



⑫

EUROPEAN PATENT SPECIFICATION

⑯ Date of publication of the patent specification: **31.10.90**

⑯ Application number: **86111706.7**

⑯ Date of filing: **23.08.86**

⑯ Int. Cl.⁵: **C11D 3/14, C11D 3/395**

④ Liquid abrasive cleaner compositions.

⑯ Priority: 11.09.85 GB 8522526	⑯ Proprietor: UNILEVER NV, Burgemeester s'Jacobplein 1 P.O. Box 760, NL-3000 DK Rotterdam(NL)
⑯ Date of publication of application: 18.03.87 Bulletin 87/12	⑯ Designated Contracting States: CH DE FR IT LI NL SE
⑯ Publication of the grant of the patent: 31.10.90 Bulletin 90/44	⑯ Proprietor: UNILEVER PLC, Unilever House Blackfriars P.O. Box 68, London EC4P 4BQ(GB)
⑯ Designated Contracting States: CH DE FR GB IT LI NL SE	⑯ Designated Contracting States: GB
⑯ References cited: EP-A-0 009 942 EP-A-0 103 325 GB-A-1 534 680 GB-A-2 055 118 US-A-4 181 633 US-A-4 396 525	⑯ Inventor: Dawson, Peter Leonard, 6 Linksway, Upton-by-Chester Chester(GB) Inventor: Machin, David, 19 Howells Avenue Great Sutton, South Wirral Cheshire L66 2SZ(GB)
	⑯ Representative: Thomas, Susan Margaret et al, UNILEVER PLC Patents Division P.O. Box 68 Unilever House, London EC4P 4BQ(GB)

EP 0 2 1 4 5 4 0 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Description

5 The present invention relates to liquid abrasive cleaner compositions comprising particulate abrasive material stably suspended in an aqueous liquid medium.

10 Liquid abrasive cleaners have been known in the art for many years. They are widely used in the ordinary household cleaning of hard surfaces as they provide a convenient means for the elimination of stubborn soils, greases, burnt-in materials and stains which are not or not completely removed by abrasive-free cleaning products.

15 Over the last two decades, a multitude of publications have dealt with the formulating of liquid abrasive cleaners. A majority of these publications focus on the stability and suspending properties of the aqueous liquid medium. Suspending media have e.g. been described in the British patent specifications Nos 1 167 597, 1 181 607, 1 262 280, 1 303 810, 1 308 190 and 1 418 671. Other disclosures are concerned with the stability of the suspending media under high shear rates during processing, such as the European patent specifications Nos. 0 050 887 and 0 080 221.

20 Over recent years liquid abrasive cleaners have become increasingly more sophisticated, the in-use properties other than straightforward cleaning efficiency becoming relevant factors in the consumer appreciation. Accordingly, the art is aiming at liquid abrasive cleaner products which display a combination of properties such as cleaning efficiency, non-scratching behaviour, rich foaming, a non-gritty creamy appearance, good rinsability, etc.

25 Unfortunately, various of these properties prove to be difficult to combine in one product. Good cleaning efficiency is difficult to achieve simultaneously with non-scratching behaviour and/or non-gritty appearance. The same applies e.g. to a combination of rich foaming and easy rinsability.

30 Although it has long been recognised that the size of the abrasive is of the greatest importance for an effective cleaner, only in the recent art has it been indicated that the specific particle size distribution of the abrasive material may play an important rôle in the formulation of liquid abrasive cleaner products which, to an acceptable extent, satisfy a number of the desired properties simultaneously.

35 In the British patent specification N° 1 581 433 it has been disclosed that rinsing properties are considerably improved if the amount of finest particles in the abrasive powder used in making the cleaner is reduced. In preferred particle distributions less than 20% by weight of the particles are of size below 10 micrometres and substantially no particles are of size above 125 micrometres.

40 In the United States patent N° 4 181 633 there are disclosed liquid abrasive cleaner compositions comprising calcium metasilicate as sole abrasive, or in conjunction with calcium carbonate, which are stated to yield abrasive cleaners of superior cleaning action and reduced abrasion. The abrasive material should have a mean particle size in the range of about 5.5 to 16 micrometres and substantially no particles above 40 micrometres.

