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(21) International Application Number: PCT/EP98/06634 (22) International Filing Date: 9 October 1998 (09.10.98) (30) Priority Data: 9721690.7 13 October 1997 (13.10.97) GB (71) Applicant (for AU BB CA CY GB GD GH GM IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZW only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB). (71) Applicant (for all designated States except AU BB CA CY GB GD GH GM IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZW): UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).		(72) Inventors: BARTOLETTI, Marcella, Margherita, Leda; Unilever Italia S.p.A., Divisione Lever Industriale, Via Lever Gibbs, 3, I-20071 Casalpusterlengo (IT). BOLZONI, Giuseppe, Vincenzo; Unilever Italia S.p.A., Divisione Lever Industriale, Via Lever Gibbs, 3, I-20071 Casalpusterlengo (IT). FERRO, Emanuela; Unilever Italia S.p.A., Divisione Lever Industriale, Via Lever Gibbs, 3, I-20071 Casalpusterlengo (IT). GALLI, Marco; Unilever Italia S.p.A., Divisione Lever Industriale, Via Lever Gibbs, 3, I-20071 Casalpusterlengo (IT). JONES, Carolyn, Elizabeth; Lever Brothers Ltd., P.O. Box 69, Port Sunlight, Wirral, Merseyside L62 4ZD (GB). MORRIS, Ronald, Meredith; Unilever Magyarország KFT, Devai u. 26-28, H-1134 Budapest XIII (HU). (74) Agent: DEKKER, Enno, Ernst, Jan; Unilever PLC, Patent Dept., Colworth House, Sharnbrook, Bedford, MK44 1LQ (GB). (81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: ACID CLEANING COMPOSITIONS CONTAINING ALKOXYLATED AMINES AND THEIR USE (57) Abstract Use of 0.01–15 wt.% of an alkoxyalted aliphatic amine with 8–20 carbon atoms and 1–8 units of alkoxylation improves the antimicrobial effectiveness of an acidic, antimicrobial composition comprising 0.01–15 wt.% of sulphamic acid. The invention also provides acidic, antimicrobial composition comprising: 0.01–15 wt.% of an alkoxyalted aliphatic amine with 8–20 carbon atoms and 1–8 units of ethoxylation, 0.01–15 wt.% of a sulphamic acid, and a source of peroxygen species and a method of disinfecting surfaces which comprises the step of treating the surface with an acidic, antimicrobial composition of that type. Typically, the alkoxyalted aliphatic amine is an ethoxyalted tertiary amine of the general formula: H(A) _x –N(R)–(A) _y H wherein R is an alkyl or alkenyl group comprising 8–20 carbon atoms, A is an ethoxy group and x and y may be the same or different and are integers from 1–4. Preferably x and y are both 1 or 2. In preferred embodiments of the invention R is C14–C18 alkyl and is most preferably derived from oleic, palmitic or myristic acid.		

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ACID CLEANING COMPOSITIONS CONTAINING ALKOXYLATED AMINES AND THEIR USE

Technical Field

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The present invention relates to acidic cleaning compositions, and in particular to acidic antimicrobial cleaning composition suitable for use on hard surfaces.

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Background to the Invention

Many formulations have been proposed in the literature for so-called 'descaler' compositions. These generally comprise sufficient acid to give a low pH and may comprise a thickening agent so as to cause the composition to cling to and be retained on sloping surfaces, such as the inside of toilet bowls. As described in more detail below, known thickeners include both ethoxylated and unethoxylated tertiary amines, either alone or in combination with a hydrotrope. Known acids for use in such compositions include sulphamic and phosphoric acids.

It is advantageous that such compositions should be antimicrobial and that they should exhibit this antimicrobial effect against a broad range of micro-organisms. In order to achieve this various bactericides have been proposed as additives to these compositions.

GB 1443244 relates to acid cleaners and descalers which comprise as a thickening agent an ethoxylated tertiary amine of which ETHOMEEN S12 (N,N-dihydroxyethyl-oleylamine) is given as an example. The composition also comprises

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acids which are selected from mineral acids and acid salts of strong inorganic acids such as sulphamic acid.

Bacteriocides are an additional, optional component.

- 5 FR 2459830 discloses compositions which comprise non-ethoxylated and ethoxylated amines together with sulphamic acid. The composition may also comprise disinfectants.

