

"LIQUID DETERGENT COMPOSITION"

This invention relates to clear and stable liquid detergent compositions, such as might be used for cleaning dishes. More particularly, this invention relates to clear, stable liquid detergent compositions containing high levels of detergent/surfactant active compounds but which do not include any of the conventional non-detergent solubilizers or hydrotropes to achieve the clarity or stability.

- Liquid detergent compositions containing sodium dodecyl benzene sulphonate and ammonium alkyl ether sulphate are known from, for example, U.S. Patent 3,231,504. However, in order to formulate compositions containing these detergent active compounds at acceptably high levels, it is necessary to include relatively high amounts of solubilizing agents or hydrotropes. The lower aliphatic alcohols (e.g. ethyl alcohol), urea, alkyl benzene sulphonate (e.g. sodium xylene sulphonate) are representative of the solubilizing agents and hydrotropes.
- Various improvements in these liquid detergent compositions have been provided by replacing all or part of the higher alkyl benzene sulphonate anionic detergent with a paraffin sulphonate anionic detergent. For instance, reference can be made to British Patent Specification B 1,339,069 (amended specification) published November 28, 1973 and its counterpart U.S. Patent 3,755,206, as well as U.S. Patent 3,812,042 and British Patent Specification 1,567,421. All of these patented formulations still require the addition of a hydrotrope or solubilizing

- agent, referred to as a "viscosity and clarity control system" in order to achieve the desired degree of clarity and concentration. Therefore, to the extent that the viscosity and clarity control
5. system (typically a mixture of ethyl alcohol and/or propyl alcohol with urea) occupies space in the composition, the relative concentration of detergent active compounds is necessarily reduced. That is, the viscosity and clarity control system does not
10. contribute to the overall cleaning performance of the liquid detergent composition.

- Other paraffin sulphonate based liquid detergent compositions are described in U.S. Patent 4,040,989, and British Patent Specifications 1,458,798 and
15. 1,458,783 - but these all require relatively specialized and expensive nonionic detergent compounds such as mixed ethylene-propylene oxide condensates, tertiary amine oxides, alkanolic acid alkanolamide, etc.

20. It would be highly desirable, therefore, and it is an object of this invention to provide still further improvements upon these prior paraffin sulphonate based clear stable liquid detergent compositions.

25. A specific object of this invention is to provide clear stable liquid detergent compositions based on paraffin sulphonate with ethoxylated alcohol sulphate and nonionic detergent which compositions can be highly concentrated, for example, up to about
30. 50 weight percent or more of active ingredients, yet

which does not include any non-detergent active solubilizer or hydrotrope material.

These and other objects of the invention which will become more readily apparent from the following detailed description and preferred embodiments of the invention have been accomplished by the discovery that the viscosity and clarity control system of hydrotropic and solubilizing agents can be replaced by a relatively low, e.g. about 8 to 10, carbon chain length alcohol sulphate anionic detergent compound in combination with a nonionic detergent, e.g. a conventional ethoxylated fatty alcohol detergent compound thereby lowering the overall cost of the compositions and permitting higher total levels of active ingredients without sacrificing clarity or stability.

Accordingly, the present invention provides clear liquid detergent composition which comprises

(A) paraffin sulphonate anionic detergent in an amount of from 15 to 40% by weight;

(B) alkyl ether sulphate anionic detergent wherein the alkyl group has from 10 to 18 carbon atoms in an amount of from 1 to 10% by weight;

(C) nonionic detergent in an amount of from 2 to 20% by weight;

(D) alkyl sulphate anionic detergent wherein the alkyl group has from 6 to 11 carbon atoms in an amount of from 0.8 to 5% by weight, the sum of (A) + (B) + (C) + (D) being at least 25% by weight of the total composition; and

(E) water.

The compositions of this invention provide rich stable high foaming cleaners, especially suitable for the hand washing of soiled dishes, glassware and cutlery.

