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(54) **Peroxygen composition**

(57) A composition comprising at least one peracid and a quaternary ammonium salt of the formula: $[R^1R^2R^3R^4N^{m+}]_n X_x^{p-} Y_y^{q-}$ wherein: R^1 , R^2 , R^3 and R^4 are independently, optionally substituted, alkyl, aryl or alkoxy groups; $m \cdot n = (x \cdot p) + (y \cdot q)$; m and n are inde-

pendently equal to 1 or 2; x and y are integers or non integers and are independently from 0 to 2; $x+y$ is at least 1; at least one of X^{p-} and Y^{q-} is R^5 -COO- and R^5 contains from 0 to 5 carbon atoms.

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DescriptionField of the invention

5 **[0001]** This invention concerns peroxygen compositions. More specifically, this invention concerns solutions of peracids and additives such as quaternary ammonium salts.

Introduction

10 **[0002]** It is well known that certain classes of compound exert a very strong microbicidal effect which renders them suitable for use as disinfectants in a wide range of applications, especially domestic and industrial hard surface disinfection. One of the most commonly employed compounds is sodium hypochlorite solution, because it is readily available at low cost and is reasonably effective as a disinfectant over short contact times. In recent years, however, there has been increasing concern expressed at the possible environmental consequences of the use of hypochlorite solutions, including the possible formation of chlorinated organic compounds, such as trihalomethanes, and so attempts have been made to identify alternative disinfectants.

15 **[0003]** Peracids and peracid compositions, for example Perestane™, are rapid acting oxidising biocides. Perestane™ is an aqueous mixture comprising peracids. Perestane™ is typically an aqueous equilibrium mixture comprising mixed peracids. Perestane™ can be formulated into compositions which are effective low temperature bleaches, colourless, non-staining liquids which are easily rinsed from surfaces without leaving a residue. Compositions including Perestane™ or other peracids may also be thickened or perfumed.

[0004] Further, Perestane™ containing compositions or other compositions containing peracids are effective instantly and react quickly with the microbial agent thereafter decomposing quickly leaving no residue.

25 **[0005]** As a consequence of these properties, Perestane™ and other peracids are typically used as household disinfectants and surface cleaners.

[0006] Quaternary ammonium salts are effective disinfecting agents active against microbial agents, e.g. yeast, virus, bacteria, moulds and spores. Known as "quats", quaternary ammonium salts have been used as antimicrobial agents for cleaning agents and for fabric softeners (US 2003/0109403). Quats have also been used in compositions to reduce the antimicrobial burden in food products (US 2002/0192340).

30 **[0007]** Quats have a longer lasting effect and provide disinfectant efficacy over a longer time period.

[0008] It is advantageous to formulate aqueous compositions containing peracids, such as Perestane™, but also quaternary ammonium salts and/or surfactants, which lead respectively to a longer term effect and better wetting properties, which will both result in a better efficacy or performance as biocide. However, formulation of peroxygen compounds is known to be difficult. The additive needs to be resistant to oxidation (as it will be in presence of powerful oxidant) and also it must not destabilize the peroxygen compound giving rise to oxygen evolution and lack of activity (as measured by available oxygen "AvOx"). The addition of quaternary ammonium salts and/or of surfactants to peracids is known to cause destabilisation of the peracids leading to loss of efficacy in the short term.

35 **[0009]** However the inventors of the present invention have found a narrow range of quats and other additives which are stable in compositions including peracids.

40 **[0010]** According to a first aspect of the invention there is provided an aqueous composition comprising at least:

- (a) one peracid and
- (b) a quaternary ammonium salt of the formula:



wherein:

50 R^1 , R^2 , R^3 and R^4 are independently, optionally substituted, alkyl, aryl or alkoxy groups;

$$m * n = (x * p) + (y * q);$$

m and n are independently equal to 1 or 2;

55 x and y are integers or non integers and are independently from 0 to 2;

x+y is at least 1;

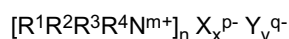
at least one of X^{p-} and Y^{q-} is R^5 -COO⁻; and

R⁵ contains from 0 to 5 carbon atoms, in particular from 1 to 4 carbon atoms, particularly from 2 to 3 carbon atoms, for instance 2 carbon atoms, which then corresponds to a propionate group with the COO⁻.

