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(54) **Detergent compositions.**

(57) A liquid detergent composition suitable especially for dishwashing by hand contains four components:
(a) any nonionic detergent except alkyl ether sulphate,
(b) an alkyl ether sulphate, the ratio of (a) to (b) being 2:1 to 1:10,
(c) a lather booster which is a betaine or amine oxide the ratio of (a) to (c) being 3:1 to 1:3 and
(d) a nonionic detergent in an amount between 35 and 50 weight %.
Compositions of the invention can provide a combination of good performance and good mildness.

EP 0 387 063 A2

DETERGENT COMPOSITIONS

The present invention relates to liquid detergent compositions suitable for use especially, but not exclusively, in fabric washing, shampoos, and above all, in manual dishwashing operations in both hard and soft water.

The term "dishes" as used herein means any utensils involved in food preparation or consumption which may be required to be washed to free them from food particles and other food residues, greases, proteins, starches, gums, dyes, oils and burnt organic residues.

Light-duty liquid detergent compositions such as are suitable for use in washing dishes are well-known. Many of the formulations in commercial use at the present time are based on a sulphonate-type anionic detergent, especially an alkyl benzene sulphonate, in conjunction with an alkyl polyethoxy sulphate (alkyl ether sulphate). The sulphonate-type detergent generally predominates.

The use of conventional dishwashing liquids based on alkyl benzene sulphonate/alkyl ether sulphate or on alkyl sulphate/alkyl ether sulphate is seen to have deleterious influence on the hand condition of users. Hence mildness in washing-up liquid is considered a desirable quality, and many specially formulated products on the market make claims for it.

Protein denaturation by surfactants is considered to be one of the major causes of skin irritation and skin roughness induced by surfactants (G Imokawa et al. JOACS 52, 484-489, Dec 1975). The degree of surfactant denaturation of protein depends on the type of surfactants and their concentration.

At present, the dishwashing formulations that are on the market which are less interactive with protein and hence considered to be milder are those based on a combination of ether sulphates and amine oxides. See for example US-A-3 928 249 (Procter & Gamble). In place of amine oxides, betaines can also be used. See for example US 4 554 098. However, such formulations - particularly with amine oxides - are expensive, not only because the active ingredients are expensive, but also because they require a large amount of expensive hydrotropes such as xylenesulphonate and/or ethanol to produce liquids which are stable and of acceptable viscosity.

EP 0232153 (Unilever) discloses detergent compositions based upon a mixture of anionic and nonionic surfactants together with lather boosters, at least some of the anionic surfactants being alkyl ether sulphate.

It is preferred to include high amounts of nonionic surfactants in order to produce a mild system because such surfactants are inert towards proteins in the skin and because nonionic-containing formulations require lesser amounts of expensive hydrotropes.

Nonionics have also been shown to have a good soil removing potential, particularly of greasy soils often found on dishes. However, nonionics as a class are low foamers and produce unstable lather.

GB 2 165 855 (Colgate) discloses mild nonionic-based light duty liquid detergents wherein the nonionic component exceeds 50% by weight of the total detergent content. However, for reasons stated above, such high nonionic-based formulations would have foam performance deficiencies.

US 4 554 098 (Colgate) mentioned above discloses a mild dishwashing formulation based on an alkyl ether sulphate containing an average of 5 to 12 moles of ethylene oxide in the molecule. However, such ether sulphates are not commercially easily available. Also, it is believed that the dioxane level in ether sulphate raw material increases with the increase in EO content of ether sulphate. Therefore, for ease of commercial exploitation the use of widely used and generally available ether sulphates containing less than 5 EO is preferred.

Therefore there is need for the development of more cost-effective mild dishwashing formulations, which are based on relatively less expensive detergent raw materials and which also require lesser amounts of expensive hydroptropes.

The present invention is based on the realisation that cost-effective mild liquid dishwashing formulations with adequate performance can be obtained by careful choice of the active ingredients and their preparation, in particular by restricting the main anionic detergent active present and including also selected amounts of alkyl ether sulphate, lather boosters and non-ionic detergent active material.

According to a first aspect of the present invention, there is provided a stable detergent composition in liquid or gel form containing from 10 to 80% by weight of an active detergent mixture and also containing water, the active detergent mixture comprising:-

(a) anionic detergent active other than alkyl ether sulphate;

(b) alkyl ether sulphate having an average ethoxylation value of between 1 and 5, the weight ratio of components (a) to (b) being in the range 2:1 to 1:10, preferably in the range 2:1 or 1.5:1 to 1:3, more preferably 2:1 to 1:2; and

(c) betaine and/or amine oxide, the molar ratio of components (a) to (c) being in the range 3:1 to 1:3,

more preferably 2:1 to 1:2; and

(d) a water-soluble nonionic detergent active material in an amount of more than 35%, but less than 50% by weight of the active detergent mixture.

