



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) **EP 1 403 360 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
**31.03.2004 Bulletin 2004/14**

(51) Int Cl.7: **C11D 3/20**, C11D 3/37,  
C11D 1/66, C11D 17/04,  
A47L 13/17

(21) Application number: **03077755.1**

(22) Date of filing: **03.09.2003**

(84) Designated Contracting States:  
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR  
HU IE IT LI LU MC NL PT RO SE SI SK TR**  
Designated Extension States:  
**AL LT LV MK**

(30) Priority: **27.09.2002 EP 02256767**  
**17.01.2003 EP 03250319**

(71) Applicants:  
• **UNILEVER N.V.**  
**3013 AL Rotterdam (NL)**  
Designated Contracting States:  
**AT BE BG CH CZ DE DK EE ES FI FR GR HU IT  
LI LU MC NL PT SE SK TR CY RO SI**  
• **UNILEVER PLC**  
**London EC4P 4BQ (GB)**  
Designated Contracting States:  
**GB IE**

(72) Inventors:  
• **Brunt, Thomas Alexander**  
**Chester CH4 7JS (GB)**  
• **Martin, Alexander**  
**Bebington, Wirral, Merseyside CH63 3JW (GB)**  
• **Newbold, Geoffrey**  
**Bebington, Wirral, Merseyside CH63 3JW (GB)**  
• **Sharples, Martin**  
**Bebington, Wirral, Merseyside CH63 3JW (GB)**

(74) Representative: **Dekker, Enno E. J. et al**  
**Unilever N.V.,**  
**Patent Department,**  
**P.O. Box 137**  
**3130 AC Vlaardingen (NL)**

(54) **Cleaning composition and wipe**

(57) The invention concerns aqueous liquid cleaning compositions for shiny hard surfaces, as well as wet wipes comprising these compositions, wherein the composition comprises a low residue surfactant, a relatively

hydrophobic alcoholic organic solvent and a copolymer of styrene and an unsaturated carboxylic acid or carboxylic acid precursor.

**EP 1 403 360 A1**

**Description**TECHNICAL FIELD

**[0001]** The present invention relates to cleaning compositions, and wipes comprising these compositions, for cleaning hard surfaces, more particularly for cleaning shiny and transparent or translucent surfaces such as enamel, ceramic, glossy paint and glass surfaces. The wipes are impregnated with the hard surface cleaning composition.

BACKGROUND AND PRIOR ART

**[0002]** Ready-to-use wipes, impregnated with a liquid cleaning composition are very popular for cleaning hard surfaces. For shiny surfaces it is very important that such wipes (generally referred to as "wet wipes") do not leave visible traces of the cleaning composition, generally known as streaks or spots, because these give the surface an unsightly appearance. Whereas on surfaces such as paint, ceramic and enamel such streaks are usually only visible when the surface is looked at under certain angles, on transparent surfaces, such as glass, streaks are nearly always clearly visible and therefore particularly annoying.

**[0003]** Thus, particular attention has been paid in the prior art to the preparation of wipes and cleaning compositions for glass which on drying leave as little streaks and spots as possible. Compositions for cleaning glass or for impregnating glass-cleaning wipes often contain a relatively low amount of a detergent surfactant, typically less than 1% of a nonionic or anionic surfactant. Furthermore they often contain one or more organic solvents with a boiling point low enough to quickly dry on the surface. Some of these compositions contain a polymeric substance. Such compositions are disclosed in WO 99/09135, in which the surfactant is alkyl sulphate, which contain propylene glycol butylether and ethanol as solvents and which preferably contain polyacrylate or a polyvinylpyrrolidone/acrylic acid copolymer. A similar composition is disclosed in WO 00/71661 comprising a linear alkyl sulphate anionic surfactant, an alkyl polyglucoside nonionic surfactant and a solvent system comprising an alkylene glycol ether and a C1-C6 alcohol.

**[0004]** WO 01/23510 discloses cleaning compositions comprising an alkyl sulphate anionic surfactant and/or an alkyl polyglucoside nonionic surfactant and a hydrophilic polymer such as polyvinyl pyridine n-oxide. The compositions may further comprise an organic solvent and a polyacrylate thickening agent. Pre-moistened wipes comprising these compositions are also disclosed.