The water soluble paraffin sulphonates, also known as alkane sulphonates, employed in the present invention are usually mixed secondary alkyl sulphonates having from 10 to 20 carbon atoms per molecule with at least about 80% thereof being either 12 to 18 carbon atoms per molecule or 10 to 17 carbon atoms per molecule. A preferred range of carbon atom contents is from 14 to 17 carbon atoms with an average carbon atom content of about 15. The preferred molecular weight normally ranges from 300 to 350.

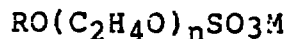
The described paraffin sulphonates are preferably prepared by subjecting a cut of paraffin, corresponding to the chain length specified above, to the action of sulphur dioxide and oxygen in accordance with the well known sulfoxidation process. The product of this reaction is a secondary sulphonic acid, which is then neutralized with a suitable base to produce the water soluble secondary alkyl sulphonate. Similar useful secondary alkyl sulphonates may be obtained by other methods, e.g. by the sulphochlorination technique, in which chlorine and sulphur dioxide are reacted with paraffin in the presence of actinic light, with the resulting sulphuryl chlorides being hydrolyzed and neutralized to form the secondary alkyl sulphonates.

The cation of the paraffin sulphonate and of the anionic sulphates to be described below is preferably an alkali metal, ammonium or lower alkanolamine, although alkaline earth metals, e.g. magnesium, and

lower amines are also useful in forming the water soluble detergent salts. The better of the alkali metals are sodium and potassium, with sodium being preferred. The lower alkanolamines may be mono-, di- or trialkanolamines containing 1 to 3 carbon atoms in the alkanol group, and most preferably, ethanolamines, e.g. triethanolamine and diethanolamine. The corresponding amines may be used instead. The most preferred of the paraffin sulphonates is the sodium paraffin sulphonate wherein the paraffin is essentially (80% or more and preferably 95% or more) of a molecular weight of about 330.

The paraffin sulphonate is present in the composition in amounts of from 15 to 40 percent by weight, preferably from 25 to 35 percent by weight. At concentrations above 40%, it is difficult to solubilize the paraffin sulphonate even at the higher levels of nonionic and alkyl sulphate such that only cloudy compositions can be obtained. At amounts below 15% cleaning performance is not sufficient.

The higher alkyl ether sulphates preferably used in the present invention are represented by the formula:

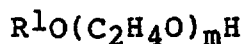


in which R is a primary or secondary alkyl group that may be straight or branched having from 10 to 13 carbon atoms, preferably 12 to 15, especially 12 to 14, and most preferably 12 to 13 carbon atoms, M is a suitable cation, as defined above for the paraffin sulphonate, and n is a number from 1 to 10, prefer-

ably 2 to 6, especially 2 or 3. These detergents are produced by sulphating the corresponding ether alcohol and then neutralizing the resulting sulphuric acid ester thereof. The sodium and ammonium salts of the ether sulphates are especially preferred.

The higher alkyl ether sulphate is present in the composition in amounts of from 1 to 10% by weight, preferably 2 to 8% by weight. At amounts of the ether sulphate above and below these ranges cleaning performance, foaming, or stability are not totally satisfactory.

The nonionic detergent which is another essential ingredient in the clear stable liquid detergent compositions of this invention functions with the alkyl sulphate to be described below to help solubilize the paraffin sulphonate and higher alkyl ether sulphate components and to provide suitable foaming characteristics, i.e. as foam builders. The nonionic detergent also helps to stabilize the composition at low temperatures. Suitable nonionics for use in this invention include the liquid ethoxylated fatty alcohols which may be represented by the following structural formula



in which

R^1 is an alkyl, which may be straight or branched, and which contains from 8 to 12 carbon atoms in the molecule, and
 m is a number of from 5 to 10, on average, generally from 5 to 8, on average.