For reasons of cost-effectiveness, and availability of materials, at least a major proportion of the component (a) is selected from secondary alkane sulphonate, alkylbenzene sulphonate, primary alkyl sulphate, fatty acid ester sulphonate, dialkylsulphosuccinate and 2-alpha olefin sulphonate.

Compositions of the invention can give performance in detergency tests as good as those of conventional compositions containing alkyl benzene sulphonate, but are considerably milder.

It is particularly surprising that mildness of predominantly nonionic-based formulations can wholly be maintained by substituting a substantial portion of the nonionic with ether sulphates containing less than 5 EO, but enhancing the foam performance significantly and thus improving cost effectiveness.

Although in principle the concentration of the active detergent mixture may be as high as desired in the range 10 to 80%, provided that a stable liquid or gel product can be obtained, the range of 5 to 60% by weight is preferred, and aqueous liquid compositions with an active detergent mixture in the range of 5 to 40% by weight are of especial interest.

Six detergent actives have been mentioned above as possibilities for component (a). Secondary alkane sulphonate may generally be produced by a free radical reaction, either a sulphochlorination reaction (Reed reaction) of a paraffin

$$RH + SO_2 + Cl_2 \rightarrow RSO_2Cl + HCl$$

followed by hydrolysis and neutralisation, or by a sulphoxidation reaction

$$RH + SO_2 + \tfrac{1}{2} O_2 \rightarrow RSO_3H$$

followed by neutralisation.

The secondary alkane sulphonate component (a) will normally be a mixture of materials of different alkyl chain lengths, of the formula

$$R_1R_2CHSO_3X$$

where R_1 and R_2 which may be the same or different are each a straight or branched chain alkyl group having at least one carbon atom, the alkyl chain length (ie. total number of carbon atoms of R_1 and R_2 plus 1) preferably being in the range 13 to 18, and X is a solubilising cation. An example of such material is SAS 60 of Hoechst (SAS is a Trade Mark) which is produced by a sulphoxidation process.

A suitable secondary alkane sulphonate produced by a sulphochlorination process is Mersolat (trade mark) of Bayer.

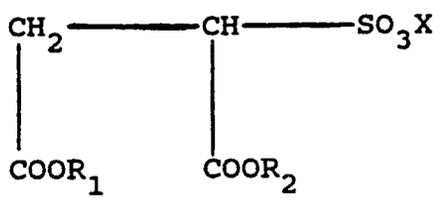
Alkylbenzene sulphonate for use in component (a) is preferably derived from an alkylbenzene with a C_8 to C_{16} primary or secondary alkyl group. This may in particular be C_8 to C_{13} alkyl. Suitable alkylbenzene sulphonates are Dobs 102 of Shell and Marlon A of Huls.

Primary alkyl sulphate is preferred (primary alcohol sulphate) for use in component (a) and is preferably of the formula

$$ROSO_3X$$

where R is a C_8 to C_{18} primary alkyl group and X is a solubilising cation. Suitable is Dobanol 23A of Shell in which R is predominantly C_{12} and C_{13}. As well be explained in more detail below alkyl sulphate is a constituent of alkyl ether sulphates which provide component (b).

Suitable detergent-active dialkyl sulphosuccinates are compounds of the formula



wherein each of R_1 and R_2, which may be the same or different, represents a straight-chain or branched-chain alkyl group having 3 to 12 carbon atoms, preferably from 4 to 10 carbon atoms and more preferably from 6 to 8 carbon atoms, and X represents a solubilising cation.

The alkyl groups R_1 and R_2 are preferably straight-chain or (in mixtures) predominantly straight-chain.

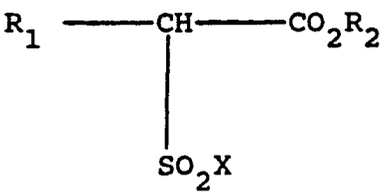
Among dialkyl sulphosuccinates that may advantageously be used in the composition of the invention are the C_6/C_8 unsymmetrical materials described and claimed in GB 2 105 325 (Unilever); the dioctyl sulphosuccinate/dihexyl sulphosuccinate mixtures described and claimed in GB 2 104 913 (Unilever); and the mixtures of symmetrical and unsymmetrical dialkyl sulphosuccinates described and claimed in GB 2

108 520 (Unilever).