**[0005]** WO 01/30128 discloses articles for wiping surfaces impregnated with a cationic surfactant or a cationic polymer.

**[0006]** EP 067016 discloses wet wipes comprising an aqueous composition with up to 1% of a nonionic surfactant and an at least partially esterified resin in a surfactant to resin ratio of from 15:1 to 1:2. It may optionally contain a water-miscible organic solvent.

**[0007]** WO 01/38480 discloses a cleaning wipe moistened with an aqueous cleaning composition comprising a low-residue surfactant (preferably 0.1% alkyl polyglucoside), a hydrophilic polymer such as polyacrylic acid and preferably a glycol ether and/or lower alcohol solvent. Similar wet wipes are disclosed in US 4,448,704. Similar wet wipes without polymer are described in US 5,342,534, WO 01/77280 and WO 01/77281. In EP 604996 the presence of a polymer is optional.

**[0008]** In US 3,696,043 it is disclosed that the reaction product of diethanolamine with a styrene/maleic anhydride copolymer reduces streaking of surfactant solutions on shiny surfaces such as glass

**[0009]** In spite of the large amount of proposed solutions for alleviating spotting and streaking problems on shiny surfaces there remains a need for further reducing this problem.

BRIEF DESCRIPTION OF THE INVENTION

**[0010]** Thus the invention provides aqueous liquid cleaning compositions for shiny hard surfaces, as well as wet wipes comprising these compositions, wherein the composition comprises a low residue surfactant, a relatively hydrophobic alcoholic organic solvent and a copolymer of styrene and an unsaturated carboxylic acid or carboxylic acid precursor. Shiny surfaces treated with the compositions according to the invention and left to dry show minimal streaking and spotting or none at all.

DETAILED DESCRIPTION OF THE INVENTION.

**[0011]** All percentages given below are by weight unless indicated otherwise.

The liquid composition

**[0012]** The liquid cleaning compositions according to the invention comprise one or more anionic and/or nonionic and/or amphoteric low residue detergent surfactants in an amount of 0.01-1%, preferably 0.02-0.5%, more preferably 0.05-0.25%. Preferably the surfactants are nonionic and particularly comprise the well known ethoxylated C8-C18 aliphatic alcohols, amine oxides comprising one C8-C18 alkyl group and 2 C1-C3 alkyl groups and C6-C18 alkyl polyglycosides with a (poly)glycoside group of 1-4 saccharide units. The alkyl polyglycosides are particularly preferred, especially those with C8-C12 alkyl groups.

**[0013]** The liquid compositions according to the invention also comprise one or more hydrophobic alcoholic solvents i.e. alcoholic solvents with a limited solubility in water of between 1% and 20% (at 20°C). The alcoholic solvents may be C4-C6 aliphatic alcohols or they may be glycol mono-ether type solvents such as mono- or di-ethylene or mono- or di-propylene glycol alkyl mono-ethers wherein the alkyl group has up to 8 carbon atoms. Preferably the solvents have a solubility in water of 2-10%. The most suitable examples are n-butanol and propylene glycol butylethers, particularly n-butylether. The solvents should easily evaporate from the surface and therefore preferably have a boiling point not exceeding 250°C, more preferably at most 200°C. The amount of solvent in the composition is 0.1-25%, preferably 0.5-10%, more preferably at most 5%, but does not exceed the limit of its solubility in water. Most preferably it is at least 1%

**[0014]** Furthermore the liquid compositions according to the invention comprise 0.0005-0.1% of a copolymer of styrene and an unsaturated carboxylic acid or carboxylic acid precursor. Such polymers may e.g. be copolymers of styrene with acrylic and/or methacrylic acid, copolymers of styrene with maleic anhydride or copolymers of styrene with (meth) acrylic acid and maleic anhydride. These polymers generally have a (weight average) molecular weight of 10,000 or more, preferably 50,000 or more even more preferably at least 100,000 or even 150,000, but generally below 1,000,000, preferably below 500,000 or even 300,000. The polymers may be modified preferably by esterification, particularly with a lower ( $\leq$  C6) alcohol. Copolymers of styrene with maleic anhydride are preferred, particularly those which are partly esterified and are soluble in aqueous alkali. Preferably the styrene/maleic anhydride ratio in the polymer is above 1, more preferably between 1.05 and 1.5, most preferably between 1.1 and 1.3. Particularly suitable polymers are those marketed by Hercules under the tradename Scripset such as Scripset 540, 740, 745 and similar polymers of other manufacturers.