- 10 WO 95/27768 discloses cleaning compositions, particularly intended for painted and plastic surfaces comprising ethoxylated C10-C18 aliphatic amines containing 3-8 ethoxy units (preferably 4-6) and C6-C10 carboxylic acids and/or organic or inorganic chelating agents. The compositions are not disclosed to have disinfecting properties.

- 15 AU-A-57022/86 relates to cleaning systems which comprise a mixture of sulphamic and phosphoric acids and an acid stable surfactant. Bacteriocides are optional and formalin is disclosed as a bacteriocide which improves the
20 antibacterial effect of the acids.

- EP-B-0276501 discloses thickened aqueous cleaning compositions which comprise 0.1-50%wt of a weak acid having a pK >2 (of which sulphamic is given as an example),
25 0.1-20%wt of an amine which can include 2% of oleyl-bis-(2-hydroxyethyl)-amine and 0.01%-5%wt hydrotrope (sodium xylenesulphonate is given as an example). Disinfecting agents are optional.

- 30 EP-A-0314232 relates to compositions which undergo a viscosity increase on dilution and discloses that thickened liquid detergent compositions can be prepared with an amine oxide, amine (such as ETHOMEEN S12TM), betaine or

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quaternary ammonium compound and hydrotrope (sodium xylene-sulphonate). It is stated in the specification that amine oxides and quaternary ammonium compounds are known to have biocidal properties and that further microbiocides
5 including organic peracids are optional. These compositions can be of acidic, neutral or alkaline pH.

From the above it can be seen that while certain thickening surfactants such as quaternary ammonium compounds and amine
10 oxides are known to have antibacterial properties it has been commonplace to suggest the addition of further antimicrobial components to descaling compositions where antimicrobial effects are desired in addition to descaling.

15

Brief Description of the Invention

We have determined that compositions which comprise both alkoxyated aliphatic amines and sulphamic acid show an
20 improved antimicrobial effect. It is believed that this is due to a synergistic interaction of these components and that the effect is obtained irrespective of the presence (i.e. also in the absence) of other antimicrobial species.

25 We have also determined that excellent scale removal and disinfection is obtained with compositions which comprise:
a) an alkoxyated aliphatic amine,
b) sulphamic acid, and,
c) a source of peroxygen species.

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Detailed Description of the Invention

According to a first aspect of the present invention there is provided the use of 0.01-15%wt of an alkoxyated
5 aliphatic amine having an aliphatic hydrocarbon group of 8-20 carbon atoms and 1-8 units of alkoxylation per mole of amine to improve the antimicrobial effectiveness of an acidic, antimicrobial composition comprising 0.01-15%wt of a sulphamic acid.

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According to a second aspect of the present invention there is provided an acidic, antimicrobial composition comprising:

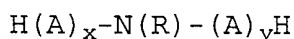
- a) 0.01-15%wt of an alkoxyated aliphatic amine with 8-20
15 carbon atoms and 1-8 units of alkoxylation;
- b) 0.01-15%wt of a sulphamic acid, and
- c) a source of peroxygen species.

According to a third aspect of the present invention there is provided a method of disinfecting surfaces which
20 comprises the step of treating the surface with an acidic, antimicrobial composition comprising:

- a) 0.01-15%wt of an alkoxyated aliphatic amine with 8-20 carbon atoms and 1-8 units of alkoxylation and
- 25 b) 0.01-15%wt of sulphamic acid.

Amines:

30 Typically, the alkoxyated aliphatic amine is a tertiary amine of the general formula:



- 5 -

wherein R is an alkyl or alkenyl group comprising 8-20 carbon atoms, A is an ethoxy or propoxy group and x and y may be the same or different and are integers from 1-4. Preferably R has 8-18, more preferably 10-18 carbon atoms; x and y are preferably 1-3, more preferably 1 or 2. The preferred materials are ethoxylated amines wherein A is -OCH₂CH₂-. In further preferred embodiments of the invention R is C14-C18 alkyl or alkenyl and is e.g. derived from oleic, palmitic or myristic acid.

10 Suitable ethoxylated aliphatic amines are e.g.:

- N,N-di(hydroxyethyl)-oleylamine which is available from AKZO under the trademark ETHOMEEN S12;
- C12-C18 aliphatic amine ethoxylates containing 2 or 3 ethoxy groups, wherein between 20 and 40% of the aliphatic groups are unsaturated (i.e. R = C12-C18 20-40% unsaturated, x=1 and y = 1 or 2). An example of such material is ETHOMEEN BTB/12TM, which is also available from AKZO and is a mixture of N,N-di(hydroxyethyl) aliphatic amine derived from fully hardened tallow and the oleyl derivative in a 65/35 ratio. Such a mixed material can be prepared by synthesis using combined starting materials mixed in the appropriate ratio, or obtained by mixing commercially available materials such as ETHOMEEN HT12TM and ETHOMEEN S12TM in the desired ratio.
- C12-C16 alkyl amines containing 2 or (even more preferably) 3 ethoxy groups (i.e. R = C12-C16 alkyl, x=1 and y = 1 or preferably 2).

