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- (75) Inventors/Applicants (*for US only*): QUELLET, Christian [CH/CH]; Sesslerstrasse 2, CH-2502 Biel (CH). For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



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(54) Title: AQUEOUS ODOR ABSORBING COMPOSITION

(57) Abstract: The invention relates to an aqueous odor absorbing composition comprising 1.8 - 14 % per weight betacyclodextrin, 0.1 - 11 % by weight of a water soluble carboxylic acid and 0.1 - 0.3 % per weight of an antimicrobial preservative. The aqueous odor absorbing composition of the invention may be used in the air or any surface with the exception of humans.

Aqueous Odor Absorbing Composition

The present invention relates to an aqueous odor absorbing composition for use in the air and on surfaces except for use directly on humans.

A wide variety of compositions are used to control
5 odor especially malodor. Such compositions comprise
perfumes, colognes, active compounds which react with
malodor, compounds comprising antibacterial and
antifungal agents etc. WO96/04937 discloses an odor
10 control composition consisting of an aqueous solution
comprising water-soluble cyclodextrins, antimicrobial
preservatives and optionally a perfume. The
cyclodextrins used are alpha-, beta- and gamma-
cyclodextrins consisting of glucose units arranged in a
donut-shaped ring which forms inclusion complexes with
15 organic molecules e.g. those of malodors. Beta-
cyclodextrin is preferred for malodor-absorption due to
its ring size and low cost, however, having a
solubility limit of about 1.85 % at room temperature it
can only be used in a concentration of up to this
20 limit. For desirable higher concentration beta-
cyclodextrin is derivatised. In such derivatives some
of the OH-groups of beta-cyclodextrin are converted to
OR-groups. The known compositions are used for malodor-
absorption or -control on textiles by spraying.

25 The US-A-5 897 854, US-A-5 879 66 and US-A-5 534 165
also describe the use of cyclodextrins for odor
absorption. Beta-cyclodextrin is used in all cases
either in a concentration up to its solubility limit of
1.85% or, if higher concentration is desired, in a
30 derivatised form. The solutions of the above documents
comprise also antimicrobial preservatives. The

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solubility of the latter is improved, if desired, by the addition of small amounts of 0.001 to 0.3% of a chelating agent.

One object of the present invention is to provide a
5 novel malodor-absorbing composition having a high malodor-control.

A further object of the present invention is to provide an aqueous malodor-absorbing composition with a low level of olfactive compounds.

10 A further object of the present invention is to provide an aqueous malodor absorbing composition with a high concentration of beta-cyclodextrin.

A further object of the present invention is to provide an aqueous malodor-absorbing composition with a low
15 viscosity and therefore with good spraying quality.

It has been surprisingly found that addition of carboxylic acids to an aqueous solution multiplies the solubility of non-derivatised beta-cyclodextrin.

Therefore, the present invention refers to an aqueous
20 odor absorbing composition comprising a cyclodextrin and an antimicrobial preservative characterized by

1.8 to 14 % by weight of the total composition of beta-cyclodextrin

0.1 to 11 % by weight of the total composition of a
25 water-soluble carboxylic acid and

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0.1 to 0.3 % by weight of the total composition of the antimicrobial preservative,

whereby all three components are in solution.

Carboxylic acids which enhance the solubility of beta-cyclodextrin are carboxylic monoacids and polyacids which may be substituted by one or more hydroxy groups such as glycolic acid, lactic acid, malonic acid, malic acid, glutaric acid, diglycolic acid, succinic acid, citramalic acid, tartaric acid, mucic acid, adipic acid and derivatives thereof. The preferred carboxylic acids are hydroxy-carboxylic polyacids such as citric acid, which may be present in an amount of 1 to 8 % preferably in an amount of 6 % per weight of the total composition.

Due to the surprising solubilizing effect of the carboxylic acid compositions according to the present invention may comprise up to 14 % of beta-cyclodextrins, amounts of 1.85 to 10 % give good results and amounts of 1.9 to 6 % are preferred.

Antimicrobial preservatives are useful for stabilizing the composition of the invention.

Preferred antimicrobial water soluble preservatives are paraben, phenyl and phenoxy compounds such as phenyl ethanol, phenoxyethanol, organic nitrogen compounds such as imidazolidinyl urea, organic sulfur compounds such as 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one, halogenated compounds such as chlorobutanol, trichlorohydroxy-diphenylether,

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parachlorometa-cresol, metallic salts such as copper salts and zinc salts e.g. ZnCl_2 .