**[0015]** The amount of polymer in the composition is preferably 0.001-0.05%, more preferably 0.002-0.02%. The weight ratio of surfactant to polymer is preferably between 10:1 and 50:1, more preferably above 15:1, even more preferably between 18:1 and 30:1

**[0016]** The compositions of the invention may optionally but preferably contain one or more hydrophilic solvents, particularly ethanol and/or isopropanol, in an amount of up to 20%, more preferably between 2 and 15%,

**[0017]** The compositions of the invention are preferably alkaline, i.e. have pH of 7.5 or higher, more preferably between 8 and 12, even more preferably between 8.5 and 11, most preferably  $\leq 10$ .

**[0018]** Furthermore the compositions may contain optional components well known in the art such as preservatives, perfumes, colouring agents, pH regulating compounds and the like.

**[0019]** Typical compositions according to the invention comprise:

C8-C12 alkyl polyglycoside	0.05-0.2%
Butanol and/or propylene glycol butylether (together)	1-5%
Esterified alkali-soluble styrene/maleic anhydride copolymer	0.002-0.01%
Optionally: ethanol and/or isopropanol	5-15%
Water	to 100%
Weight ratio of surfactant to polymer 18:1 - 30:1.	

**[0020]** The compositions according to the invention can be used as such to clean all kind of shiny and/or transparent hard surfaces and may be applied by spraying followed by wiping with a cloth, towel, sponge or similar implement. They are particularly suitable for application with a wipe that is pre-wetted with the composition, as more particularly set out below.

The wipes

**[0021]** The wet wipes according to the invention comprise a flexible substrate made of one or more layers of woven or non-woven fibrous material impregnated with a composition according to the invention.

**[0022]** Suitable substrates for wet wipes are well known in the art and include nonwoven material with sufficient wet strength and liquid absorption capacity to contain a suitable amount of the liquid composition according to the invention

and deliver it to the surface to be cleaned. The fibres may be from natural sources e.g. viscose or cellulose such as wood pulp or cotton or synthetic origin such as polypropylene, polyester and nylon. Mixed fibres from different sources may be used in one layer of substrate.

[0023] Optionally, one or more polymeric binders can be added. These binders can typically include one or more monomers selected from styrene/2-ethylhexyl acrylate, butyl acrylate, methyl methacrylate, ethyl acrylate, methyl acrylate, acrylonitrile and vinyl acetate. Any binder material present should not be soluble in the liquid composition to such an extent that it causes the wipe to cause streaking on the cleaned surface.

[0024] The materials can be formed into webs using technologies generally known in the art such as carding, drylaid, wetlaid, airlaid and extrusion.

[0025] Webs can be bonded using technologies known in the art such as needlepunch, stitchbond, hydro-entangling, chemical bonding, thermal bonding, spunbonding, spunlacing and meltblowing. A preferred method is spunlacing.

[0026] The wipe may be a single layer structure or a multilayer structure formed from layers of materials of the above general type, which may be the same or different.

[0027] It is important that the substrate be free from impurities that can be leached out by the liquid composition and can cause streaking on the wiped surface. If necessary, the substrate may be pre-washed prior to impregnation with the composition of the invention in order to remove such impurities.

[0028] Prior to impregnation with the composition of the invention, the wipe typically has an average thickness ranging from 0.1 to 3.0mm, preferably from 0.2 to 1.0mm, more preferably from 0.3 to 0.6mm.

[0029] Prior to impregnation with the composition of the invention, the wipe typically has a maximum absorbency of from 1 to 20g/g (grams water per gram of wipe), preferably from 2 to 12g/g, more preferably from 4 to 10g/g.

[0030] Prior to impregnation with the composition of the invention, the wipe typically has a baseweight of from 20 to 100 g/m<sup>2</sup>, preferably from 30 to 90 g/m<sup>2</sup>, more preferably from 40 to 80 g/m<sup>2</sup>.