Usually R¹ will be a mixture of straight alkyl groups with, for example, chain lengths of 9-11 carbon atoms, 8-10 carbon atoms, 10-12 carbon atoms, etc. Mixed alkyl chain lengths of from 9 to 11 carbon atoms are particularly useful. Similarly, the alkyl groups of the ether sulphates will typically be mixtures of varying carbon chain lengths.

The nonionic detergents can be treated, as by distillation, to remove the free starting alcohol and low ethoxylates and such "topped" nonionics are commercially available.

The nonionic detergent is present in the composition in amounts of from 2 to 20% by weight, preferably from 5 to 15% by weight. At amounts of the nonionic below about 2 wt% in the compositions scarcely any effect in foam boosting or solubilizing the remaining ingredients is observed. Amounts of the nonionic larger than about 20 wt%, on the other hand do not provide any significant improvement in cleaning performance and so the use of such high amounts of nonionic should be avoided. On the other hand, within the range of 2 to 20 wt%, especially 5 to 15 wt%, the presence of the nonionics together with the alkyl sulphate, especially at very high total levels of detergent active ingredients, promotes the solubility of the detergent compounds and enables clear, stable solutions to be formed.

The alkyl sulphate anionic detergent compounds which are useful in the present invention have from 6 to 11, especially from 8 to 10 carbon atoms in the alkyl group and can be represented by the following

5. general formula



in which R^2 is straight or branched chain alkyl of from 6 to 11, especially from 8 to 10 carbon atom chain length and M is as defined above, especially
10. sodium. Straight chain alkyl groups are preferred.

With alkyl chain lengths of the alkyl sulphate of 12 or more carbon atoms, for example 12 to 14 carbon atoms, the detergent active compounds, particularly at high total levels of detergent active
15. ingredients, for example, at least 40 percent by weight of the total compositions, especially at least 45 wt%, are not totally soluble and the resulting compositions are cloudy at room temperature.

For example, the following compositions "A" and
20. "B" at a 40 weight percent total active ingredient concentration are prepared by mixing all of the ingredients at room temperature.

<u>Ingredient</u>	A	B
	<u>Weight%</u>	<u>Weight%</u>
25. C ₁₄ -C ₁₇ alkane sulphonate, Na	26.0	26.0
C ₁₂ -C ₁₅ alcohol EO (3:1) Na sulphate	4.2	4.2
C ₉ -C ₁₁ fatty alcohol EO (8:1)	8.4	8.4
C ₈ -C ₁₀ alkyl sulphate	1.2	-
C ₁₂ -C ₁₄ alkyl sulphate	-	1.2
30. Water	balance	balance

Composition "B" is cloudy, whereas Composition "A" is clear. Such cloudy compositions are generally unacceptable to the consumer, especially where the compositions are provided in clear glass or plastic bottles.

The amount of the alkyl sulphate is also important. At concentration of alkyl sulphate of less than about 0.8 percent by weight, the solubilizing effect is insufficient. At concentration above about 5 weight% for any given total concentration of detergent active ingredients, the overall cleaning performance is diminished. Therefore, the amount of the alkyl sulphate anionic detergent component should be in the range of from 0.8 to 5 weight%, preferably from 1 to 3 weight%.

It is one of the features of the present invention that the clear aqueous liquid dishwashing detergent compositions can be prepared with high total levels of the detergent active compounds as described above, especially at levels of at least about 40%, preferably at least about 45%, and especially preferably at least about 50%, by weight of the total composition. Clear stable compositions containing as much as about 70 weight%, for example, up to about 65%, especially up to about 60%, such as from 50 to 60% by weight of the total composition can be prepared.

The detergent compositions according to this invention should have clear point temperatures of at most about 15°C (59°F), preferably no more than about

13°C (55.5°F). The clear point temperature can be easily determined by the following procedure. A sample composition is prepared and placed in a glass test tube which is then placed overnight in a freezer (about -4°C). The test tube is then removed from the freezer and the temperature is increased at a rate of about 1°C per minute. The temperature at which the composition changes from cloudy to clear is the clear point temperature.