[0011] In this first aspect of the invention, R¹ may further be of the formula [R⁶-O]_p wherein p is from 1 to 10, in particular from 2 to 5. In this first aspect of the invention, R⁶ may for instance have from 1 to 5 carbon atoms, particularly from 2 to 4 carbon atoms, for instance 2 or 3 carbon atoms, advantageously 2 carbon atoms.

[0012] According to a second aspect of the invention, there is provided an aqueous composition comprising at least:

- (a) one peracid and
- (b) a quaternary ammonium salt of the formula:



wherein:

R¹, R², R³ and R⁴ are independently, optionally substituted, alkyl, aryl or alkoxy groups;

$$m * n = (x * p) + (y * q);$$

m and n are independently equal to 1 or 2;

x and y are integers or non integers and are independently from 0 to 2;

x+y is at least 1;

R¹ is of the formula [R⁶-O]_p wherein p is from 1 to 10, in particular from 1 to 5; and

R⁶ has from 1 to 5 carbon atoms, particularly from 2 to 4 carbon atoms, for instance 2 or 3 carbon atoms, advantageously 2 carbon atoms.

[0013] The following may apply to both the first and the second aspects of the present invention as defined above, independently from one another, but also combined to one another, advantageously combined to one another.

[0014] Typically, at least one of, and more frequently only two of R¹, R², R³ and R⁴, comprises 5 to 15 carbon atoms, for instance 9 to 11 carbon atoms. Conveniently, these chains may be saturated.

[0015] Also typically, at least one of the other of the R¹, R², R³ and R⁴ groups, particularly only one of these groups, comprises 1 to 3 carbon atoms, in particular 1 carbon atom (i.e. a methyl group). Conveniently, this chain may be saturated.

[0016] Often, n is 1.

[0017] X^{p-} and Y^{q-} are the anions which act as counterpart of the ammonium cation. X^{p-} and Y^{q-} can be selected from any kind of typical anions, including chloride, bromide, and carboxylates, advantageously carboxylates.

[0018] In many cases, y is 0.

[0019] In a certain embodiment of the present invention, the first and second aspects described above may be combined together. An example of quaternary ammonium salt corresponding to this certain embodiment is didecyl-methyl-poly(oxyethyl) ammonium carboxylate, preferably N,N-didecyl-N-methyl-poly(oxyethyl) ammonium propionate.

[0020] The quaternary ammonium may be present in the composition according to the first or second aspect of the present invention or according to the certain embodiment of the present invention, in an amount from 1 to 5 wt%.

[0021] According to a third aspect of the present invention, there is provided a composition comprising at least:

- (a) one peracid; and
 - (b) an alcohol ethoxylate;
- wherein the alcohol ethoxylate comprises carbon chains in the range of from C₉ to C₁₁ which have been condensed with from 2.5 to 10 moles of ethylene oxide per mole of alcohol.

[0022] The alcohol ethoxylate may typically be present in the composition according to the third aspect of the present invention in an amount from 0.5 to 5 wt%.

[0023] In a further aspect of the present invention, the various aspects as defined above can be combined to one another, to provide a composition comprising at least:

- (a) one peracid,
- (b) a quaternary ammonium salt of the formula [R¹R²R³R⁴N^{m+}]_n X_x^{p-} Y_y^{q-} as defined in the first or second aspects of the invention, and

(c) an alcohol ethoxylate as defined in the third aspect of the invention.

[0024] The following applies to the various aspects and embodiments of the present invention, as defined above. The following may apply, independently from one another, but also combined to one another, advantageously combined to one another.

[0025] The at least one peracid present into the compositions according to any of the above-mentioned aspects and embodiments of the present invention may typically comprise from 3 to 10 carbon atoms, in particular from 4 to 6 carbon atoms. For instance, it can be a mixture of from C4 to C6 peracids.

[0026] The peracid may be present in the composition of the present invention in an amount from 0.1 to 7 wt%, in particular from 1 to 5 wt%, especially from 3 to 5wt%.