30 As can be seen from the above, particularly suitable ethoxylated amines or mixtures of such amines are those wherein the aliphatic group is predominantly (for more than

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50%) derived from C16 and C18 fatty acids and wherein
(average) x+y is 2-3

Preferred levels of the alkoxyated aliphatic amine are
5 1-10%wt on product with levels of 2-6%wt on product being
particularly preferred.

Acids:

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Typical levels of sulphamic acid (i.e. amino-sulphonic
acid) range from 1-10%wt on product with levels of 2-6% on
product being particularly preferred.

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Peroxygen Sources:

Where present, typical sources of peroxygen species include
one or more of hydrogen peroxide, peracetic acid and/or
20 other organic or inorganic peroxygen sources. Hydrogen
peroxide is a preferred source of peroxygen species.
Typical levels of hydrogen peroxide range from 1-10%wt on
product with levels of 3-8% being particularly preferred.

25

Surfactants:

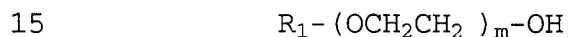
Preferred compositions according to the invention
additionally comprise nonionic surfactant and/or
30 hydrotrope.

Suitable nonionic detergent active compounds (surfactants)
can be broadly described as compounds produced by the

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condensation of alkylene oxide groups, which are hydrophilic in nature, with an organic hydrophobic compound which may be aliphatic or alkyl aromatic in nature. The length of the hydrophilic polyoxyalkylene radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements. Suitable nonionic surfactants include alkoxyated alcohols and alkyl phenols, preferably ethoxyated alcohols

The preferred ethoxyated alcohols are of the general formula:



wherein R_1 is straight or branched C8-C18 alkyl or hydroxyalkyl (preferably alkyl) and m is, on average, 1-14. Ethoxyated alcohols suitable for use in the present invention include the LIAL series available in the marketplace from DAC, such as LIAL 111.10EO [TM]. Typical levels of nonionic surfactant in products according to the present invention range from 0-5%.

Suitable hydrotropes include lower aliphatic alcohols, especially ethanol, urea and/or alkylaryl-sulphonates such as salts of, particularly alkali metal salts of toluene-, cumene- or xylene-sulphonate.

The preferred hydrotropes are alkylaryl-sulphonates, most preferably sodium cumene-sulphonate. A suitable material is ELTESOL SC 40 (TM Albright and Wilson). Typical levels of hydrotrope range from 0.05-2%wt on product.

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In particularly preferred embodiments of the invention the alkoxyated aliphatic amine is present together with an anionic surfactant at levels of these materials are such
5 that they interact so as to thicken the composition

Preferably, formulations comprising the alkylaryl sulphonates are formulated at a pH below 2, more preferably below 1.5, even more preferably below 1. Without wishing to
10 limit the invention by reference to any theory of operation, it is believed that at such a low pH, the ethoxylated amine behaves as a cationic surfactant and interacts with the alkylaryl sulphonate to form a water-insoluble gel which deposits as a monolayer on surfaces.
15 It is believed that this monolayer lowers the surface energy of the surface and retards or prevents the deposition of further limescale.

The preferred mole ratio of the ethoxylated amine and the
20 anionic surfactant is 3-3.5, more preferably 3.25-3.5.

The preferred viscosity of the cleaning compositions according to the present invention is between 50 mPas and 1000 mPas when measured at 11.7 sec⁻¹ shear and at 25
25 Celcius using Haake RV2 rotoviscometerTM and an MV1 bob.