[0031] The wipes are impregnated with at least 0.5g liquid composition per g substrate dry weight, preferably 1.0-4.0g liquid per g substrate, more preferably 1.0-2.0g liquid per g substrate.

[0032] The wipes according to the invention may also comprise an additional non-fibrous layer of absorbent or liquid-carrying material such as a spongy layer or a layer of super absorbent material that is capable of releasing the liquid again under the application of pressure.

[0033] Preferred wipes are made of a combination of hydrophobic and hydrophilic fibres. More preferably the wipes are made of a mixture of hydrophobic polyester, nylon or polypropylene fibres and hydrophilic cellulose (preferably cotton) or viscose fibres in the same layer. The wipes may comprise one or more of such layers. Most preferred are wipes comprising a mixture of polyester fibres and viscose or cotton fibres. Preferably, the amount of hydrophobic fibres is 10-70% of the wipe, more preferably at most 60%. An amount of between 20 and 60% hydrophobic fibres is particularly suitable.

#### EXAMPLE

[0034] An aqueous cleaning liquid of the following composition was prepared:

Scripset 740	0.005%
Propylene glycol n-butyl ether	2.5%
Glucopon 215CS UP*	0.10%
Ethanol	12.0%
3-Iodo-2-propynyl butyl carbamate	0.005%
Perfume	0.05%
Demineralised water	to 100%

[0035] A wipe substrate consisting of 50% polyester and 50% viscose fibres and having a baseweight of 50g/m<sup>2</sup> is wetted with the above composition to a liquid loading of 1.5g liquid per g of substrate.

[0036] When used to clean window glass the above wipes gave excellent and completely streak-free cleaning.

#### Claims

1. An aqueous liquid cleaning composition for shiny hard surfaces comprising a low residue surfactant, an alcoholic organic solvent and a polymer **characterized in that:**

- the amount of surfactant is 0.01-1%

- the alcoholic solvent is a hydrophobic solvent chosen from C4-C6 aliphatic alcohol and glycol mono-ether in an amount of 0.1-25%
- the polymer is a copolymer of styrene and an unsaturated carboxylic acid or carboxylic acid precursor in an amount of 0.0005-0.1%.

2. A cleaning composition according to claim 1 **characterized in that** the surfactant is a nonionic surfactant used in an amount of 0.02-0.5%, preferably a C6-C18 alkyl polyglycoside with 1-4 saccharide units.

3. A cleaning composition according to claims 1 or 2 **characterized in that** the hydrophobic solvent has a solubility in water of between 1 and 20% and a boiling point not exceeding 250°C and is present in an amount of 0.5-10%.

4. A cleaning composition according to claims 1-3 **characterized in that** the polymer is an alkali-soluble esterified styrene/maleic anhydride copolymer with a mol. weight of at least 50,000 and is present in an amount of 0.001-0.05%.

5. A cleaning composition according to claims 1-4 **characterized in that** the weight ratio of surfactant to polymer is between 10:1 and 50:1.

6. A cleaning composition according to claims 1-5 **characterized in that** it additionally contains up to 20% of ethanol and/or isopropanol.

7. A cleaning composition according to claims 1-6 comprising:

C8-C12 alkyl polyglycoside	0.05-0.2%
Butanol and/or propylene glycol butylether (together)	1-5%
Esterified alkali-soluble styrene/maleic anhydride copolymer	0.002-0.01%
Ethanol and/or isopropanol	5-15%
Water	to 100%;

wherein the surfactant to polymer ratio is between 18:1 and 30:1.

8. A wet wipe comprising a flexible substrate made of one or more layers of woven or non-woven fibrous material impregnated with a composition according to any one of claims 1-7.

9. A wet wipe according to claim 8 **characterized in that** the substrate consists of a mixture of hydrophobic and hydrophilic fibres in the same layer wherein the amount of hydrophobic fibres is between 10 and 70% of the substrate.