45 In the United States patent N° 4 302 347 all-purpose liquid abrasive cleaners are disclosed comprising from 1 to 20% by weight of water-insoluble particulate abrasive of particle sizes in the range of 1 to 40 micrometres. Compositions are stated to have a creamy consistency and to exhibit effective removal of grease and other soils with effective polishing action and virtually no scratching.

50 In the British patent specification N° 2 125 428 liquid scouring cleanser compositions are described comprising an abrasive powder of mean particle size between 4 and 17.5 micrometres with substantially no particles of size above 75 micrometres. An improved soft and smooth consistency is combined with acceptable cleaning performance.

55 Compared to the conventional household liquid abrasive cleaners comprising abrasive powders with particle sizes ranging from 1 to about 150 micrometres and mean particle size of between 10 and 50 micrometres, recent prior art suggests a considerable shift to lower particle size ranges and sharper distributions, thereby improving consistency and rinsing properties without unacceptable loss of cleaning performance.

60 A drawback of liquid abrasive cleaner compositions formulated with relatively high amounts of fine mineral abrasives, in particular very fine calcite, is that on storage the fine mineral will grow to particles of much larger size which consequently adversely affect the consistency of the product and the non-scratching behaviour thereof on the softer substrates such as e.g. plastic surfaces.

65 It has now been found that in compositions which are free from phosphates, a specific selection of electrolyte type effectively reduces this tendency to particle growth.

70 In accordance with these findings, the present invention provides a liquid abrasive cleaner composition which is free from phosphates, comprising, stably suspended in a liquid medium, from 40 to 70% by weight of a mineral abrasive having particles in the size range of from 1 to 10 micrometres with less than 10% by weight of the abrasive particles having sizes above 10 micrometres and less than 30% by weight of the abrasive particles having sizes below 1 micrometre, and up to 20% by weight of one or more electrolytes selected from the group consisting of alkali metal and ammonium salts of citric, carbonic, sulphuric, hydrochloric, succinic, adipic and glutaric acids.

75 Suitable for use as the abrasive material are both natural and synthetic mineral abrasives, for example dolomite, precipitated calcium carbonate (aragonite), feldspar, alumina, silica, abrasives, such as quartz and quartzite; and preferably an abrasive material is used with a hardness on Moh's scale of

from 1 to 4. Particularly suitable is calcite, for instance limestone, chalk or marble such as those forms of calcite referred to in the British Patent 1 345 119.

The mineral abrasive is included in an amount of from 40 to 70% by weight of the composition, preferably of from 45 to 55% by weight.

5 Abrasive distributions in accordance with the present invention are highly classified distributions. The classification at the upperside preferably results in distributions having less than 5 or even 3% by weight of particles having sizes above 10 micrometres. A very sharp classification at the lower side is less pertinent, but preferably results in distributions comprising less than 20% by weight of particles having sizes below 1 micrometre.

10 The mean particle size of the distribution according to the present invention lies in general within the range of from 1 to 5 micrometres, optimal results being obtained with mean particle sizes within the preferred range of from 2 to 4 micrometres.

15 The mineral abrasive is stably suspended in a liquid medium, which normally comprises an aqueous medium in which an anionic detergent material is present, preferably in combination with a nonionic or zwitterionic detergent material. Suitable anionic surfactants are alkali metal or alkanol amine salts of C₁₂-C₁₈ branched or straight chain alkylaryl sulphonates, of C₁₀-C₁₈ alkyl (EO)₁₋₁₀ sulphates, of C₁₀-C₂₄ fatty acid soaps etc. In general the amount of anionic surfactant will vary between 0.5 and 15 percent, preferably between 1 and 5 percent by weight of the final composition.

20 It is often desirable to include also a nonionic or zwitterionic detergent material in the aqueous medium in an amount of from 0.3 to 7 percent, preferably from 0.5 to 5 percent by weight. Suitable examples of nonionic detergents are water-soluble condensation products of ethylene oxide and/or propylene oxide with linear primary or secondary C₈-C₁₈ alcohols, with C₈-C₁₈ fatty acid amides or fatty acid alkylolamides (both mono- and diamides), with C₉-C₁₈ alkyl phenols and so on. The alkoxyLATED C₈-C₁₈ fatty acid mono- and dialkyloamides should contain more than one alkylene oxide unit; for example, they should be condensed with e.g. 2-5 moles of alkylene oxide such as ethylene oxide. Fatty acid mono- or dialkyloamides in which the fatty acid radical contains 10-16 carbon atoms are also suitable nonionics, such as for instance coco fatty acid mono- or diethanolamide.

