



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification <sup>6</sup> : C07C 409/24, 407/00, A01N 37/16</p>	<p>A1</p>	<p>(11) International Publication Number: <b>WO 95/24388</b></p> <p>(43) International Publication Date: 14 September 1995 (14.09.95)</p>
<p>(21) International Application Number: PCT/NL94/00059</p> <p>(22) International Filing Date: 9 March 1994 (09.03.94)</p> <p>(71) Applicant (for all designated States except US): KEMIRA PEROXIDES B.V. [NL/NL]; P.O. Box 1015, NL-3180 AA Rozenburg (NL).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): MATTILA, Tapio [FI/NL]; De Poortstraat 24, NL-2597 CS The Hague (NL). AKSELA, Tapio [FI/FI]; Sookan Rantatie 8.c.27, FIN-02360 Espoo (FI).</p> <p>(74) Agent: DE BRUIJN, Leendert, C.; Nederlandsch Octrooibureau, Scheveningseweg 82, P.O. Box 29720, NL-2502 LS The Hague (NL).</p>	<p>(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, GE, HU, JP, KP, KR, KZ, LK, LU, LV, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b> <i>With international search report.</i></p>	
<p>(54) Title: A METHOD FOR THE PREPARATION OF AQUEOUS SOLUTIONS CONTAINING PERFORMIC ACID AS WELL AS THEIR USE</p> <p>(57) Abstract</p> <p>The invention relates to a method for the preparation of aqueous solutions containing performic acid formed by reaction of formic acid and hydrogen peroxide in the presence of a catalyst, wherein the catalyst is a compound containing at least one ester group and/or group (a) differing from a carboxylic acid group and an alcoholic group, preferably a carboxylic acid ester. The invention also comprises aqueous solutions containing performic acid, formic acid, hydrogen peroxide, and a compound containing at least one ester group and/or group (a) differing from a carboxylic acid group, and the use of such solutions.</p>		

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A method for the preparation of aqueous solutions containing performic acid as well as their use.

5 The present invention relates to a method for the preparation of aqueous solutions containing performic acid formed by reaction of formic acid and hydrogen peroxide in the presence of a catalyst.

Such a method is known from the book Organic Peroxides, Vol. 1, ed. by B. Swern in 1970 (Wiley Interscience). Dilute performic acid solutions suitable for disinfection are most conveniently prepared by mixing 70-90 wt.% of formic acid and 35-50 wt.% of hydrogen peroxide. Performic acid is unstable at higher concentrations and therefore it is usually prepared by mixing solutions of formic acid and hydrogen peroxide just prior to use (in situ preparation). According to Swern an acid catalyst may be used.

15 The bactericidal and sporicidal disinfectant properties of performic, peracetic and perpropionic acid has been described by Merka et al., in J.Hyg.Epidem.Microbiol.Immunol. 1965 (IX) 220. Performic acid has demonstrated superior results in the studies concerning the fungicidal (mycocidal) properties of these acids (J.Hyg.Epidem.Microbiol.Immunol. 1968, 12, 115).

20 The exceptional microbicidal properties of performic acid have later been described in EP-A-0 231 623.

A specific use of aqueous performic acid containing solutions is described in not republished Dutch patent application 9300445. This reference relates to a method for preventing and combating harmful microorganisms such as fungi, viruses, bacteria, yeasts and algae in water circulation systems, wherein the water including feed solutions and drain water, has a disinfectant added to it which at least comprises performic acid. The contents of this Dutch patent application is incorporated here by reference.

30 It is an object of the present invention to increase the equilibrium concentration of performic acid in aqueous solution of formic acid and hydrogen peroxide.

This object was achieved by the use of a compound containing at least one ester group and/or

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·C-O· group differing from a carboxylic acid group as a catalyst.

