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

(11) Publication number: 0 054 436
A1

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: 81305889.8

(22) Date of filing: 15.12.81

(51) Int. Cl.³: C 11 D 3/065
C 11 D 1/12, C 11 D 3/00

(30) Priority: 17.12.80 GB 8040446

(43) Date of publication of application:
23.06.82 Bulletin 82/25

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

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

(84) Designated Contracting States:
GB

(71) Applicant: UNILEVER NV
Burgemeester s'Jacobplein 1
NL-3000 DK Rotterdam(NL)

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

(72) Inventor: Butler, Gregory
137 Dearnford Avenue Bromborough
Wirral Merseyside(GB)

(72) Inventor: Carter, Malcolm Nigel Alan
14 Rickaby Close Bromborough
Wirral Merseyside(GB)

(72) Inventor: Curtis, Michael
6 Eastleigh Drive Irby
Wirral Merseyside(GB)

(72) Inventor: Davies, Roger Maxwell
9 Kings Crescent East
Great Boughton Chester(GB)

(74) Representative: Mole, Peter Geoffrey et al,
Unilever PLC, Patent Division PO Box 31 Salisbury
Square House Salisbury Square
London EC4P 4AN(GB)

(54) **Controlled-sudsing detergent compositions.**

(57) Low sudsing washing powder containing a suds-controller in the form of an alkyl phosphoric acid or salt has improved foaming properties if the carbon chain length of the alkyl benzene sulphonate is carefully selected. The carbon chain length should be such that the proportion of alkyl groups having 14 or more carbon atoms is less than 15, preferably less than 5% by weight. The mean molecular weight perferably is from 235 to 245.

EP 0 054 436 A1

cC.1078

CONTROLLED-SUDSING DETERGENT COMPOSITIONS

This invention relates to controlled suds washing powders containing alkyl benzene sulphonate as a detergent active component primarily designed for use in front loading or drum type washing machines.

Most controlled suds washing powders contain anionic surfactants usually in admixture with nonionic surfactants, and the suds generated by the surfactants is controlled by a suds suppressant, soap being the one most commonly used. However, manufacturers are beginning to be willing to accept the cost penalty of using suds controllers other than soap because of the increased flexibility they give in formulation of the detergent active component. Even so, it is necessary to minimise the additional cost which use of these compounds involves.

We have now discovered that when an alkyl benzene sulphonate is used as the anionic surfact component of the washing powder, and an alkyl phosphoric acid or a salt thereof is used as the suds controller, then very effective suds control can be achieved by a selection of the type of alkyl benzene sulphonate used.

Accordingly the present invention provides a washing powder comprising 5% or more by weight of water-soluble salts of alkyl benzene sulphonates in which the total content of alkyl groups containing 14 or more carbon atoms is less than 15% by weight of the alkyl material, and a suds controller comprising an alkyl phosphoric acid or a salt thereof.

The alkyl benzene precursors of the sulphonates of the invention may be prepared from cracked wax olefines, from polymerized lower olefines or by any other desired route, provided that they conform to the chain length and molecular weight criteria of the invention.

The characteristics of the alkyl benzene sulphonates are extremely important to the present invention, since we have discovered that if sulphonates containing high proportions of alkyl groups having 14 or more carbon atoms are used, the suds produced requires significantly greater amounts of suds controller to be used in order to achieve the target suds profile.

It is preferred that the total content of alkyl sulphonates having 14 or more carbon atoms is less than 5% by weight. Also preferred is that the mean molecular weight of the unsulphonated hydrocarbon is from 235 to 245.

The alkyl benzene sulphonates may be used in combination with other anionic detergent active species. Examples of such materials are sodium primary and secondary alkyl sulphates, sodium olefine sulphonates and sodium alkane sulphonates. Of these, the C_{12}-C_{20} primary and secondary alkyl sulphates are preferred.

