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(54) Title: WASTE WATER TREATMENT WITH A MN (III) OR MN (IV) COMPLEX AS CATALYST

(57) Abstract: A method of treating aqueous industrial waste comprising the following steps : (i) storing the aqueous industrial waste in a holding vessel (ii) adding to the aqueous industrial waste a transition metal catalyst or precursor thereof and hydrogen peroxide to provide a concentration of the transition metal catalyst in a concentration from 0.1 to 100 mM and a concentration of the hydrogen peroxide from 1 to 1500 mM and (iii) releasing the effluent after treatment for further processing or directly into the environment, wherein the transition metal catalyst is a specific mononuclear or dinuclear complex of a Mn (iii) or Mn (IV) transition metal catalyst, and wherein the pH of the aqueous solution is maintained within the operating window of 2.5 pH units in the pH range 7.5 to 11.5. The preformed catalyst is subjected to an electrochemical reduction step before addition to the waste solution.



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WASTE WATER TREATMENT WITH A MN (III) OR MN (IV)
COMPLEX AS CATALYST

FIELD OF INVENTION

The present invention relates to the catalytic treatment of
5 waste water with hydrogen peroxide.

BACKGROUND OF INVENTION

Disposal and treatment of industrial aqueous waste is
significant. Problems encountered in the industry include
10 excessive coloured waste streams, waste streams with high
Biological Oxygen Demand (BOD) or Chemical Oxygen Demand
(COD), chlorinated phenolic materials, low levels of
pharmaceutical intermediates or end products or a variety of
other organic materials that may give bio-accumulation or
15 problems with aquatic environments.

EP 1078033 and Science, 296, 326 (2002) disclose the use of
an anionic iron-based transition metal catalyst for treating
waste water, particularly so in the area of waste streams
20 from the paper/pulp industry where bleaching processes with
chlorine-based oxidants are common practice.

WO98/39098 discloses that crossed-bridged macrocycles may be
used for the oxidative destruction of waste materials or
25 effluents.

The macrocyclic triazacyclic molecules have been known for
several decades, and their complexation chemistry with a
large variety of metal ions has been studied thoroughly. The
30 azacyclic molecules often lead to complexes with enhanced

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thermodynamic and kinetic stability with respect to metal ion dissociation, compared to their open-chain analogues.

United States Application 2001/0025695A1, Patt et al,
5 discloses the use of PF_6^- salts of 1,2-bis-(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)-ethane (Me₄-DTNE).

United States Application 2002/010120 discloses the bleaching of substrates in an aqueous medium, the aqueous
10 medium comprising a transition metal catalyst and hydrogen peroxide.

WO 2006/125517 discloses a method of catalytically treating a cellulose or starch substrate with a Mn(III) or Mn(IV)
15 preformed transition metal catalyst salt and hydrogen peroxide in an aqueous solution. The preformed transition metal catalyst salt is described as having a non-coordinating counter ion and having a water solubility of at least 30 g/l at 20 °C. Exemplified ligands of the catalysts
20 described in WO 2006/125517 are 1,4,7-Trimethyl-1,4,7-triazacyclononane (Me₃-TACN) and 1,2-bis-(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)-ethane (Me₄-DTNE).

EP 0733594 discloses the use of 1,4,7-Trimethyl-1,4,7-triazacyclononane (Me₃-TACN) for removing noxious compounds
25 in water or gas.

SUMMARY OF INVENTION

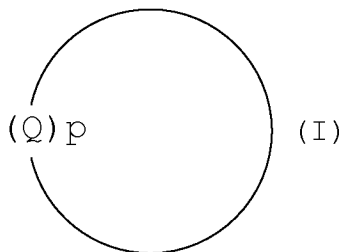
We have found that in contrast to the process described in
30 EP 0733594 subjecting the transition metal catalyst to an electrochemical reducing step facilitates use at a low

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concentration whilst reducing the loss of hydrogen peroxide during the process. Further, we have found that this aids maintenance of the pH of the process medium within limits. We have found that the use of a holding vessel permits
 5 aggressive treatment of aqueous industrial waste and insulates the environment before discharge thereto.