25 Suitable zwitterionic detergents are trialkyl amine oxides having one long alkyl chain (C₈-C₁₈) and two short (C₁-C₄) alkyl chains; betaines and sulphobetaines.

30 It is highly desirable that the liquid medium should exhibit Bingham plastic characteristics, thus forming a stable suspending medium for the mineral abrasive. Such media using the above-mentioned surfactants, possibly in combination with other surfactants, are described in British patent specifications 1 167 597, 1 181 607, 1 262 280, 1 303 810, 1 308 190 and 1 418 671.

35 As a further essential component of the suspending medium, one or more electrolytes are included, which must not be of the phosphate type.

Suitable electrolytes are selected from the group consisting of alkali metal and ammonium salts of citric, carbonic, sulphuric, hydrochloric, succinic, adipic and glutaric acids.

40 Preferred electrolytes are the alkali metal salts of citric and carbonic acid, such as sodium citrate, sodium carbonate and sodium bicarbonate. The level of electrolyte depends on any choice of surfactant system but in general ranges from 0.5 to 20% by weight, preferably from 1 to 7% by weight.

The compositions of the present invention optimally include a bleaching agent of the chlorine-releasing type, such as sodium hypochlorite and isocyanurate.

45 Other adjuncts for liquid abrasive cleansers may be included, such as colouring agents, perfumes, fluorescers, hydrotropes, soil-suspending agents, enzymes, opacifiers, germicides, humectants, etc.

The invention will further be described by way of example, in which quantities are expressed by percentages by weight of the total composition unless otherwise indicated.

50

55

60

65

Example-

Ingredients	I	II
sodiumdodecylbenzene sulphonate	2.35	—
5 sodium (C ₁₄ —C ₁₇) alkane sulphonate	—	1.87
coconut soap	—	0.46
monococonut dimethyl amine oxide	—	1.87
10 sodium citrate	0.47	—
sodium carbonate	—	4.32
sodium bicarbonate	1.43	—
sodium hypochlorite	—	11.4
15 magnesium hydroxide	—	0.3
calcite abrasive	52.5	45.7
(mean particle size: 3 µm, above 10 µm 3%, below 1 µm 20%)		
20 water, minor adjuncts	balance	

Claims

25 1. A liquid abrasive cleaner composition which is free from phosphates, comprising, suspended, in an aqueous medium, from 40 to 70% by weight of a mineral abrasive having particles in the size range of from 1 to 10 micrometres with less than 10% by weight of the abrasive particles having sizes above 10 micrometres and less than 30% by weight of the abrasive particles having sizes below 1 micrometre, and up to 20% by weight of one or more electrolytes selected from the group consisting of alkali metal and ammonium salts of citric, carbonic, sulphuric, hydrochloric, succinic, adipic and glutaric acids.

30 2. A composition according to claim 1, wherein the abrasive has a Moh's hardness of between 1 and 4.

3. A composition according to claim 1 or 2, wherein the abrasive is calcite.

4. A composition according to any one of the preceding claims, comprising from 45 to 55% by weight of the abrasive.

35 5. A composition according to any one of the preceding claims, wherein the abrasive has a mean particle size within the range of from 1 to 5 micrometres.

6. A composition according to any one of the preceding claims, wherein the abrasive has a mean particle size within the range of from 2 to 4 micrometres.

7. A composition according to any one of the preceding claims wherein less than 5% by weight of the abrasive particles have sizes above 10 micrometres.

40 8. A composition according to any one of the preceding claims, wherein the aqueous medium comprises from 0.5 to 15% by weight of an anionic surfactant, from 0.3 to 7% by weight of a nonionic surfactant, and from 0.5 to 20% by weight of the electrolyte.

9. A composition according to any one of the preceding claims, wherein the electrolyte is selected from the group consisting of the alkali metal salts of citric and carbonic acid.

45 10. A composition according to any one of the preceding claims, which further includes a bleaching agent of the chlorine-releasing type.

