
%NTA
STABLE
0
0.25
0.50
0.75
1.0
NONIONIC
$C_{13-15}E_7$
WEIGHT FRACTION LAS
B
%NTA
STABLE
LE$_3$S
WEIGHT FRACTION LAS
C
% NTA
STABLE
LE$_{4.5}$C
WEIGHT FRACTION LAS