In one aspect the present invention provides a method of treating aqueous industrial waste comprising the following
 10 steps:

- (i) storing the aqueous industrial waste in a holding vessel, the holding vessel a batch or a continuous vessel;
- (ii) adding to the aqueous industrial waste in the holding
 15 vessel a transition metal catalyst or precursor thereof and hydrogen peroxide to provide a concentration of the transition metal catalyst in a concentration from 0.1 to 100 micromolar and a concentration of the hydrogen peroxide from 1 to 1500
 20 mM; and,
- (iii) releasing the effluent after treatment for further processing or directly into the environment wherein, the transition metal catalyst is a mononuclear or dinuclear complex of a Mn(III) or Mn(IV) transition
 25 metal catalyst wherein the ligand of the transition metal catalyst is of formula (I):



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wherein: $Q = \begin{array}{c} R \\ | \\ \text{---N---} \end{array} [CR_1R_2CR_3R_4) \text{---} ;$

p is 3;

R is independently selected from: hydrogen, C1-C6-alkyl, CH₂CH₂OH, and CH₂COOH, or one of R is linked to the N of

5 another Q via an ethylene bridge;

R₁, R₂, R₃, and R₄ are independently selected from: H, C1-C4-alkyl, and C1-C4-alkylhydroxy, wherein the pH of the aqueous solution is maintained within the operating window of 2.5 pH units in the pH range 7.5 to 11.5, preferably 8 to
10 11, wherein the preformed transition metal catalyst is subjected to a reducing step that is an electron transfer electrochemical step provided by a cathode having a reduction potential in the range 0.4 to -2V.

15 The present invention is particularly applicable to aqueous industrial waste containing phenolics, including, but not limiting to chlorinated phenolics, quinones, azo-containing molecules, lignin waste, various dyes, alkenes, alcohols and sulphur containing compounds. A preferred industrial waste
20 for treatment is that of waste from pharmaceutical preparation so that active pharmaceuticals are degraded before release into the environment. Another preferred waste for treatment is the dyeing baths from textile processing mills that furnish, if untreated, an undesired coloured
25 waste stream.

Most preferably the method is other than that of a cleaning or bleaching process. The method is other than that applied in a laundry washing machine or dishwasher. In this regard,

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the term industrial waste is other than that of laundry or dish water. That is to say, most preferably the process is other than that applied by default to an effluent stream arising from treating a solid or particulate substrate with a preformed transition metal catalyst or ligand thereof together with hydrogen peroxide.

DETAILED DESCRIPTION OF INVENTION

TRANSITION METAL CATALYST

It is preferred that a preformed transition metal catalyst is added. However, a precursor for the transition metal catalyst may be used instead. The precursor is the free ligand that may be added which complexes *in situ* with adventitious Mn ions but if the free ligand is employed it preferred that Mn ions are provided by the addition of manganese salts, e.g., manganese(II)chloride, manganese(II) sulphate or manganese [(II) or (III)] acetate. The free ligand can be provided as pure ligand, or in its protonated form as chloride, sulphate, nitrate, acetate salts, for example. The most preferred ligand that can be employed this way is 1,4,7-trimethyl-1,4,7-triazacyclononane.

The manganese transition metal catalyst used may be non-deliquescent by using counter ions such as PF_6^- or ClO_4^- , it is preferred for industrial substrates that the transition metal complex is water soluble. It is preferred that the preformed transition metal is in the form of a salt such that it has a water solubility of at least 50 g/l at 20 °C. Preferred salts are those of chloride, acetate, sulphate, and nitrate. These salts are described in WO 2006/125517.

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Preferably, R1, R2, R3, and R4 are independently selected from: H and Me. Most preferably, the catalyst is derived from a ligand selected from the group consisting 1,4,7-Trimethyl-1,4,7-triazacyclononane (Me₃-TACN) and 1,2-bis-
5 (4,7-dimethyl-1,4,7-triazacyclonon-1-yl)-ethane (Me₄-DTNE).

The preformed transition metal catalyst salt is preferably a dinuclear Mn(III) or Mn(IV) complex with at least one O²⁻ bridge.

10 The preformed transition metal catalyst is first reduced before adding it to the solution containing the substrate that needs to be degraded. Electrochemical reduction using suitable electrodes, including platinum, gold, glassy
15 carbon, may be employed to activate the catalyst. A description on the electrochemical reduction processes to activate the catalyst can be found in literature (J.W. de Boer, et al., Inorg. Chem., 46, 6353 (2007) and references cited herein).

20 STORAGE OF THE AQUEOUS INDUSTRIAL WASTE DURING TREATMENT

The aqueous industrial waste is stored during treatment as a batch or a continuous process for treating waste water. In a batch process, material is placed in the vessel at the
25 start and removed at the end of the process. In a continuous process, material flows into and out of the process during the duration of the process. In this regard the holding vessel may be a conduit or discreet vessel.