Particularly preferred compositions according to the present invention comprise:

- a) 1-10%wt, preferably 3-5%wt sulphamic acid,
- 30 b) 1-10%wt, preferably 2-5%wt ethoxylated amine,
- c) 0-5%wt, preferably 0.05-1%wt, nonionic surfactant,
- d) 0.05-2%wt, preferably 0.4-1.1%wt, anionic surfactant hydrotrope

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e) 1-10%wt, preferably 4-6%wt, hydrogen peroxide

Minors:

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While the combination of the surfactants in the compositions of the invention provide a thickening effect it is possible to add other thickeners. Gums, particularly xanthan gums are suitable thickeners. Preferred xanthan
10 gums are the Kelzan (RTM) series (available from Kelco Corp). If present, typical levels of xanthan gum range from 0.05-1wt%. The resulting viscosity of the composition, as measured on a Haake RV2 rotoviscometer (RTM) is preferably in the range 10-200 mPas at 20
15 reciprocal seconds shear and 25°C, using an MV1 bob. More preferably the viscosity is 10-100 mPas under the conditions mentioned above.

Metal ion sequestrants such as ethylenediamine tetra-
20 acetate, amino-poly-phosphonates (such as those in the DEQUESTTM range ex. Monsanto) and phosphates and a wide variety of other poly-functional organic acids and salts, can also optionally be employed. Preferred metal ion complexing agents are selected from dipicolinic acid,
25 ethylenediamine tetra-acetic acid (EDTA) and its salts, hydroxyethylidene-diphosphonic acid (Dequest 2010), ethylenediamine-tetra(methylene-phosphonic acid) (Dequest 2040), diethylenetriamine-penta(methylene-phosphonic acid) (Dequest 2060).

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Optional, minor components also include those typically found in cleaning compositions and are selected from opacifiers, colours perfumes and fluorescers.

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Preferred levels of perfume range from 0.05-2%wt. Acid stable perfumes are available from a variety of sources.

- 5 A particularly preferred composition according to the present invention comprises:

ETHOMEEN BTB/12	ex AKZO	2-5%	Ethoxylated amine
SULPHAMIC ACID		4%	
HYDROGEN PEROXIDE		5%	
LIAL 111.10EO	ex DAC	0.1%	Nonionic surfactant
ELTESOL SC40	ex Albright	0.4-1.1%*	Sodium Cumene-Sulphonate
BRILLIANT BLUE 9	ex WJE	0.0021%	CI 307047/colour
PERFUME	ex IFF	0.12%	Othello 39
DEQUEST 2066	ex Monsanto	0-0.3%	
WATER		to 100%	

- 10 *variable to adjust viscosity

Typical products having the above formulation made with 3.0%wt of the amine and around 0.56%wt of the SCS are clear, have a specific gravity of 1.040 g/ml, an initial
 15 viscosity at 106 sec⁻¹ (at 25°C) of 120mPas, an initial viscosity at 11.7 sec⁻¹ (at 25°C) of 300mPas and pH 0.9 (at 25°C).

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In order that the present invention may be further understood it will be illustrated hereafter with reference to the following non-limiting examples.

Examples:

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Example 1: Antibacterial Synergy

Suspension tests were carried out with compositions of the invention and comparative compositions at typical in-use
10 dilutions (2%) of a composition according to the invention. The following bacterial strains were used in the suspension tests.

	<i>Pseudomonas aeruginosa</i>	ATCC 15442
15	<i>Staphylococcus aureus</i>	ATCC 6538
	<i>Enterococcus faecium</i>	DVG 8582
	<i>Proteus mirabilis</i>	ATCC 14153

Antibacterial activity was determined according to EST
20 (DD177:1988) and performed under soil conditions of 0.03%wt bovine serum albumen (BSA) at 19.5 Celcius. Total viable count was determined after a five minute and a 30 minute contact time using solutions as listed below and water of standard hardness for controls. Log reduction relative to
25 water were determined. Viable organisms were determines by culturing on Nutrient or Tryptone-soya agar for 48 hours at 37°C. Log decimal reductions were determined from the viable counts. Table 1 below gives the results for 5 and 30 minutes contact time.

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Concentrations in the assay, which were representative of those encountered in a toilet bowl after use of the product according to the invention, were as follows:

- Sulphamic acid: 0.08%wt
 5 Hydrogen peroxide: 0.10%wt
 Amine ethoxylate: 0.06%wt Ethomeen S/12 [TM]

TABLE 1 (log kill).