5. 10. The viscosities of the detergent compositions may be further varied by the addition of thickening agents such as gums and cellulose derivatives. The product viscosity and flow properties should be such as to make it pourable from a bottle and not so thin
15. as to tend to splash or pour too readily, since usually only small quantities of the liquid detergent are to be utilized in use. Viscosities from 20 to 500 centipoises (Brookfield Viscometer) are found useful with those from 50 to 300 cps. being preferred
20. and a viscosity of about 200 centipoises being considered best by most consumers, although at somewhat lower viscosities. e.g. 100 cps, consumer acceptance is almost the same.

- The liquid detergents of the present invention
25. may also contain any of the additives heretofore used in other liquid detergent compositions such as sequestrants, e.g. salts of ethylenediamine tetra-acetic acid, such as the sodium and potassium salts, and salts of hydroxyl ether ethylene diamine tri-
 30. acetate. It is desirable in some cases to tint or

colour the liquid detergent composition and any suitable dyes may be used for this purpose. Perfume may also be added to these compositions to give them a pleasant odour. Preservatives, germicides, bacteriocides and the like also may be included in the compositions.

Water is used as the liquid vehicle for the liquid detergent compositions of the present invention. It will typically vary in proportion from about 20 to 60 percent, depending upon the content of the other ingredients of the composition.

The compositions generally have a neutral pH (7) but pH's of from 5 to 9, preferably from 6 to 8, are satisfactory.

The invention also extends to a method of washing up, the method comprising cleaning items to be washed up in an aqueous solution of a detergent composition in accordance with the invention.

The invention is illustrated by the following examples.

In order to demonstrate the various advantages of the liquid detergent compositions of this invention, the following formulation are prepared:

<u>Ingredient</u>	WEIGHT%					
	EXAMPLE/RUN NO.					
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
Paraffin sulphonate, Na salt (C ₁₄ -C ₁₇)	27	32.5	30	26	34.15	31.5
Alkyl ether sulphate, Na salt (C ₁₂ -C ₁₅ alcohol EO 3:1)	3.8	5.25	3	4.2	5.5	5.5
Nonionic detergent (C ₉ -C ₁₁ fatty alcohol EO 8:1)	5.4	10.5	6	8.4	11.0	13.65
Alkyl sulphate, Na salt (C ₈ -C ₁₀ alkyl)	3.8	1.75	1	1.4	1.85	1.85
Perfume/dye/water	B A L A N C E					
Total Active Ingredients	40	50	40	40	52.5	52.5
Clear Point	13°C	9°C	7°C	4°C	25°C	12°C
Viscosity (cps)*		280	200	200		300

*Measured with Brookfield viscometer-LVT, spindle No. 2 at 30 r.p.m. and 20°C.

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		WEIGHT%				
		EXAMPLE/RUN NO.				
	<u>Ingredient</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>	<u>11</u>
	Paraffin sulphonate,	20	16.25	24	19.5	26
5.	Na salt (C ₁₄ -C ₁₇)					
	Alkyl ether sulphate,	5	2.6	6	3.25	4.6
	Na salt (C ₁₂ -C ₁₅					
	alcohol EO 3:1)					
	Nonionic detergent	-	5.25	-	6.25	4.7
10.	(C ₉ -C ₁₁ fatty					
	alcohol EO 8:1)					
	Alkyl sulphate, Na	-	0.9	-	1.0	4.7
	salt (C ₈ -C ₁₀ alkyl)					
	Perfume/dye/water		B	A	L	A
					N	C
						E
15.						
	Total Active Ingre-	25	25	30	30	40
	dients					
	Clear Point	21°C	4°C	>13°C	6°C	14°C
	Viscosity (cps)*	150	150	375	160	240
20.						
	*Measured with Brookfield viscometer-LVT, spindle					
	No. 2 at 30 r.p.m. and 20°C.					
	Example/Run Nos. 5, 7 and 9 are comparison examples.					
25.						