Appropriate alpha-olefin sulphonates will generally be in the range having from twelve to sixteen carbon atoms.

An example of such a material is Liporan 440, a C_{14} alpha-olefin sulphonate from Lion Corporation, Japan.

Appropriate fatty acid ester sulphonates are of formula



where

R_1 is straight or branched C_8 to C_{16} alkyl

R_2 is straight or branched C_1 to C_4 alkyl

and

X is a solubising cation

R_1 is preferably C_{10} to C_{12} and

R_2 is preferably butyl.

Component (a) of the active detergent mixture may also include one or more other detergent actives used in liquid compositions, for example alkyl glyceryl ether sulphonates, or alkyl sarcosinates. The amount is preferably less than half of component (a), more preferably not more than a quarter of it.

The second essential component (b) of the active detergent mixture is alkyl ether sulphate (sometimes called alcohol ether sulphate or alkyl polyethoxy sulphate) having at least one ethylene oxide residue per molecule. This will normally be provided by incorporating into the composition an alkyl ether sulphate which is a mixture of materials of the general formula:

$R - (OCH_2CH_2)_n OSO_3X$

wherein R is a C_{10} to C_{18} primary or secondary alkyl group, X is a solubilising cation, and $\underline{n}$, the average degree of ethoxylation, is from 1 to 5, preferably from 3 to 4. Particularly preferred values of $\underline{n}$ are 3 and 4. R_3 is preferably a C_{10} to C_{16} alkyl group. In any given alkyl ether sulphate, a range of differently ethoxylated materials, and some unethoxylated material, will be present and the value of $\underline{n}$ represents an average. The unethoxylated material is, of course, alkyl sulphate and this contributes to component (a).

The amount of alkyl sulphate in any alkyl ether sulphate will depend on average degree of ethoxylation $\underline{n}$. When $\underline{n}$ is 3, alkyl sulphate typically constitutes 15 to 20% of the mixture, and less than this when $\underline{n}$ is 4 or more. When the proportion of alkyl sulphate is low, it may prove convenient to ignore it. Nevertheless, it contributes to component (a).

When the average degree of ethoxylation is 2, alkyl sulphate typically constitutes 30% of the mixture provided as "alkyl ether sulphate". Such a mixture can provide both component (b) and component (a), with the latter then consisting entirely of alkyl sulphate.

We have found that it is not feasible to use alkyl ether sulphate with an average degree of ethoxylation below 1.5. Unless the alkyl sulphate content of the ether sulphate is providing much or the whole of component (a), it is preferred that the alkyl ether sulphate is provided by material with an average of at least 2 or 2.5 ethylene oxide residues per molecule.

Alkyl ether sulphate contains molecules with differing numbers of ethylene oxide residues in a statistical distribution. In an alkyl ether sulphate where the average degree of ethoxylation is 1.5 or greater, the proportion of molecules with a single ethylene oxide residue will not be substantially greater than the proportion with two ethylene oxide residues, nor the proportion with the most frequently encountered number of ethylene oxide residues (if this is more than two). Therefore this feature is an observable characteristic of component (b). If the average degree of ethoxylation is 2 or more, as preferred, the proportion of molecules with a single ethylene oxide residue will be less than the proportion with two ethylene oxide residues and the proportion with the most frequently encountered number.

Preferred alkyl ether sulphates of the component (b), excluding alkyl sulphate, are mixtures of compounds of the above formula

$R\text{-}(OCH_2CH_2)_n\text{-}OSO_3X$

in which $\underline{n}$ is any positive integer, with the proviso that the average EO value is less than 5.

Examples of preferred alkyl ether sulphates for use in the present invention are Dobanol (Trade Mark) 23-3 from Shell in which the degree of ethoxylation (n) is 3 and the equivalent material in which the degree of ethoxylation is 4. These materials which are based on C_{12}-C_{13} (50% of each) primary alcohol (about 75% straight chain, 25% 2-methyl branched). Another preferred material is an alkyl ether sulphate based on Lial (Trade Mark) 123 from Chimica Augusta, which is a branched chain primary alcohol with a degree of ethoxylation of 3 to 4 and with a similar alkyl chain length distribution to Dobanol 23. Also preferred is Empicol MD (Trade Mark) from Albright and Wilson, with degree of ethoxylation of 4 and based on middle-cut coconut alkyl group.