The amount of beta-cyclodextrin dissolved in the compositions of the present invention alone is
5 sufficient to control malodor in an appreciable extent, however, olfactive compounds can be added to impart pleasant odors to a substrate the composition is applied to. Small amounts of olfactive compounds give
10 surprisingly good results i.e. additionally improving control of malodor and adding a pleasant odor at the use of the compositions of the present invention.

Further solubilizing agents for the olfactive compounds, such as fragrances, may be added. Such solubilizing agents are nonionic, anionic, cationic and
15 amphoteric surfactants. Nonionic surfactants are block copolymers, graft copolymers and homopolymers all being more hydrophylic than hydrophobic. Preferred anionic surfactants are alkyl sulfonate. Such solubilizing agents may be present in an amount of 0.01 to 5 %
20 preferably 0.01 to 4 %.

The compositions of the invention may be used to control odor especially malodor in the environment (air-freshener) and on any structured surface such as textiles, rugs, walls etc. In liquid form they may be
25 sprayed or if containing a thickener and thus having a higher viscosity applied with conventional means such as a paintbrush.

The invention is further described in the examples.

Examples 1 to 11

The ingredients given in Table I and II are mixed and dissolved to form a clear solution.

Table I

Ingredients	1 Wt %	2 Wt %	3 Wt %	4 Wt %	5 Wt %	6 Wt %
beta-Cyclodextrin	5	2.5	5	5	2.5	5
Citric acid	6	6	10	10	10	10
Perfume 1*	-	-	-	-	0.008	0.008
Calone	-	-	0.04	-	-	-
Alc.phenyl.ethyl.	-	-	-	0.05	-	-
Preservatives	0.01	0.01	0.01	0.01	0.01	0.01
Water	Qsp 100	Qsp 100	Qsp 100	Qsp 100	Qsp 100	Qsp 100

5

Perfume 1* is a composition of the following 15 compounds: amylacetate, eucalyptol, dymethyloctenon, Cyclal C, linalool, Aldehyde C12 MNA, viridine, terpeneol, benzylacetat, irisone, verdylacetat, phenyl ethyl alcohol, diphenyloxid, prunolide, lilial.

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Table II

Ingredients	7 Wt %	8 Wt %	9 Wt %	10 Wt %	11 Wt %
beta-Cyclodextrin	2.5	5	2.5	5	2.5
Citric acid	6	6	6	6	6
Perfume 2*	0.015	0.015	0.02	0.02	0.02
Surfactant	0.8	0.8	1.05	1.05	1.05
Thickener	0	0	0	0	0.4
Preservatives	0.01	0.01	0.01	0.01	0.01
Water	Qsp 100	Qsp 100	Qsp 100	Qsp 100	Qsp 100

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Perfume 2* is a composition of the following 15 compounds: limonen, tetrahydrolinalool, dihydromyrcenol, anethol, citronellol, alpha-methyl ionone, phenyl ethyl alcohol, lilial, γ -nonalacton, 5 vertofix, γ -decalactone, methyl dihydrojasmonale, cumarin, verdyl-propionate, verdylacetat.

In a first set of evaluation the malodor control or coverage is evaluated directly in the gas phase against tobacco and kitchen malodors by a panel of 4 trained 10 individuals. The panelist evaluate systems with different beta-cyclodextrin concentrations of Examples 1-11 at a constant concentration of malodor. The results are shown in Table III. The best malodor control is denoted by 3.

15 Table III

Examples	1	2	7	8	9	10	11
Coverage effectiveness in air	2	1	2	3	3	3	3

In a second set of evaluation the malodor control is evaluated in situ by a group of 10 trained individuals. The compositions are sprayed on a fabric with tobacco 20 malodor. Fabrics sprayed with the compositions and unsprayed fabrics are compared. The results are shown in Table IV.

Table IV

Example	1	2	3	4	5	6	7	8	9	10
Coverage on smoked cotton	2	1	2	1	1	2	2	3	3	3

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Claims

1. An aqueous odor absorbing composition comprising a cyclodextrin and an antimicrobial preservative characterized by
 - 5 1.8 to 14 % by weight of the total composition of beta-cyclodextrin
 - 0.1 to 11 % by weight of the total composition of a water-soluble carboxylic acid and
 - 10 0.1 to 0.3 % by weight of the total composition of the antimicrobial preservative,whereby all three components are in solution.
2. Composition according to claim 1 wherein the carboxylic acid is a carboxylic monoacid which may be substituted by a hydroxy group.
- 15 3. Composition according to claim 1 wherein the carboxylic acid is a carboxylic polyacid which may be substituted by one or more hydroxy groups.
4. Composition according to claim 1 wherein the carboxylic acid is selected from a group consisting
 - 20 of glycolic acid, lactic acid, malonic acid, malic acid, glutaric acid, diglycolic acid, succinic acid, citramalic acid, tartaric acid, mucic acid, adipic acid and polyacrylic acid or derivatives thereof.