[0027] Said peracid may comprise at least one monopercarboxylic acid and/or at least one ester percarboxylic acid (or ester peracid, i.e. a compound comprising an ester group and a CO₃H group), such as methylester percarboxylic acid(s). Advantageously, the peracid comprises both at least one monopercarboxylic acid and at least one ester percarboxylic acid. Said monopercarboxylic acid may for instance be present into the composition of the present invention in an amount from 1 to 3 wt%. Said ester percarboxylic acid may for example be present into the composition of the present invention in an amount from 1 to 3 wt%. The composition could also comprise from 1 to 3 wt% of monopercarboxylic acid(s) and from 1 to 3 wt% of ester percarboxylic acid(s).

[0028] Other components may also be present in the composition according to any previous aspects and embodiments of the invention, and these may include at least one of hydrogen peroxide, dicarboxylic acids, dipercarboxylic acids (that is with two CO₃H groups), esters, diesters, and ester acids (that is with an ester group and a COOH group). For these additional components, typically the carbon chains lengths are in the range of from 3 to 10 carbon atoms, especially from 4 to 6 carbon atoms, for instance a mixture of from C4 to C6 chain lengths.

[0029] In particular, the composition according to any aspects or embodiments of the present invention may comprise the reaction mixture of an acid or an ester, especially an ester acid (i.e. a compound comprising an ester group and a COOH group) or a diester, and hydrogen peroxide.

[0030] In especially preferred aspects and embodiments, the composition of the present invention comprises the composition sold by Solvay SA under the brand name Perestane™.

[0031] The present invention also provides a use of a composition as described herein as a biocide, usually after dilution in water.

[0032] Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it might render a term unclear, the present description shall take precedence.

Examples

[0033] Embodiments of the present invention will now be described, by way of example only, without limiting the scope of the invention thereto.

Example 1 (samples A1, B1 and C1)

[0034] Three samples were made, all comprising Perestane™. Perestane™ is a mixture including C4 to C6 dicarboxylic acids, monocarboxylic percarboxylic acids, di-percarboxylic acids, monoester percarboxylic acids (or ester peracids), ester acids, diesters and hydrogen peroxide. Perestane™ is available from Solvay SA.

[0035] The samples were:

(A1) 3.5g water + 96.6 g Perestane™.

(B1) 3.5g benzalkonium chloride + 96.5 g Perestane™ as a comparative experiment.

(C1) 3.5g Bardap™ 26 + 96.5 g Perestane™ in accordance with the present invention. Bardap™ is a brand of Lonza Group Ltd, Switzerland and Bardap™ 26 corresponds to the chemical N,N-didecyl-N-methyl-poly(oxyethyl) ammonium propionate.

[0036] To determine the stability of the samples, their peracid content as well as the percentage of available oxygen (AvOx) were determined over a period of time up to 91 days. The total available oxygen (AvOx) in the compositions was calculated from the free H₂O₂ content and peracid content. The H₂O₂ content was measured by a standard ceric sulphate titration method. The peracid content was determined by iodometric titration. Between the measurements, samples A1, B1 and C1 were stored in the same conditions, at about 20°C in glass brown bottles with screw caps (non vented). The results are presented below in tables 1 and 2.

Table 1: Results expressed as %w/w peracid

Days after mixing	Sample A1 Perestane™ & water	Sample B1 Perestane™ & benzalkonium chloride	Sample C1 Perestane™ & Bardap-26™
3	4	2.2	4
9	4.1	1.6	4
16	4.2	1.2	4
41	4		4.1
91	4.2		4.5

Table 2: Results expressed as % available oxygen (AvOx)

Days after mixing	Sample A1 Perestane™ & water	Sample B1 Perestane™ & benzalkonium chloride	Sample C1 Perestane™ & Bardap-26™
3	6.1	5.1	6.2
9	6.3	3.0	6.2
16	6.2	0.5	6.2
41	6.2		6.1
91	6.2		6.1

[0037] As noted above, sample A1 (comprising water) is stable, showing no loss of peracid or of available oxygen. However when Perestane™ is combined with a known quat, such as benzalkonium chloride (sample B1), the stability is lost: a strong decrease of the peracids concentration and an almost total loss of available oxygen are observed after 16 days.