Preferred total amounts of anionic surfactant in the compositions of the invention are from 5 to 25% by weight, most preferably 5 to 15% by weight. Desirably the selected alkyl benzene sulphonates will constitute at least half of these amounts and in any event at least 5% by weight of the composition.

Nonionic surfactants may also be present in the compositions of the invention in amounts of up to 15% by weight. Preferred nonionic surfactants are the C_8-C_{24} primary and secondary aliphatic alcohols, ethoxylated with from 3 to 25 moles of ethylene oxide per mole of alcohol. Particularly preferred are the C_{10}-C_{18} primary alcohol ethoxylates containing from 5 to 15 moles of ethylene oxide. We have found C_{12-15} primary alcohol 7EO ethoxylate to be best from the point of view of detergency.

The second essential component of the compositions of the invention is an alkyl phosphoric acid, or a salt thereof, preferably mixed with a hydrocarbon oil or wax. The preferred alkyl phosphoric acids have the general formula

$$R_1O(EO)_n - \underset{\underset{A}{|}}{\overset{\overset{O}{|}}{P}} - OH \qquad (I)$$

where A is -OH or $R_2O(EO)_m$-, R_1 and R_2 are the same or different C_{12}-C_{24}, preferably C_{16}-C_{22}, straight or branched chain, saturated or unsaturated alkyl groups, most preferably C_{16}-C_{18} linear saturated groups, and m and n are the same or different and are O or an integer of from 1 to 6. Preferably A is -OH and n is O, so that the compounds are monoalkyl phosphoric acids, preferably with linear alkyl groups. These compounds may be present either as the free acid or as a sodium, potassium, calcium or magnesium salt or as a mixture thereof.

The amount of the alkyl phosphoric acid or salt thereof used in the detergent compositions can be varied widely from a minimum level of about 0.05% up to a practical maximum of about 5, preferably about 0.1% to about 3% by weight. Higher levels than 5% can be employed but this would be uneconomical and would generally not give any product advantages.

Suitable hydrocarbon waxes for use in the detergent compositions are water insoluble materials of either synthetic, mineral, vegetable or animal origin, which are dispersible in the detergent solutions. The waxes should normally melt at a temperature between about 20°C and about 120°C, preferably not more than about 90°C and especially in the range of about 30°C to about 70°C, i.e. lower than the maximum intended wash temperatures for the detergent compositions.

The preferred waxes are of mineral origin, especially those derived from petroleum, including microcrystalline and oxidised microcrystalline petroleum waxes, petroleum jelly ('Vaseline') and paraffin waxes. Petroleum jelly is correctly a semi-solid wax, usually having a drop melting point of about 50°C, but is for convenience here grouped with other solid waxes. Synthetic waxes such as Fischer-Tropsch and oxidised Fischer-Tropsch waxes, or Montan waxes, or natural waxes such as beeswax, candelilla and carnauba waxes may be used if desired. Any of the waxes described may be used alone or in admixture with other waxes. The waxes should be readily dispersible in the detergent liquor but not soluble therein, and preferably they should not have very high saponification values, e.g. not in excess of about 100. Emulsifying or stabilising agents for the waxes can also be included in the detergent composition.

The amount of wax is normally from about 0.05% to about 10%, preferably about 0.1% to about 5% and especially about 0.5% to about 3% in the composition. The total

BAD ORIGINAL

amount of the alkyl phosphoric acid or salt and the hydrocarbon wax is generally from about 0.2% to about 20% by weight of the composition, preferably about 0.5% to about 5% by weight. The ratio of the amount of the alkyl phosphoric acid or salt to the wax can be varied widely from about 1:25 to about 10:1 parts by weight but is generally from about 1:20 to about 10:1 parts by weight, preferably from about 1:10 to about 1:1 parts by weight.

In addition to the wax which may be used with the alkyl phosphoric acid or salt in the detergent composition, a hydrocarbon oil may also be present, either added separately or jointly with the wax, for example in order to facilitate addition of the wax or to modify its melting point or dispersion characteristics.