30 Often biological treatment units are in use to treat most of the waste streams. The catalytic degradation solution may be

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used in combination with such a biological treatment unit. The vessel may be located before or after a biological treating system. When located before the biological treatment system, one can destroy most of the undesired
5 molecules from the effluent in a more concentrated form, i.e. just after the process where it has been formed (e.g. dyeing bath or chemical reactor). This will lead to an increased selectivity of destruction, as there are less or no components other than the component that needs to be
10 degraded. Further, the volumes to treat the solutions are much lower, which leads to a reduced chemical (catalyst and hydrogen peroxide) demand. Another advantage of carrying out the reaction before the biological treatment unit is that there is a reduced chance of destroying hydrogen peroxide by
15 catalase enzymes, which may be found in biological treatment systems. Optionally to the with catalyst/hydrogen peroxide treated waste stream, catalase enzyme may be added to destroy hydrogen peroxide before it enters the biological treatment unit (excessive hydrogen peroxide may lead to
20 reduced biological activity). The catalytic oxidation treatment unit may be placed after the biological treatment tank. An advantage can be that most of the undesired waste products are degraded by the biological treatment unit and therefore less of the catalyst and hydrogen peroxide is
25 needed to remove the last traces of the undesired components.

The extent of degradation of the pollutant by the catalyst and hydrogen peroxide depends on many factors, including
30 time, pH of the reaction, optionally addition of sequestrant, temperature of the reaction, type of pollutant,

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level of pollutant, level of other organic materials, level of transition-metal ions, like Fe or Cu, which could give hydrogen peroxide decomposition, and presence of catalase enzyme, which gives hydrogen peroxide decomposition. For each application these optimal conditions need to be assessed.

The solvent is not necessarily limited to water; also organic solvents may be employed to degrade the pollutant, such as methanol, ethanol, acetonitrile, or acetone. This could be the case where industrial processes to produce fine or bulk chemicals. In the case where an organic solvent is used, it is desired to use the same solvent(s) for the oxidative degradation process as used in the industrial processes. After the treatment with the catalyst and hydrogen peroxide, the organic solvent is preferably removed.

It is preferred that the maximum treatment time is 4 hours.

ADDITION OF CATALYST AND HYDROGEN PEROXIDE

The preformed transition metal catalyst may be added in one batch, multiple additions, or as a continuous flow. The use of a continuous flow is particularly applicable to continuous processes.

The hydrogen peroxide may also be generated electrochemically or using oxidase enzymes, including glucose oxidase, methanol oxidase and the like.

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MAINTANANCE of pH

Stabilization of the pH provides better treatment of the aqueous industrial waste. The requirement that the pH of the aqueous solution is prevented from decreasing by more than 2.5 pH units during treatment of the aqueous industrial waste in the presence of the catalyst may be provided for in a number of ways. Below are four ways that are preferred.

First high pH without catalyst

- 1) Pretreating the aqueous industrial waste with base (preferably NaOH) to pH 10 to 12 and optionally lowering the pH to the range from 8 to 11 and then adding the manganese catalyst. If no H₂O₂ was used in the pretreatment stage then H₂O₂ must be added after or as the pH is lowered. Optionally, also low amounts of hydrogen peroxide may be employed in the pretreatment phase, and additional hydrogen peroxide may be added after or as the pH is lowered.

Single stage process, starting at the appropriate pH window

- 2) Commencing treatment of the aqueous industrial waste at pH in the range from 8.5 to 11.5 with sequestrant/H₂O₂/NaOH/ manganese catalyst and letting the pH reduce naturally as a consequence of the bleaching (typically from pH 8 to 11).

Single stage process at lower pH with maintaining the pH constant

- 3) Maintaining the pH in the range 8 to 11 during the treatment by addition, preferably continuous, of aqueous NaOH. This may be provided by the use of a pH probe together with a feed back loop which controls the addition of sodium hydroxide.

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Single stage process using a buffered solution to keep the pH constant

4) Maintaining the pH in the range 8 to 11 during the
5 treatment by using a buffered aqueous solution. Preferably
carbonate buffer, with an ionic strength between 1 mM and 1
M or more preferred between 0.01 and 0.1 M is used.
Alternatively, phosphate or borate buffer with the same
ionic strengths may be used. However, the choice of buffer
10 is not limited to these buffers.

Other ways of maintaining the pH in the range 8 to 11 during
the treatment such as by applying ion exchange resins may be
used.