50 Patentansprüche

1. Flüssige Scheuermittel-Reinigungszusammensetzung, die frei von Phosphaten ist, umfassend, suspendiert in einem wässrigen Medium, 40 bis 70 Gew.-% eines Mineral-Scheuermittels mit Teilchen im Größenbereich von 1 bis 10 Mikrometern, wobei weniger als 10 Gew.-% der Scheuermittel-Teilchen Größen über 10 Mikrometer und weniger als 30 Gew.-% der Scheuermittel-Teilchen Größen unter 1 Mikrometer aufweisen, und bis zu 20 Gew.-% eines oder mehrerer Elektrolyten, ausgewählt aus der Gruppe bestehend aus Alkalimetall- und Ammoniumsalzen von Zitronen-, Kohlen-, Schwefel-, Salz-, Bernstein-, Adipin- und Glutarsäure.

2. Zusammensetzung nach Anspruch 1, worin das Scheuermittel eine Mohssche Härte zwischen 1 und 4 aufweist.

3. Zusammensetzung nach Anspruch 1 oder 2, worin das Scheuermittel Kalzit ist.

4. Zusammensetzung nach einem der vorhergehenden Ansprüche, umfassend 45 bis 55 Gew.-% des Scheuermittels.

5. Zusammensetzung nach einem der vorhergehenden Ansprüche, worin das Scheuermittel eine mittlere Teilchengröße im Bereich von 1 bis 5 Mikrometern aufweist.

6. Zusammensetzung nach einem der vorhergehenden Ansprüche, worin das Scheuermittel eine mittlere Teilchengröße im Bereich von 2 bis 4 Mikrometern aufweist.

7. Zusammensetzung nach einem der vorhergehenden Ansprüche, worin weniger als 5 Gew.-% der Scheuermittel-Teilchen Größen über 10 Mikrometer aufweisen.

5 8. Zusammensetzung nach einem der vorhergehenden Ansprüche, worin das wäßrige Medium 0,5 bis 15 Gew.-% eines anionischen oberflächenaktiven Materials, 0,3 bis 7 Gew.-% eines nicht-ionischen oberflächenaktiven Materials und 0,5 bis 20 Gew.-% des Elektrolyten umfaßt.

9. Zusammensetzung nach einem der vorhergehenden Ansprüche, worin der Elektrolyt ausgewählt ist aus der Gruppe bestehend aus den Alkalimetallsalzen von Zitronen- und Kohlensäure.

10 10. Zusammensetzung nach einem der vorhergehenden Ansprüche, die weiterhin ein Bleichmittel vom Chlor-Freisetzungstyp einschließt.

Revendications

15 1. Composition abrasive liquide de nettoyage qui est exempte de phosphates, comprenant en suspension dans un milieu liquide, de 40 à 70% en poids d'un abrasif minéral ayant des particules d'une grosseur comprise entre 1 et 10 μm et moins de 10% en poids de particules abrasives d'une dimension au dessus de 10 μm et moins de 30% en poids de particules abrasives d'une grosseur au dessous de 1 μm , et jusqu'à 20% en poids d'un ou plusieurs électrolyte(s) choisi(s) parmi les sels de métaux alcalins et d'ammonium des acides citrique, carbonique, sulfurique, chlorhydrique, succinique, adipique et glutarique.

2. Composition selon la revendication 1, dans laquelle l'abrasif présente une dureté Moh de 1 à 4.

3. Composition selon la revendication 1 ou 2, dans laquelle l'abrasif est une calcite.

4. Composition selon l'une quelconque des revendications précédentes, qui comprend de 45 à 55% en poids d'abrasif.

25 5. Composition selon l'une quelconque des revendications précédentes, dans laquelle l'abrasif présente une granulométrie moyenne de 1 à 5 μm .

6. Composition selon l'une quelconque des revendications précédentes, dans laquelle l'abrasif présente une granulométrie moyenne de 2 à 4 μm .

7. Composition selon l'une quelconque des revendications précédentes, dans laquelle moins de 5% en poids de particules abrasives sont d'une dimension au dessus de 10 μm .

30 8. Composition selon l'une quelconque des revendications précédentes, dans laquelle le milieu aqueux contient de 0,5 à 15% en poids d'un surfactif anionique, de 0,3 à 7% en poids d'un surfactif non ionique et de 0,5 à 20% en poids d'électrolyte.

9. Composition selon l'une quelconque des revendications précédentes, dans laquelle l'électrolyte est choisi parmi les sels de métaux alcalins des acides citrique et carbonique.

35 10. Composition selon l'une quelconque des revendications précédentes, qui contient en outre un agent de blanchiment du type à dégagement de chlore.

40

45

50

55

60

65