Examples of suitable liquid hydrocarbons are mineral, vegetable or animal oils of which colourless mineral oils are preferred. Either light or heavy mineral oil or mixtures thereof may be employed, but of course any liquid hydrocarbon used must be of low volatility at normal fabric washing temperatures. Other oils which could be used if desired are vegetable oils such as sesame oil, cottonseed oil, corn oil, sweet almond oil, olive oil, wheat germ oil, rice bran oil, or peanut oil, or animal oils such as lanolin, neat's foot oil, bone oil, sperm oil or cod liver oil. Any such oils used should of course not be highly coloured, of strong odour or otherwise unacceptable for use in a detergent composition.

Other suds controllers may also be used in combination with the alkyl phosphoric acid-based suds controllers. Examples of these are silicone-based controllers, for example particles of granular sodium tripolyphosphate impregnated with organopolysiloxane and encapsulated in wax, or hydrophobic silica particles impregnated with an organopolysiloxane. Another example, which is of particular interest, is a particle having a spherical or cylindrical core, desirably of sucrose, coated with an

BAD ORIGINAL

absorbent such as titanium dioxide which is impregnated with polysiloxane, the whole particle being coated with wax. Mixtures of polysiloxanes and waxes or ethylene distearamides either alone or in admixture with waxes can also be used as auxiliary suds controllers.

A detergency builder will normally be included within the compositions of the invention. Several suitable detergency builders are well-known and commercially available, examples being alkali metal, ortho-, pyro- and tripolyphosphates, alkali metal carbonates and bicarbonates, alkali metal polyphosphonates, alkali metal nitrilotriacetates and the host of organic builders which have been suggested as a response to the anti-phosphate lobby, examples of which are sodium carboxymethyloxy-succinate, sodium citrate, and sodium polyacrylate.

Other detergency builders are the sodium carbonate/finely divided calcite combination, and the crystalline or amorphous aluminosilicate cation exchange materials. These builders may be used in an amount of from 5 to 80% by weight of the composition, preferably 10 to 60% by weight.

The compositions of the invention may also contain oxygen bleaches such as sodium perborate and sodium percarbonate, fillers such as sodium sulphate, and moisture and minor components such as slurry hydrotropes, corrosion inhibitors, anti-redeposition agents, anti-ashing agents, anti-oxidants, fluorescers and optical brighteners, enzymes, blue-whiteners and pigments and dyestuffs.

The invention will be further illustrated by the following Examples.

BAD ORIGINAL

Example 1

A series of spray-dried powders was produced to the following general formulation and by the following general method:

	Parts by Weight
Sodium alkylbenzene sulphonate	8.0
Primary C_{12-15} alcohol ethoxylate 7EO	3.0
Sodium silicate	8.0
Sodium tripolyphosphate	35.0
Sodium sulphate	7.0
Sodium carboxymethylcellulose	1.0
Moisture, fluorescers and stabilisers	14.0

A suds suppressant in the form of a mixture of one part of C_{16} alkyl phosphoric acid ester with three parts of petroleum jelly was sprayed onto this powder as it fell in a cascade from one conveyor belt to another. 24 parts of sodium perborate tetrahydrate were then mixed with the spray-dried powder, together with perfume.

The suds produced by each powder, varying one from the other as shown below, were assessed as follows:

2½ kg loads of white terry cotton towelling were washed in Hoover (registered trade mark) front-loading automatic washing machines using water of 26°H hardness and 200 g of powder. The washing programme used washes at 90°C.

The suds height of each wash liquor was measured using an arbitrary scale attached to the window of the machines. Each suds assessment was performed four times, the average suds height being quoted in the following tables, which are interpolations from a graph. The graph was produced directly from the results in the experiments.

In the first series of experiments, three sets of powder were used, Set A, the control set, containing a sulphonate of an alkyl benzene having a molecular weight of

BAD ORIGINAL

255 and Sets B and C, the sets in accordance with the invention, containing a sulphonate of an alkyl benzene having a molecular weight of 241 and 242 respectively. The actual alkyl chain length distribution is shown in Table 1.