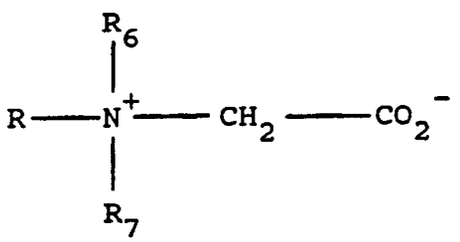
A suitable example of a secondary alcohol ether sulphate is a material derived from an alcohol such as Tergitol 15/S/3 (trade mark) of Union Carbide (this material itself is not at present available). The conventional process of manufacture of secondary alkyl ether sulphates is such that there is only a very small quantity of alkyl sulphate in the product.

Component (b) provides at least 12% of the active detergent mixture, preferably it provides at least 20 or 30%. It preferably provides not more than 40% of the active detergent mixture. However, component (b) could form up to 50% of the mixture if component (b) contributes substantially or wholly to component (a).

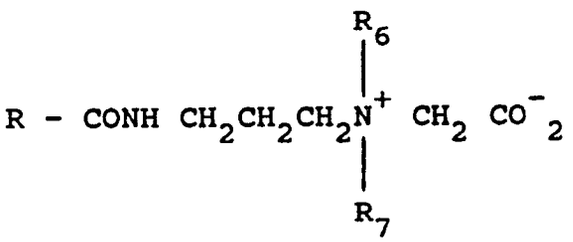
The solubilising cations of the anionic detergent actives of components (a) and (b), denoted as X in the formulae above, may be any which provide the desired solubility of the anionic material. Monovalent cations such as alkali metal ions, ammonium and substituted ammonium are typical. Divalent ions giving adequate solubility may be used, and especially magnesium ions may be present to improve soft water performance and can be incorporated as magnesium salt of the anionic actives or as inorganic magnesium salts, or in the hydrotrope system.

Component (c) is a betaine or amine oxide or a mixture thereof. It is preferred to avoid using substantial amounts of these, especially amine oxides, for the sake of economy and consequent cost effectiveness. Preferably then the amount of amine oxide is not more than 10% by weight of the active detergent mixture. Preferably the amount of betaine is not more than 30% by weight of this mixture. The total amount of amine oxide and betaine is preferably not more than 30% and more preferably not more than 15% or 10% by weight of the active detergent mixture. It is preferred to use betaines alone.

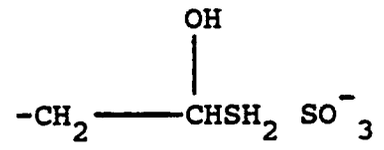
Suitable betaines include simple betaines of formula



and amido betaines of formula:



In both formulae R is a C_8 to C_{18} straight or branched alkyl group. It may be a lauryl group or a middle cut coconut alkyl group. R_6 and R_7 are each C_1 to C_3 alkyl or C_1 to C_3 hydroxyalkyl. Examples of sulphobetaines have the above formulae with $-CH_2CO^-_2$ replaced by $-(CH_2)_3SO^-_3$ or



A suitable simple betaine is Empigen BB from Albright & Wilson. It has the formula quoted above in which R is C_{12} to C_{14} alkyl, derived from coconut, and R_6 and R_7 are both methyl. Also preferred is Tego L7 from Goldsmidt, which has a whole coconut alkyl group.

Suitable amine oxides have the formula

R R_6 R_7 N-O

wherein R is a straight or branched chain C_8 to C_{18} alkyl group and R_6 and R_7 are each C_1 to C_3 alkyl, or C_1 to C_3 hydroxyalkyl. A suitable amine oxide is Empigen OB from Albright & Wilson. In it R is middle-cut coconut alkyl and R_6 and R_7 are both methyl.

Component (d) is one or more water-soluble non-ionic detergent active materials, eg. materials conventionally used in detergent formulations. The betaines and amine oxides of component (c) do not form part of component (d).

Component (d) is preferably a polyalkoxylated material, notably it is one or more ethoxylated non-ionic detergent active materials. It is then desirable that such material should have an HLB value in the range from 12.0 to 16.0.

Component (d) may be a polyethoxylated aliphatic alcohol having an alkyl chain length of from C_8 to C_{18} preferably C_8 to C_{16}, and an average degree of ethoxylation of from 4 to 14. Suitable nonionic detergents include short-chain high-foaming ethoxylated alcohols of the general formula

R - $(OCH_2CH_2)_m$ - OH

wherein R is an alkyl group, preferably straight-chain, having from 8 to 18 better 8 to 16 and yet more preferably 9 to 12, carbon atoms, and the average degree of ethoxylation m is from 5 to 14, more preferably 6 to 12. An especially preferred nonionic detergent is Dobanol 91-8 from Shell, in which R is C_9-C_{11} (predominantly straight-chain) and m is 8, or alternatively Lialet C_{11}-10 EO.