[0038] In contrast when a quat in accordance with the present invention is used (sample C1), the mixture shows surprising stability, maintaining the peracid and available oxygen content even after 91 days. Surprisingly this stability is comparable to that of the water sample A1 rather than the known quat B1.

Example 2 (samples A2, B2 and C2)

[0039] A further series of experiments were conducted to show that the combination of Neodol™ 91-8 with Perestane™ provides a stable composition, as measured by peracid content and available oxygen (AvOx) over time.

[0040] Three samples were made:

(A2) 1.1 g water + 98.1 g Perestane™.

(B2) 1.1g Mirataine™ D40 + 98.1 g Perestane™ as a comparative experiment. Mirataine™ D40 is a brand name for lauryldimethylbetaine which is a type of surfactant used in household formulations supplied by Rhodia and has an aqueous composition comprising water and an alkyldimethylbetaine, wherein the alkyl is a mixture of about 70 weight % lauryl (C12) and 30 weight % tetradecyl (C14), the composition having a solid content of the alkyldimethylbetaine of 40 weight %.

(C2) 1.1g Neodol™ 91-8 + 98.1 g Perestane™ in accordance with the present invention. Neodol™ is a brand name for Shell Chemicals Ltd and Neodol™ 91-8 corresponds to a soluble C₉₋₁₁ linear alcohol ethoxylate, ethoxylated with an average of approximately 8 moles of ethylene oxide per mole of alcohol. An alternative supplier of such a chemical is Croda, under the brand Synperonic™ 91/8.

[0041] The peracid content and available oxygen (AvOx) of these three samples were determined using the same method as in Example 1. The results are shown in tables 3 and 4 below.

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Table 3: Results expressed as %w/w peracid

Days after mixing	Sample A2 Perestane™ & water	Sample B2 Perestane™ & Mirataine™ D40	Sample C2 Perestane™ & Neodol™ 91/8
3	4	3.6	4.1%
9	4.1	3.4	4.7
16	4.2	3.1	4.2
41	4	2.3	4.2
91	4.2	1.1	4.2

Table 4: Results expressed as % available oxygen (AvOx)

Days after mixing	Sample A2 Perestane™ & water	Sample B2 Perestane™ & Mirataine™ D40	Sample C2 Perestane™ & Neodol™ 91/8
3	6.3	6.0	6.3
9	6.3	5.5	6.4
16	6.3	5.0	6.3
41	6.3	3.5	6.3
91	6.3	1.8	6.3

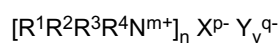
[0042] Thus, as shown above, the stability of the peracid composition is maintained in the control experiment, with water. When mixed with Mirataine™ D40 however, the stability is lost: after 91 days, the content in peracid and the available oxygen are significantly reduced. However, on using Neodol™ 91/8 in accordance with the present invention the stability of the peracid composition was maintained.

[0043] Thus the above results demonstrate a good stability of a peracid composition with different embodiments of the invention in comparison to similar compositions which are outwith the scope of the invention, which exhibit a poor stability.

Claims

1. A composition comprising at least:

- (a) one peracid and
- (b) a quaternary ammonium salt of the formula:



wherein:

R^1 , R^2 , R^3 and R^4 are independently, optionally substituted, alkyl, aryl or alkoxy groups;

$$m * n = (x * p) + (y * q);$$

m and n are independently equal to 1 or 2;

x and y are integers or non integers and are independently from 0 to 2;

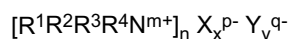
x+y is at least 1;

at least one of X^{p-} and Y^{q-} is R^5-COO^- ; and

R^5 contains from 0 to 5 carbon atoms.