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5. Composition according to claim 3 wherein the carboxylic polyacid is citric acid in an amount of 1 to 8 % per weight of the total composition.
- 5 6. Composition according to one of the preceding claims comprising 1.85 to 10 % per weight of the total composition of beta-cyclodextrin.
7. Composition according to claim 6 comprising 1.9 to 6 % per weight of beta-cyclodextrin.
- 10 8. Composition according to any of the preceding claims comprising 0.001 to 1 % per weight of the total composition of a fragrance or fragrance composition.
- 15 9. Composition according to any of the preceding claims comprising 0.01 to 5 % per weight of the total composition of a solubilizing agent for the fragrance or fragrance composition.
10. Composition according to claim 1 comprising 0.0002 to 0.2 % per weight of the total composition of the antimicrobial preservative.
- 20 11. Composition according to anyone of the preceding claims in liquid form.
12. Composition according to claim 13 in form of a spray.
- 25 13. Composition according to any of the preceding claims comprising a thickening agent.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/CH 00/00280

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A61L9/01 A61L9/14

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A61L

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)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 897 854 A (BUCKNER ROBIN YAGER ET AL) 27 April 1999 (1999-04-27) cited in the application column 8, line 11 column 9, line 54 - line 58 * claims *	1-13
X	US 5 879 666 A (BUCKNER ROBIN YAGER ET AL) 9 March 1999 (1999-03-09) cited in the application column 7, line 29 - line 37 column 8, line 51 - line 54 column 9, line 26 - line 29 examples 1-3 * claims *	1-7, 10-13

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 534 165 A (PILOSOF DAVID ET AL) 9 July 1996 (1996-07-09) cited in the application column 13, line 19 - line 21 column 14, line 22 - line 29 column 15, line 56 - line 57 * claims * ----	1-4,6,7, 10-13
X	WO 96 04937 A (PROCTER & GAMBLE) 22 February 1996 (1996-02-22) cited in the application * claims * page 24, line 11 - line 12 page 25, line 26 - line 28 ----	1,3,4, 6-13
A	DATABASE WPI Section Ch, Week 198906 Derwent Publications Ltd., London, GB; Class D15, AN 1989-043082 XP002121540 & JP 63 315200 A (JOLEABE KK), 22 December 1988 (1988-12-22) abstract ----	1,2,4,5, 8,11
A	DATABASE WPI Section Ch, Week 199616 Derwent Publications Ltd., London, GB; Class D25, AN 1996-157617 XP002121541 & JP 08 041780 A (NIKKA KAGAKU KK), 13 February 1996 (1996-02-13) abstract -----	1,2,4,5, 8,11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/CH 00/00280

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5897854 A	27-04-1999	AU 7825998 A EP 0996414 A NO 996053 A WO 9856342 A	30-12-1998 03-05-2000 04-02-2000 17-12-1998
US 5879666 A	09-03-1999	AU 4910897 A CZ 9901450 A EP 1006993 A NO 991897 A WO 9817240 A	15-05-1998 15-09-1999 14-06-2000 22-06-1999 30-04-1998
US 5534165 A	09-07-1996	AU 3148395 A CA 2196294 A CN 1157574 A EP 0776220 A JP 10503955 T WO 9604939 A	07-03-1996 22-02-1996 20-08-1997 04-06-1997 14-04-1998 22-02-1996
WO 9604937 A	22-02-1996	US 5714137 A CA 2197441 A CN 1159762 A CZ 9700402 A EP 0774978 A HU 76679 A JP 10503953 T TR 960139 A US 5668097 A	03-02-1998 22-02-1996 17-09-1997 16-07-1997 28-05-1997 28-10-1997 14-04-1998 21-06-1996 16-09-1997
JP 63315200 A	22-12-1988	JP 1688359 C JP 3056800 B	11-08-1992 29-08-1991
JP 8041780 A	13-02-1996	NONE	