Alternative suitable materials are those in which R is a secondary alkyl having from 8 to 18, preferably 11-15, carbon atoms and m is from 5 to 14 preferably 6-12. An example is Tergitol 15/S/12 of Union Carbide (not available at present) or the material of the Softanol A series (from Japan Catalytic).

Preferably the polyethoxylated alcohol mixture is stripped, to reduce odour imparted to the composition.

Another possibility for the component (d) is an ethoxylated alkanolamide of the general formula

R-CO- N(R_8)$(OCH_2CH_2O)_pH$
|
Y

wherein R is a straight or branched alkyl having from 7 to carbon atoms,

R_8 is an ethyleneoxy or propyleneoxy group

Y is hydrogen or $-R_8(CH_2CH_2O)_qH$

p is 1 or more and q is 0, 1 or more

R may be lauryl or coconut alkyl. Examples of ethoxylated alkanolamide are Amidox L5 and Amidox C5 from Stepan Chemical Company.

Further possibilities for component (d) are ethoxylated alkylphenols and ethoxylated fatty acids, ie. polyethyleneglycol esters of fatty acids.

Component (d) constitutes at least 35% by weight of the active detergent mixture, but less than 50%.

Optionally present within the active detergent mixture of the composition of the invention may be one or more mono- or dialkanolamides, preferably C_8 to C_{18}, more preferably C_{10}-C_{18} carboxylic acid mono- or di-(C_2-C_3) alkanolamides. These have the general formulae

R_4 - CO - NHR_5 and R_4 - CO - $N(R_5)_2$ respectively

wherein R_4 is a C_7-C_{17} aliphatic group, preferably straight-chain and preferably saturated, and R_5 is a hydroxyethyl or hydroxypropyl group. R_5 is preferably a 2-hydroxyethyl group.

Materials of this type are generally made from fatty acids of natural origin and contain a range of molecules having R_4 groups of different chain lengths; for example, coconut ethanolamides consist predominantly of C_{12} and C_{14} material, with varying amounts of C_8,C_{10}, C_{16} and C_{18} material. Preferred are ethanolamides derived from so-called middle cut coconut fatty acid, most preferably from lauric acid.

The mono- and di-ethanolamides may range from 5% to 20% of the detergent mixture.

As well as the active detergent mixture and water, the liquid detergent compositions of the invention will generally need to contain one or more hydrotropes. Hydrotropes are materials present in a formulation to

control solubility, viscosity, clarity and stability but which themselves make no active contribution to the performance of the product. Examples of hydrotropes include lower aliphatic alcohols, especially ethanol; urea; lower alkylbenzene sulphonates such as sodium, toluene and xylene sulphonates and combinations of these. Preferred are alcohol, urea and xylene sulphonate. Hydrotropes are expensive and take up room in a formulation without contributing to its performance, and it is therefore desirable to use as small quantities of them as possible.

For example, the use of amine oxides as mentioned above requires a large amount of alcohol as hydrotrope. For this reason and because of expense, it is preferred to avoid the use of a substantial amount of any tertiary amine oxide in the present invention.

In preferred forms of this invention the weight of hydrotrope in the composition is not more than 12% of the weight of the active detergent mixture.

The compositions of the invention may also contain the usual minor ingredients such as perfume, colour, preservatives and germicides.

The stable liquid detergent compositions of the invention may be used for all normal detergent purposes especially where foaming is advantageous, for example, fabric washing products, general purpose domestic and industrial cleaning compositions, carpet shampoos, car wash products, personal washing products, shampoos, foam bath products, and above all, manual dishwashing.

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

EXAMPLES

Examples 1-4

The foaming performance and mildness of various aqueous formulations were compared. These formulations I and II falling within the scope of the present application were compared with a comparable composition (A) containing over 50% by weight of nonionic active.