From the above results, the following conclusions can be drawn.

Stable and clear formulations with useful viscosities can be prepared over a wide range of concentrations of active ingredients to and including total active ingredients in excess of 50 weight%.

At the same total active ingredient level (52.5 wt%) increasing the amount of the nonionic (with a corresponding decrease in paraffin sulphonate) results in clarification of an otherwise cloudy composition - Compare Run No. 5 (comparison) with Run No. 6 (Invention).

At low total active ingredient levels of about 25% and 30%, the mixture of paraffin sulphonate and alkyl ether sulphate is at the borderline or slightly above acceptable clear points (see Comparative Run Nos. 7 and 9, respectively); at the same total active ingredient levels of 25% and 30% replacing a portion of the paraffin sulphonate and alkyl ether sulphate with the nonionic detergent and C₈-C₁₀ alkyl sulphate results in perfectly acceptable clear compositions, albeit at relatively low total concentration of active ingredients (see Run Nos. 8 and 10, respectively).

As the amount of the C₈-C₁₀ alkyl sulphate anionic detergent approaches 5 wt% (Run No. 11), the clear point is still acceptable, but outside the preferred value of less than about 13°C.

The compositions of Run Nos. 3, 4 and 11 are tested to measure cleaning performance of several

- typical formulations according to the invention. For comparison, the cleaning performance of a composition (Run No. 12) in which each of the paraffin sulphonate, alkyl ether sulphate, nonionic and alkyl sulphate are used at the 10 wt% level (total active ingredients 40 wt%, clear point 7°C, viscosity 235 cps) is also measured. The performance test is a dishwashing test which was carried out at two different levels of water hardness, viz. at 50 and 300 parts per million (ppm) of hardness, and at a concentration of detergent of 1.25 grams per litre, for each level of water hardness.

- The dishwashing tests are carried out by uniformly soiling standard plates with a soil which consists of a commercial hydrogenated fatty (cottonseed) oil by spreading a small amount, equally, on each plate.

- The plates are washed in dishpans which contain 6 litres of wash water at 43°C. Each of the compositions to be tested (at the two different water hardnesses) is prepared and placed, separately, in different dishpans. The plates are then washed in the dishpans to an end point of a permanent break in the foam covering the dishpan; the number of plates which can be washed to that end point is noted and recorded. A difference of 2 plates in the results obtained is generally considered necessary in order to be significant at a 95% confidence level. The results reported below are based on the average of 3 replicate runs.

Run No.	Composition	Total AI	Cleaning Performance	
			50 ppm	300 ppm
3	30%PS/3%ES/6%NI/1%AS	40	53.5	57
4	26%PS/4.2%ES/8.4%NI/1.4%AS	40	44.5	52
11	26%PS/4.6%ES/4.7%NI/4.7%AS	40	42	52
12	10%PS/10%ES/10%NI/10%AS	40	16	31

PS = Paraffin sulphonate AS = alkyl sulphate
 ES = alkyl ether sulphate
 AI = active ingredients, wt% NI = nonionic

From these results, it can be seen that the composition with the most paraffin sulphonate (Run No. 3) provides the most outstanding cleaning performance, while the cleaning performance of Run Nos. 4 and 11 is very good. The composition of Run No. 12 which is outside the scope of the invention is inferior in cleaning performance at both hardness levels even though its clarity and viscosity are otherwise acceptable.

If, in the compositions of Run Nos. 1, 2, 3, 4, 6 or 11, a C₉-C₁₁ fatty alcohol EO 5:1 is used in place of the C₉-C₁₁ fatty alcohol EO 8:1 similar results are obtained. Similarly, if in any of these compositions a C₁₂-C₁₅ alkyl ether sulphate EO 2:1, Na salt, or ammonium salt is used in place of the C₁₂-C₁₅ alkyl ether sulphate EO 3:1, Na salt, similar results are obtained.