Consequently, the present invention relates to a method for the preparation of aqueous solutions containing performic acid formed by reaction of formic acid and hydrogen peroxide in the presence of a catalyst, characterized in that the catalyst is a  
5 compound containing at least one ester group and/or

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·C-O·group differing from a carboxylic acid group.

The compound may be used in catalytic amounts, which expression is well-known to men skilled in the art. However, it is  
10 preferred that a minimum amount of 10 ppm, calculated on the aqueous solution, is used. In general an amount of more than 10.000 ppm will not bring additional advantages. The particularly preferred range is 200-5000 ppm, again calculated on the total aqueous solution containing the reactants.

15 Preferably, the catalytic compound is a carboxylic acid ester which is not toxic. However, other ester compounds such as sulfate esters, sulfonate esters/lactones and phosphate esters and similar compounds may be successfully used.

According to a preferred embodiment of the method of the  
20 invention the catalytic compound is selected from the group consisting of carboxylic acid esters where the carboxylic acid is:

- a) aromatic or aliphatic C<sub>1</sub>-C<sub>20</sub> carboxylic acid;
- b) aromatic or aliphatic di- or polyfunctional carboxylic acid;

and wherein the alcohol part is

- 25 a) aliphatic or aromatic C<sub>1</sub>-C<sub>6</sub> mono- of polyfunctional alcohol,
- b) sugar alcohol,
- c) polymer containing hydroxyl groups.

Suitable are a.o. compounds like glyceryl mono-, di- and tri-  
30 esters, wherein the carboxylic acid is C<sub>1</sub>-C<sub>20</sub> carboxylic acid, polymers such as (partially hydrolysed) polyvinylacetate.

The use of the catalyst in accordance with the invention causes an enormous increase, e.g. of 100-300 % of the concentration of performic acid. Consequently, performic acid containing preparations prepared in accordance with the invention are more  
35 efficient than the prior art solutions.

The present invention also relates to an aqueous solution containing performic acid, formic acid, hydrogen peroxide as well as

a compound containing at least one ester group and/or

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·C - O· group differing from a carboxylic acid group.

The same preferences as mentioned with respect to the method of the  
5 invention can be mentioned here.

Further, the invention relates to the use of the above  
aqueous solutions of the invention for sterilization, sanitization  
and disinfection purposes. In this respect reference is e.g. made to  
the above cited EP-A-0 231 623 and NL 9300445.

10 It appeared from many tests that any compound of the ester  
type may be used with a certain degree of success. An average  
chemist will immediately understand what is meant by "ester type".

The inventors find the effect of the ester type compound on  
the amount of performic acid in the solution surprising.

15 The invention is explained in more detail in the following  
examples.

#### Example 1

20 A 35 % (w/w) solution of hydrogen peroxide (515 g, 5.38 mol)  
is added dropwise with stirring in 98 % (w/w) formic acid (100 ml,  
122 g, 2.65 mol) at room temperature. The resulting solution was  
stirred for 30 minutes at room temperature and diluted with de-  
ionized water (1911 g). The solution was divided into 50 ml portions  
and 50 mg of the following alkyl esters of carboxylic acids were  
25 added into each solution:

#### **Sample Carboxylic acid ester**

1. no additives
2. caproic acid mono- and diglyceride (Grinstedt TS-T 104)
3. 1,2,3-triacetoxypropane
- 30 4. ethyl acetate
5. methyl formate
6. sorbitan monolaurate (ICI Span 20)
7. dibutyl phthalate

35 The solutions were allowed to stand at room temperature and the  
concentrations of hydrogen peroxide and performic acid were  
determined by titration with Ceric sulfate and sodium thiosulfate,  
respectively, according to the method of Swern et al. (Swern,

Organic Peroxides, Vol. 1, page 501, Wiley Interscience, 1970). The concentrations obtained by titrations are collected in tables 1 and 2.