Five variants of each set of powder were prepared by spraying the powder with 0.6, 0.8, 1.0, 1.2 and 1.4% by weight respectively of the alkyl phosphoric acid/petroleum jelly mixture and the suds height was assessed as described. The results are shown in Table 2.

It can be seen that whereas Powder A containing an alkyl benzene sulphonate having substantial proportions of C_{14}, C_{15} and C_{16} alkyl groups in the composition produces over-foaming at the lower levels of suds-suppressant, the powders in accordance with the invention do not, and indeed produce only a trace of suds at the higher levels of suppressant.

Table 1

Alkyl chain length distribution of the various alkyl benzene sulphonates (ABS)

ABS	Alkyl chain length / Mean Molecular Weight	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}
A	255	8	20	20	20	19	11	2
B	241	9	37	32	19	2	trace	nil
C	242	10	33	33	20	2	trace	nil

0054436
CC.1078

Unilever PLC

Table 2

Maximum Suds Height Produced by 5 Variants of 3 Powders

Suds Suppressant (%)		0.6	0.8	1.0	1.2	1.4
ABS	Mean Molecular Weight					
A	255	over-foam	over-foam	21	16	12
B	241	19	13	9	7	6
C	242	15	8	5	trace	trace

00544436
cc.1078

CLAIMS

1. A washing powder comprising 5% or more by weight of water soluble salts of alkyl benzene sulphonates and a suds controller comprising an alkyl phosphoric acid or a salt thereof, characterised in that the total content of alkyl groups containing 14 or more carbon atoms in the alkyl benzene sulphonates is less than 15% by weight of the alkyl material.

2. A washing powder according to claim 1 characterised in that the total content of alkyl groups containing 14 or more carbon atoms is less than 5% by weight of the alkyl material.

3. A washing powder according to claim 1 or claim 2 characterised in that the average molecular weight of the alkyl benzene from which the alkyl benzene sulphonate is prepared is 235 to 245.

4. A washing powder according to any one of the preceding claims characterised in that the alkyl benzene sulphonate is combined with a C_8-C_{24} primary or secondry alcohol ethoxylated with from 3 to 25 moles of ethylene oxide per mole of alcohol.

5. A washing powder according to claim 4 characterised in that the ethoxylated alcohol is a C_{12}-C_{15} primary alcohol ethoxylated with from 5 to 10 moles of ethylene oxide.

6. A washing powder according to any one of the preceding claims characterised that the suds controller comprises an alkyl phosphoric acid or a salt thereof, in combination with a hydrocarbon oil or wax.

7. A washing powder comprising an alkyl benzene sulphonate and an alkyl phosphoric acid suds controller, substantially as herein before described in compositions B and C of the Example.

0054436

European Patent Office

EUROPEAN SEARCH REPORT

Application number
EP 81 30 5889.8

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.³)
X	DE - A1 - 2 701 663 (UNILEVER N.V.) * claims 1,4,5,7,18; page 10, paragraph 2; page 11, paragraph 2; pages 19 to 21; example 1 * & FR - A1 - 2 338 990	1,2,4, 6,7	C 11 D 3/065 C 11 D 1/12 C 11 D 3/00
A	GB - A - 1 159 643 (MO OCH DOMSJO AB) * claims 1,7,8 *		
A	GB - A - 1 128 330 (UNILEVER LTD.) * claims 1,4 *		TECHNICAL FIELDS SEARCHED (Int. Cl.³)
P,A	EP - A2 - 0 030 859 (UNILEVER N.V.) * claims 1, 5 to 8 *		C 11 D 1/00 C 11 D 3/00

CATEGORY OF CITED DOCUMENTS

- X: particularly relevant
- A: technological background
- O: non-written disclosure
- P: intermediate document
- T: theory or principle underlying the invention
- E: conflicting application
- D: document cited in the application
- L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Berlin	28-01-1982	SCHULTZE