15 Preferably, the pH of the aqueous solution is prevented from
decreasing by more than 2 pH units during treatment of the
aqueous industrial waste in the presence of the manganese
catalyst, more preferably 1.5 pH units, even more preferably
20 1 pH units, most preferably 0.7 pH units.

One will appreciate the closer the pH tolerances the greater
the cost of treatment.

REDUCTANT

25 The electrochemical step is provided by a cathode having a
reduction potential in the range 0.4 to -2V, preferably 0.2
to -1V, more preferably 0 to -0.4V.

It is most preferred that a reducing step is used with
30 Mn(IV) transition metal catalyst of 1,4,7-Trimethyl-1,4,7-
triazacyclononane (Me₃-TACN).

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The reducing step is particularly useful when employed for the treatment of aqueous industrial waste containing Phthalocyanine dyes.

5

There are three possible ways to treat the catalyst electrochemically:

- 1) In a separate vessel and then adding the reduced catalyst solution into aqueous industrial waste;
- 10 2) Treating the catalyst electrochemically in presence of the aqueous industrial waste with no H₂O₂ present and then after the electrochemical treatment adding H₂O₂;
- 3) Treating the catalyst electrochemically in presence of aqueous industrial waste and in the presence of H₂O₂.

15

MONITORING OF TREATMENT

The aqueous industrial waste is preferably monitored during treatment by UV or UV-visible spectroscopy. The wavelength of monitoring depends upon the nature of the waste. When
20 coloured dyes or lignin residues are being treated it is preferred that monitoring is conducted with UV-visible spectroscopy. The absorption of the aqueous industrial waste is preferably linked to a set threshold value that when met results in an automated step taking place. This step may be
25 step (iii) or the addition of further actives to the aqueous industrial waste. Also the monitoring device may include HPLC or other chromatographic methods to analyse the degradation of the undesired product. Further standard analytical methods to determine COD (chemical oxygen demand)

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or BOD (biological oxygen demand) may be used. This may include an automatic feedback loop as described above.

The invention is illustrated by the list of non-limiting
5 examples.

Example 1

Bleaching of dye Reactive Red 239 by electrochemically
reduced $[\text{Mn}_2\text{O}_3(\text{Me}_3\text{-TACN})_2](\text{PF}_6)_2$

10 The progress of the dye bleaching was followed by UV-Vis spectroscopy using a Hewlett-Packard 8453 UV-Vis diode array spectrophotometer monitoring the absorbance at around 540 nm. The dye solution was contained in a reactor consisting of a 10 mm quartz cuvette at around 50 °C.

15 A solution containing the dye Reactive Red 239 in a circa 50 mM carbonate buffer at around pH 9 was contained in a reactor consisting of a 10 mm quartz cuvette. Furthermore, the solution contained a sequestrant (around 60 µM
20 diethylenetriaminepentaacetic acid pentasodium salt) and hydrogen peroxide (around 10 mM at the start).

The catalyst stock solution was prepared by mixing the catalyst $[\text{Mn}_2\text{O}_3(\text{Me}_3\text{-TACN})_2](\text{PF}_6)_2$ (around 1 mM), acetic acid (around 10 mM) and tetrabutylammonium hexafluorophosphate
25 (around 0.1 M) in acetonitrile (the concentrations in brackets refer to the concentrations of the reagents in the catalyst stock solution). An aliquot of this catalyst stock solution (about 20 µl) was added to the solution containing the dye (about 2 ml). Only minor bleaching of the dye was
30 observed after circa 12.5 min (22%).

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A similar experiment was conducted using the same setup, but this time the catalyst stock solution was placed in a quartz holding vessel which was equipped with a platinum gauze working electrode, a platinum wire counter electrode and a silver wire pseudo-reference electrode and the electrodes were connected to a Model CHI600c electrochemical workstation (CH Instruments). The catalyst stock solution was subjected to bulk reduction (-0.4 V versus silver pseudo-reference electrode) before adding an aliquot of the thus treated catalyst stock solution (about 20 μ l) to the solution containing the dye (about 2 ml). Bleaching of the dye (50%) was observed after circa 12.5 min.

Example 2

Bleaching of dye Reactive Blue 71 by electrochemically reduced $[\text{Mn}_2\text{O}_3(\text{Me}_3\text{-TACN})_2](\text{PF}_6)_2$

The progress of the dye bleaching was followed by UV-Vis spectroscopy using a Hewlett-Packard 8453 UV-Vis diode array spectrophotometer monitoring the absorbance at around 620 nm. The dye solution was contained in a reactor consisting of a 10 mm quartz cuvette at around 50 °C.