Table 1

5 Concentrations of performic acid obtained from the samples 1-6,  
1 hour after dilution.

Sample No.	additive 1)	performic acid (g/l)
1.	no additives	3.41
2.	monoglyceride	6.51
10 3.	1,2,3-triacetoxyp propane	6.51
4.	ethyl acetate	6.51
5.	methylformate	6.20
6.	sugar ester	6.82
15 7.	dibutyl phthalate <sup>1,2</sup>	11.16

1) concentration 2500 mg/l

2) titrated after 4 hours stirring at room temperature.

Table 2

20 Concentrations of performic acid obtained from the samples  
24 hours after dilution

Sample No.	additive	performic acid (g/l)
1.	no additives	2.63
25 2.	monoglyceride	6.36
3.	1,2,3-triacetoxyp propane	7.13
4.	ethyl acetate	7.29
5.	methylformate	6.66
30 6.	sugar ester	5.43

Example 2

A 30 wt.% solution of hydrogen peroxide (610 g, 5.38 mol) was added dropwise into 98 wt.% formic acid (100 ml, 122 g, 2.65 mol).

The solution was stirred at room temperature for 30 minutes, where-  
after it was divided into five portions. Carboxylic acid esters  
listed in Table 3, were added into the solutions and they were  
stirred at room temperature for 4 hours. Concentrations of performic  
acid and hydrogen peroxide were determined by using the method  
mentioned above.

Table 3

Concentrations of performic acid obtained from the samples  
4 hours after dilution.

Sample	additive	(mg/l)	performic acid (mg/l)
1.	no additives		27.28
2.	ethyl acetate	1300	31.00
3.	ethyl propionate	1500	28.52
4.	dibutyl phthalate	2500	31.93
6.	glycolic acid butyl ester	1500	44.64

C L A I M S.

1. A method for the preparation of aqueous solutions containing performic acid formed by reaction of formic acid and hydrogen peroxide in the presence of a catalyst, characterized in that the catalyst is a compound containing at least one ester group and/or

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·C - O· group differing from a carboxylic acid group.

2. The method according to claim 1, wherein the catalyst is present in an amount of 100-5000 ppm, calculated on the aqueous solution.

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3. The method according to claim 1 or 2, wherein the catalytic compound is a carboxylic acid ester.

4. The method according to any of claims 1-3, wherein the catalytic compound is selected from the group consisting of carboxylic acid esters where the carboxylic acid is:

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a) aromatic or aliphatic C<sub>1</sub>-C<sub>20</sub> carboxylic acid;

b) aromatic or aliphatic polyfunctional carboxylic acid;

and wherein the alcohol part is:

a) aliphatic or aromatic mono- or polyfunctional C<sub>1</sub>-C<sub>6</sub> alcohol;

b) sugar alcohol,

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c) polymer containing alcohol groups.

5. Aqueous solutions containing performic acid, formic acid, hydrogen peroxide, and a compound containing at least one ester group and/or

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·C - O· group differing from a carboxylic acid group.

6. Use of a solution according to any of the preceding claims for sterilization, sanitization and disinfection purposes.

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**INTERNATIONAL SEARCH REPORT**

Internat. Application No  
PCT/NL 94/00059

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C07C409/24 C07C407/00 A01N37/16

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 6 C07C 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,A,2 008 896 (PETROCARBON DEVELOPMENTS LIMITED) 30 January 1970 see claims ---	1-4
A	DE,A,19 62 671 (DEUTSCHE GOLD- UND SILBER-SCHNEIDANSTALT, VORM. ROESSLER) 24 June 1971 see claims ---	1
A	FR,A,2 101 175 (FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT) 31 March 1972 see page 7 - page 9; claims ---	1
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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

11 November 1994

Date of mailing of the international search report

21. 11. 94

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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.
A	DATABASE WPI Week 8609, Derwent Publications Ltd., London, GB; AN 86-060814 & SU,A,1 172 514 (TARTU UNIV) 15 August 1985 see abstract  -----	1,6

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Internati	Application No
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