10 Suspension test results showing mean log kill, cfu/ml.

CK = Complete Kill

NSK = No Significant Kill

Organism	<i>S.aureus</i>		<i>E.faecium</i>		<i>P. mirabilis</i>		<i>P. aerugi-nosa</i>	
Soil	0.03% BSA		0.03% BSA		0.03% BSA		0.03% BSA	
Contact Time (in min)	5	30	5	30	5	30	5	30
Sulphamic acid	0.99 NSK	2.00	0.00 NSK	0.05	1.95 NSK	0.96 NSK	2.45	0.00 NSK
Sulphamic acid + peroxide	1.62 NSK	2.15	0.00 NSK	0.14	1.74 NSK	0.93 NSK	2.36	1.64 NSK
sulphamic acid + peroxide + amine ethoxylate	3.54	3.99	1.01 NSK	5.01	4.3	4.85	6.95	4.36 CK
sulphamic acid + amine ethoxylate	3.29	3.91	1.56 NSK	5.01	2.69	4.85	6.95	4.36 CK

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Initial Counts:

	<i>Staphylococcus aureus</i> ATCC 6538	6.99
5	<i>Enterococcus faecium</i> DVG 8582	6.99
	<i>Pseudomonas aeruginosa</i> ATCC 15442	4.36
	<i>Proteus mirabilis</i> ATCC 14153	4.95

A neutraliser of Tween (TM) Peptone, volume of 49ml was
10 used. Therefore where counts are zero this is equivalent
to <50cfu/ml or $\log 50 = 1.70$ survivors. From this table it
can be seen that the combination of sulphamic acid and
amine ethoxylate has improved bacteriocidal properties over
15 sulphamic acid per se, against this broad range of
bacteria. In the table figures above 3, indicating
disinfectant behaviour are printed in bold.

In particular, it can be seen that sulphamic acid alone
(first example) has poor antimicrobial properties which are
20 not significantly improved by the presence of hydrogen
peroxide (compare first two examples), but that the
compositions which comprise both sulphamic acid and the
amine ethoxylate (compare bottom two examples) have
antimicrobial properties which are almost as good as those
25 of systems which further comprise hydrogen peroxide (bottom
example).

Claims

- 5 1. The use of 0.01-15%wt of an alkoxyated aliphatic amine with 8-18 carbon atoms and 1-8 units of alkoxylation to improve the antimicrobial effectiveness of an acidic, antimicrobial composition comprising 0.01-15%wt of sulphamic acid.
- 10 2. An acidic, antimicrobial composition comprising:
- a) 0.01-15%wt of an alkoxyated aliphatic amine with 8-20 carbon atoms and 1-8 units of alkoxylation;
 - b) 0.01-15%wt of a sulphamic acid; and
 - 15 c) a source of peroxygen species.
3. A composition of according to claim 2 wherein the alkoxyated aliphatic amine is an ethoxyated tertiary amine of the general formula:
- 20
- $$H(A)_x-N(R)-(A)_yH$$
- wherein R is an alkyl or alkenyl group comprising 8-18 carbon atoms, A is an ethoxy group and x and y may be the same or different and are integers from 1-4.
- 25
4. A composition according to any one of claims 2-3 wherein the source of peroxygen species is hydrogen peroxide.
- 30

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5. A composition according to any one of claims 2-4 wherein the antimicrobial composition comprises:
- a) 1-10%wt sulphamic acid,
 - b) 1-10%wt ethoxylated amine,
 - 5 c) 0-5%wt nonionic surfactant,
 - d) 0.05-2%wt hydrotrope, and,
 - e) 1-10%wt hydrogen peroxide
- 10 6. A method of disinfecting surfaces which comprises the step of treating the surface with an acidic, antimicrobial composition comprising:
- 15 a) 0.01-15%wt of an alkoxyated aliphatic amine with 8-20 carbon atoms and 1-8 moles of ethoxylation and
 - b) 0.01-15%wt of a sulphamic acid.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 98/06634

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D1/44 C11D3/00 C11D3/02 C11D3/39 C11D1/835
C11D7/08 A01N59/02 A01N33/08

According to International Patent Classification (IPC) or to both national classification and IPC

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IPC 6 C11D A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR 2 207 984 A (RECKITT & COLMAN) 21 June 1974 see page 6, line 26-31; claims 1,3 & GB 1 443 244 A (...) cited in the application ----	1,2,6
A	FR 2 459 830 A (INDUSTRIES CHIMIQUES DE VOREPPE) 16 January 1981 cited in the application see page 2, line 34-35; claim 1 ----	1,2,6
A	EP 0 231 886 A (HENKEL) 12 August 1987 see claim 1 ----	1,3
A	EP 0 276 501 A (AKZO) 3 August 1988 see claim 1 -----	3

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☒ Patent family members are listed in annex.

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Information on patent family members

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PCT/EP 98/06634

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