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 03 07 7755

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.7)
D,X	WO 01 38480 A (CLOROX CO) 31 May 2001 (2001-05-31) * page 11, line 4 - line 12; table III *	1-3,6,8,9	C11D3/20 C11D3/37 C11D1/66 C11D17/04 A47L13/17
A	* page 19, line 2 - line 5; table 1 * ---	5,7	
D,X	US 3 696 043 A (HANSON ALDEN W ET AL) 3 October 1972 (1972-10-03) * column 4, line 45 - line 56; claims 1,3; example 5 *	1,3,5,6,7	
A	---		
D,X	US 5 342 534 A (SKROBALA CATHERINE J ET AL) 30 August 1994 (1994-08-30) * claim 1; example 1M *	1,2,6-9	
D,A	WO 00 71661 A (RECKITT & COLMANN PROD LTD; RECKITT BENCKISER INC (US)) 30 November 2000 (2000-11-30) * page 11, line 16 - line 18; example 1 *	1-3,6-9	
A	---		
A	WO 99 36499 A (UNILEVER PLC; UNILEVER NV (NL)) 22 July 1999 (1999-07-22) * page 10, line 14 - line 24; claims 1-3 *	1,2,5-7	TECHNICAL FIELDS SEARCHED (Int.Cl.7) C11D A47L A61K
A	US 5 753 605 A (MCBRIDE SR DANIEL M ET AL) 19 May 1998 (1998-05-19) * column 5, line 34 - line 41; example 1 *	1-3,6,7	
A	---		
A	EP 0 358 984 A (STERLING DRUG INC) 21 March 1990 (1990-03-21) * claim 10; example 1 *	1,3,5,7	
A	---		
A	EP 0 244 006 A (UNILEVER PLC; UNILEVER NV (NL)) 4 November 1987 (1987-11-04) * page 2, line 50 - line 55; example 1 *	1,3-7	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 22 October 2003	Examiner Saunders, T
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 03 07 7755

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

22-10-2003

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 0138480	A	31-05-2001	US 6340663 B1	22-01-2002
			AU 1455801 A	04-06-2001
			CA 2394626 A1	31-05-2001
			WO 0138480 A1	31-05-2001
-----				
US 3696043	A	03-10-1972	DE 2220540 A1	15-11-1973
			NL 7205261 A	23-10-1973
			FR 2111579 A5	02-06-1972
			BE 783492 A1	16-11-1972
-----				
US 5342534	A	30-08-1994	DE 69330305 D1	12-07-2001
			DE 69330305 T2	22-11-2001
			EP 0604996 A2	06-07-1994
-----				
WO 0071661	A	30-11-2000	AU 4933800 A	12-12-2000
			BR 0010813 A	12-03-2002
			CA 2372895 A1	30-11-2000
			CN 1351648 T	29-05-2002
			EP 1179039 A1	13-02-2002
			WO 0071661 A1	30-11-2000
			GB 2353043 A ,B	14-02-2001
			PL 351588 A1	05-05-2003
			US 2002119902 A1	29-08-2002
			ZA 200109515 A	19-11-2002
-----				
WO 9936499	A	22-07-1999	AU 3249599 A	02-08-1999
			BR 9900073 A	11-01-2000
			CA 2317544 A1	22-07-1999
			WO 9936499 A1	22-07-1999
			EP 1049762 A1	08-11-2000
			HU 0100524 A2	28-06-2001
			JP 2002509186 T	26-03-2002
			TR 200002087 T2	21-12-2000
			ZA 9900188 A	12-07-2000
-----				
US 5753605	A	19-05-1998	NONE	
-----				
EP 0358984	A	21-03-1990	US 4869934 A	26-09-1989
			AU 614655 B2	05-09-1991
			AU 3947089 A	22-03-1990
			DK 424289 A	17-03-1990
			EP 0358984 A2	21-03-1990
			NO 893459 A	19-03-1990
-----				
EP 0244006	A	04-11-1987	AU 580210 B2	05-01-1989
			AU 7159387 A	29-10-1987

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 03 07 7755

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

22-10-2003

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0244006 A	BR	8701914 A	02-02-1988
	CA	1288019 C	27-08-1991
	DE	3765685 D1	29-11-1990
	EP	0244006 A1	04-11-1987
	JP	1726122 C	19-01-1993
	JP	4009840 B	21-02-1992
	JP	62256898 A	09-11-1987
	TR	24506 A	12-11-1991
	US	4759868 A	26-07-1988
	ZA	8702834 A	28-12-1988
-----			