2. A composition as claimed in claim 1, wherein R¹ is of the formula [R⁶-O]_p wherein p is from 1 to 10, in particular from 2 to 5; and R⁶ has from 1 to 5 carbon atoms, particularly from 2 to 4 carbon atoms, more particularly 2 carbon atoms.
3. A composition as claimed in either preceding claim, wherein at least one, preferably only two, of R¹, R², R³ and R⁴, comprises 5 to 15 carbon atoms, in particular 9 to 11 carbon atoms, these chains being conveniently saturated.
4. A composition as claimed in any preceding claim, wherein at least one, particularly only one, of R¹, R², R³ and R⁴ groups comprises 1 to 3 carbon atoms, in particular 1 carbon atom, these chains being conveniently saturated.
5. A composition as claimed in any preceding claim, wherein R⁵ comprises 1 to 4 carbon atoms, preferably 2 carbon atoms.
6. A composition as claimed in any preceding claim, wherein the quaternary ammonium salt is didecyl-methyl-poly (oxyethyl) ammonium carboxylate, preferably N,N-didecyl-N-methyl-poly(oxyethyl) ammonium propionate.
7. A composition as claimed in any preceding claim wherein the composition includes an amount of peracid from 0.1 to 7 wt%, in particular from 1 to 5 wt%, especially from 3 to 5 wt%.
8. A composition as claimed in any preceding claim wherein the peracid comprises at least one monopercarboxylic acid, preferably present into the composition in an amount from 1 to 3 wt%.
9. A composition as claimed in any preceding claim wherein the peracid comprises at least one ester percarboxylic acid, preferably present into the composition in an amount from 1 to 3 wt%.
10. A composition as claimed in any preceding claim wherein the composition comprises from 1 to 5 wt% of the quaternary ammonium salt.
11. A composition as claimed in any preceding claim, wherein the peracid comprises from 3 to 10 carbon atoms, especially from 4 to 6 carbon atoms.
12. A composition comprising at least

- (a) one peracid and
- (b) a quaternary ammonium salt of the formula:



wherein:

R¹, R², R³ and R⁴ are independently, optionally substituted, alkyl, aryl or alkoxy groups;

$$m * n = (x * p) + (y * q);$$

m and n are independently equal to 1 or 2;

x and y are integers or non integers and are independently from 0 to 2;

x+y is at least 1;

R¹ is of the formula [R⁶-O]_p wherein p is from 1 to 10, preferably from 1 to 5; and

R⁶ has from 1 to 5 carbon atoms, particularly from 2 to 4 carbon atoms.

13. A composition comprising at least:

- (a) one peracid and
 - (b) an alcohol ethoxylate;
- wherein the alcohol ethoxylate comprises carbon chains in the range of from C₉ to C₁₁ which have been condensed with from 2.5 to 10 moles of ethylene oxide per mole of alcohol.

- 14.** A composition according to claim 13, wherein the peracid comprises from 3 to 10 carbon atoms, especially from 4 to 6 carbon atoms.
- 15.** Use of a composition as claimed in any preceding claim as a biocide.

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EUROPEAN SEARCH REPORT

Application Number
EP 10 16 9207

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	WO 94/00548 A1 (LAPORTE E S D LTD [GB]) 6 January 1994 (1994-01-06) * page 1, line 22 - page 4, line 23; examples *	1-12,15	INV. C11D1/62 C11D1/835 C11D3/00 C11D3/39
X	US 2002/128164 A1 (HARA YASUSHI [JP] ET AL) 12 September 2002 (2002-09-12) * paragraphs [0018] - [0021], [0025]; claims; examples *	1-12	
A		15	
A	EP 1 192 860 A1 (AIR LIQUIDE SANTE INT [FR]) 3 April 2002 (2002-04-03) * paragraphs [0015] - [0019]; table 2 *	1-12,15	
			TECHNICAL FIELDS SEARCHED (IPC)
			C11D
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 30 November 2010	Examiner Péntek, Eric
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			

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EPO FORM 1503 03.82 (P04C01)



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CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing claims for which payment was due.

☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due and for those claims for which claims fees have been paid, namely claim(s):

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.

☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:

☒ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

1-12(completely); 15(partially)

☐ The present supplementary European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims (Rule 164 (1) EPC).

**LACK OF UNITY OF INVENTION
SHEET B**

Application Number

EP 10 16 9207

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. claims: 1-12(completely); 15(partially)

Composition comprising at least one peracid and a quaternary ammonium salt as specified in independent claim 1; use of said composition as a biocide.

2. claims: 13, 14(completely); 15(partially)

Composition comprising at least one peracid and an alcohol ethoxylate as specified in independent claim 13; use of said composition as a biocide.

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

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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
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30-11-2010

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9400548	A1	06-01-1994	NONE
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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 20030109403 A [0006]
- US 20020192340 A [0006]