A clear, stable but more highly viscous composition is prepared containing 60 wt% of the

active ingredients used in Run Nos. 1, 2, 3, 4, 6 and 11:

	Paraffin Sulphonate	36%
	Alkyl ether sulphate	6.3%
5.	Nonionic	15.6%
	Alkyl sulphate	<u>2.1%</u>
	Total Actives	60%
	Clear Point	<13%
10.	Viscosity	500 cps.

CLAIMS

1. A clear aqueous detergent composition which comprises

(A) paraffin sulphonate anionic detergent in an amount of from 15 to 40% by weight;

(B) alkyl ether sulphate anionic detergent wherein the alkyl group has from 10 to 18 carbon atoms in an amount of from 1 to 10% by weight;

(C) nonionic detergent in an amount of from 2 to 20% by weight;

(D) alkyl sulphate anionic detergent wherein the alkyl group has from 6 to 11 carbon atoms in an amount of from 0.8 to 5% by weight, the sum of (A) + (B) + (C) + (D) being at least 25% by weight of the total composition; and

(E) water.

2. A composition as claimed in Claim 1 wherein the sum of (A) + (B) + (C) + (D) is at least 40% by weight of the total composition.

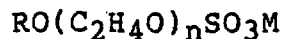
3. A composition as claimed in Claim 1 wherein the sum of (A) + (B) + (C) + (D) is from 40% to 60% of the total weight of the composition.

4. A composition as claimed in Claim 3 wherein the sum is at least 50% by weight.

5. A composition as claimed in any one of Claims 1 to 4, wherein the paraffin sulphonate has from 14 to 17 carbon atoms.



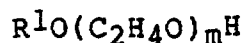
6. A composition as claimed in any one of Claims 1 to 5, wherein the alkyl ether sulphate is a compound of the formula



in which R is a primary or secondary branched or straight chain alkyl group having from 12 to 14 carbon atoms, M is an alkali metal, ammonium or lower alkanolamine, and n is a number of from 1 to 10.

7. A composition as claimed in Claim 6 wherein R is an alkyl group of from 12 to 13 carbon atoms, M is a sodium or ammonium cation, and n is a number of from 2 to 6.

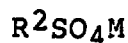
8. A composition as claimed in any one of Claims 1 to 7, wherein the nonionic detergent is an ethoxylated fatty alcohol of the formula



in which R^1 is a straight or branched alkyl group of from 8 to 12 carbon atoms and m is a number of from 5 to 10.

9. A composition as claimed in Claim 8 wherein R^1 is an alkyl group having from 9 to 11 carbon atoms and m is a number of from 5 to 8.

10. A composition as claimed in any one of Claims 1 to 9, wherein the alkyl sulphate is a compound of the formula



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in which R^2 is a straight or branched chain alkyl group of from 6 to 11 carbon atoms and M is an alkali metal, ammonium or lower alkanolamine.

11. A composition as claimed in any one of Claims 1 to 10, which comprises

- (A) from 25 to 35% by weight,
- (B) from 2 to 8% by weight,
- (C) from 5 to 15% by weight,
- (D) from 1 to 3% by weight,

and

- (E) water.

12. A composition as claimed in any one of Claims 1 to 10, which comprises

- (A) C_{14} - C_{17} paraffin sulphonate in an amount of from 25 to 35 weight percent,
- (B) C_{12} - C_{15} alkyl ether sulphate EO 3:1 in an amount of from 2 to 8 weight percent,
- (C) C_9 - C_{11} fatty alcohol EO 8:1 in an amount of from 5 to 15 weight percent,
- (D) C_8 - C_{10} alkyl sulphate in an amount of from 1 to 3 weight percent, and
- (E) water.

13. A composition substantially as herein described with reference to any one of Example/Run Nos. 1 to 4, 6, 8, 10 and 11.

14. A method of washing up, the method comprising cleaning items to be washed up in an aqueous solution of a detergent composition as claimed in any one of Claims 1 to 13.