Foaming performance was assessed by means of a modified Schlachter-Dierkes test based on the principle described in Fette und Seifen 1951, 53, 207. A 100 ml aqueous solution of each material tested, having a concentration of 0.04% active detergent in 24° H water (French hardness) at 45° C was rapidly oscillated using a vertically oscillating perforated disc within a graduated cylinder. After the initial generation of foam, increments (0.2 g) of soil (9.5 parts commercial cooking fat, 0.25 partsoleic acid 0.25 parts stearic acid and 10 parts wheat starch in 120 parts water) were added at 15 second intervals (10 seconds' mild agitation and 5 seconds' rest) until the foam collapsed. The result was recorded as the number of soil increments (NSI score): a score difference of 6 or less is generally regarded as insignificant. Each result was typically the average of 3 or 4 runs.

Several in-vitro and in-vivo methods for evaluating protein denaturation potency of surfactants and their mixtures have been reported (see Miyazowa et al, Int J Cos Sci 6 33-46 1984, and the references cited therein). One such method is the study of interaction of detergents with acid phosphatase enzyme either from skin (Prottey et al, Int J Cos Sci 6 263-273 1984) or from Wheatgerm (Tanaka et al, Anal Biochem 66 489-498 1975).

In vivo mildness of formulations can be assessed using a flex wash test. In this test neat products were rubbed on the forearm of panellists and rinsed. The process was repeated four times a day for five days and the level of erythema developed was assessed by trained assessors.

A comparison of wheatgerm acid phosphatase (WGAP) test and flex wash test results indicated that formulations giving less than 50% enzyme inhibition under the test conditions are substantially mild; any mildness differences between products giving <40% inhibition do not show any detectable mildness differences in flex wash test, indicating that the enzyme test is very sensitive an that in a real life situation there is a threshold level of protein denaturation below which all actives and products are indistinguishably mild. The results of the WGAP test are expressed as percentage inhibition (ie 100% minus percentage activity remaining). Water gave no inhibition at all, ie 100% of activity remained.

	I	II	A
Lialet 123-3S[1]	10	-	-
Lialet 123-4S[1]	-	10	-
Dobanol 23-A[2]	-	-	8
Lialet 123-S[2]	5	5	-
Lialet C_{11} 10EO[3]	15	15	22
Empigen BB[4]	6	6	6
Empigen LME[5]	4	4	4
Plunger Test (0.04% AD)			
24° FH	46	46	41
5° FH	45	46	43
% WGAP Inhibition	23	21	12

1 - Alkyl Ether Sulphate
2 - Primary Alkyl Sulphate
3 - Nonionic
4 - Betaine
5 - Ethanolamide

The Examples show that formulations I and II give a greater foaming performance than A. Although % WGAP inhibition of A is less than I and II, the effective mildness is no different, as explained above. Thus compositions of the present invention give a combination of mildness and performance.

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Claims

1. A stable detergent composition in liquid or gel form containing from 10 to 80% by weight of an active detergent mixture and also containing water, the active detergent mixture comprising:

(a) anionic detergent active other than alkyl ether sulphate;

(b) alkyl ether sulphate having an average ethoxylation value of between 1 and 5, the weight ratio of components (a) to (b) being in the range 2:1 to 1:10; and

(c) betaine and/or amine oxide, the molar ratio of components (a) to (c) being in the range 3:1 to 1:3; and

(d) a water-soluble nonionic detergent active material in an amount of more than 35%, but less than 50% by weight of the active detergent mixture.

2. A composition according to claim 1 wherein at least a major proportion of said component (a) is selected from secondary alkane sulphonate, fatty acyl ester sulphonate, dialkyl sulphosuccinate, alpha-olefin sulphonate, primary alkyl sulphate, alylbenzene sulphonate and mixtures thereof.

3. A composition according to any one of the preceding claims wherein the weight ratio of components (a) to (b) is in the range 2:1 to 1:2.

4. A Composition according to any one of the preceding claims wherein the total amount of amine oxide and betaine is not more than 20% by weight of the active detergent mixture.

5. A composition according to any one of the preceding claims wherein component (c) contains substantially no amine oxide.

6. A composition according to any one of the preceding claims wherein the alkyl ether sulphate (b) is provided by a mixture of materials of the general formula:

$R - (OCH_2CH_2)_n - OSO_3X$

wherein R is a C_{10} to C_{18} alkyl group, X is a solubilising cation, and n, the average degree of ethoxylation, is from 2 to 12.

7. A detergent composition according to the alkyl ether sulphate (b) is provided by a primary alkyl ether sulphate in which the alkyl groups R are such that less than 20% of material of alkyl chain length C_{14} and above is present, and the average degree of ethoxylation n is from 3 to 8.

8. A composition according to any one of the preceding claims wherein the nonionic (d) is a material of

chain length less than C_{12}.