A solution containing the dye Reactive Blue 71 in a circa 50 mM carbonate buffer at around pH 9 was contained in a reactor consisting of a 10 mm quartz cuvette. Furthermore, the solution contained hydrogen peroxide (around 10 mM at the start).

The catalyst stock solution was prepared by mixing the catalyst $[\text{Mn}_2\text{O}_3(\text{Me}_3\text{-TACN})_2](\text{PF}_6)_2$ (around 1 mM), acetic acid (around 10 mM) and tetrabutylammonium hexafluorophosphate

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(around 0.1 M) in acetonitrile (the concentrations in brackets refer to the concentrations of the reagents in the catalyst stock solution). An aliquot of this catalyst stock solution (about 20 μ l) was added to the solution containing
5 the dye (about 2 ml). Only minor bleaching of the dye was observed after circa 5 min (3%).

A similar experiment was conducted using the same setup, but this time the catalyst stock solution was placed in a quartz
10 holding vessel which was equipped with a platinum gauze working electrode, a platinum wire counter electrode and a silver wire pseudo-reference electrode and the electrodes were connected to a Model CHI600c electrochemical
workstation (CH Instruments). The catalyst stock solution
15 was subjected to bulk reduction (-0.4 V versus silver pseudo-reference electrode) before adding an aliquot of the thus treated catalyst stock solution (about 20 μ l) to the solution containing the dye (about 2 ml). After circa 5 min partly bleaching of the dye was observed (28%).

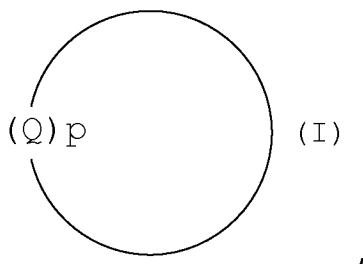
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We claim:

1. A method of treating aqueous industrial waste comprising the following steps:

- 5 (i) storing the aqueous industrial waste in a holding vessel, the holding vessel a batch or a continuous vessel;
- (ii) adding to the aqueous industrial waste in the holding vessel a transition metal catalyst or precursor thereof and hydrogen peroxide to provide a
- 10 concentration of the transition metal catalyst in a concentration from 0.1 to 100 micromolar and a concentration of the hydrogen peroxide from 1 to 1500 mM; and,
- 15 (iii) releasing the effluent after treatment for further processing or directly into the environment wherein, the transition metal catalyst is a mononuclear or dinuclear complex of a Mn(III) or Mn(IV) transition metal catalyst, wherein the ligand of the transition
- 20 metal catalyst is of formula (I):



wherein: $Q = \begin{array}{c} R \\ | \\ \text{---N---} \end{array} [CR_1R_2CR_3R_4) \text{---} ;$

p is 3;

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R is independently selected from: hydrogen, C1-C6-alkyl, CH₂CH₂OH, and CH₂COOH, or one of R is linked to the N of another Q via an ethylene bridge;

R₁, R₂, R₃, and R₄ are independently selected from: H, C1-C4-alkyl, and C1-C4-alkylhydroxy, wherein the pH of the aqueous solution is maintained within the operating window of 2.5 pH units in the pH range 7.5 to 11.5, wherein the preformed transition metal catalyst is subjected to a reducing step that is an electron transfer electrochemical step provided by a cathode having a reduction potential in the range 0.4 to -2V.

2. A method according to claim 1, wherein R₁, R₂, R₃, and R₄ are independently selected from: H and Me.

3. A method according to claim 1, wherein the catalyst is derived from a ligand selected from the group consisting 1,4,7-Trimethyl-1,4,7-triazacyclononane (Me₃-TACN) and 1,2-bis-(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)-ethane (Me₄-DTNE).

4. A method according to claim any preceding claim, wherein the preformed transition metal catalyst salt is a dinuclear Mn(III) or Mn(IV) complex with at least one O²⁻ bridge.

5. A method according to any preceding claim, wherein the method is a continuous process.

6. A method according to any preceding claim, wherein the method is a batch process.

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7. A method according to any preceding claim, wherein the time of treatment in the holding vessel is at least 5 minutes.
- 5 8. A method according to claim 7, wherein the time of treatment in the holding vessel is from 15 minutes to 24 hrs.
- 10 9. A method according to any preceding claim, wherein the aqueous medium is monitored in the holding vessel by UV, UV-visible or chromatography or by COD or BOD determination methods, and the monitoring is determinative of the time of treatment in the holding vessel before step (iii).
- 15 10. A method according to any preceding claim, wherein the aqueous industrial waste in the holding vessel contains an aminocarboxylate or aminophosphonate.
- 20 11. A method according to claim 10, wherein the aminocarboxylate sequestrant is selected from the group consisting of: ethylenediaminetetraacetic acid (EDTA), N-hydroxyethylenediaminetetraacetic acid (HEDTA), nitrilotriacetic acid (NTA),
- 25 N-hydroxyethylaminodiacetic acid, diethylenetriaminepentaacetic acid (DTPA), methylglycinediacetic acid (MGDA), and alanine-N,N-diacetic acid.

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12. A method according to claim 10, wherein the aminophosphonate is selected from Dequest 2066™ and Dequest 2047™.

5 13. A method according to any preceding claim wherein the pH of the aqueous industrial waste in the holding vessel is in the range from 8 to 11.

10 14. A method according to claim 13, wherein the pH of the aqueous solution in the holding vessel is maintained within an operating window such that the initial pH does not decrease by more than 2 pH units during the treatment of the aqueous industrial waste in the presence of the catalyst.

15 15. A method according to claim 13, wherein the pH is maintained by using an inorganic buffer consisting of carbonate, borate or phosphate buffer.

20 16. A method according to any preceding claim, wherein the temperature is in the range from 15 °C to 100 °C.

25 17. A method according to claim 16, wherein the temperature is in the range from 30 °C to 80 °C.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/051616

A. CLASSIFICATION OF SUBJECT MATTER

INV. C02F1/72

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)

C02F C11D

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2006/125517 A (UNILEVER PLC [GB]; UNILEVER NV [NL]; LEVER HINDUSTAN LTD [IN]; HAGE RO) 30 November 2006 (2006-11-30) page 6, line 10 - line 12 page 7, line 1 - page 8, line 18 claims 1-25	1-19
A	EP 0 733 594 A (TNO [NL]) 25 September 1996 (1996-09-25) column 3, line 14 - column 4, line 7 column 2, line 38 - line 54 column 1, line 49 - column 2, line 21 ----- -/--	1-19

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

☒ See patent family annex.

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Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

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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	WO 2007/042192 A (UNILEVER PLC [GB]; UNILEVER NV [NL]; DE ALMEIDA JOAQUIM MANUEL HENR [G] 19 April 2007 (2007-04-19) paragraph [0018] - paragraph [0019] paragraphs [0011], [0013], [0036]; claims 1-12 -----	1-19
A	WO 01/45842 A (UNILEVER PLC [GB]; UNILEVER NV [NL]; LEVER HINDUSTAN LTD [IN]) 28 June 2001 (2001-06-28) page 3, line 10 - line 15 page 2, line 1 - line 5 page 1, line 18 - line 23 page 3, line 29 - page 4, line 2 page 8, line 22 - line 25 -----	1-19
A	US 2002/010120 A1 (HAGE RONALD [NL] ET AL HAGE RONALD [NL] ET AL) 24 January 2002 (2002-01-24) paragraphs [0058], [0060], [0061] -----	1-19

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2009/051616

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 2006125517	A	30-11-2006	AR 056367 A1	10-10-2007
			AU 2006251406 A1	30-11-2006
			CA 2608440 A1	30-11-2006
			CN 101253292 A	27-08-2008
EP 0733594	A	25-09-1996	NL 9500551 A	01-11-1996
			US 5667690 A	16-09-1997
WO 2007042192	A	19-04-2007	AR 056692 A1	17-10-2007
			AT 428818 T	15-05-2009
			AU 2006301605 A1	19-04-2007
			CA 2624846 A1	19-04-2007
			CN 101331260 A	24-12-2008
			US 2009126121 A1	21-05-2009
WO 0145842	A	28-06-2001	AR 027022 A1	12-03-2003
			AU 3008401 A	03-07-2001
			US 2001044402 A1	22-11-2001
US 2002010120	A1	24-01-2002	AU 5615501 A	12-09-2001
			BR 0108772 A	26-11-2002
			CA 2401039 A1	07-09-2001
			CN 1426451 A	25-06-2003
			WO 0164826 A2	07-09-2001
			EP 1259588 A2	27-11-2002
			TR 200202075 T2	21-01-2003