



(51) International Patent Classification:

C02F 1/72 (2006.01) C02F 11/00 (2006.01)

(21) International Application Number:

PCT/FI2017/050791

(22) International Filing Date:

17 November 2017 (17.11.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/423,870 18 November 2016 (18.11.2016) US

(71) Applicant: **KEMIRA OYJ** [FI/FI]; Porkkalankatu 3,
FI-00180 Helsinki (FI).

(72) Inventors: **ALLEN, James Currie**; c/o Kemira Water So-
lutions Canada Inc., 626 Oak Park Road, Brantford, Ontario
N3T 5V6 (CA). **MARIGA, Tafadzwa**; 4021 Shady Forge
Trail, Arlington, Texas 76005 (US).

(74) Agent: **BERGGREN OY**; P.O.Box 99, Tykistökatu 2-4 B,
FI-20521 Turku (FI).

(81) Designated States (*unless otherwise indicated, for every
kind of national protection available*): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ,
CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO,
DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN,
HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP,
KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME,
MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ,
OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA,
SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every
kind of regional protection available*): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ,
UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,
TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,
EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,
MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— of inventorship (Rule 4.17(iv))

Published:

— with international search report (Art. 21(3))

(54) Title: METHOD FOR TREATING WASTEWATER AND WASTEWATER SLUDGE USING A PERCARBOXYLIC ACID

(57) Abstract: The present invention provides a method for treating wastewater or wastewater sludge, in which method percarboxylic acid is used as an odor controlling agent and/or corrosion controlling agent.



METHOD FOR TREATING WASTEWATER AND WASTEWATER
SLUDGE USING A PERCARBOXYLIC ACID

Field of the invention

5

The present invention relates to a method for treating wastewater and/or wastewater sludge according to the independent claim presented below. The invention relates also to use of percarboxylic acid in odor control and/or in corrosion control.

10

Background of the invention

15

Various organic and inorganic compounds can cause problems in wastewater treatment processes, one of the most remarkable of which is bad odor. Hydrogen sulfide is often identified as the predominant odor- and corrosion-causing compound of concern in wastewater treatment systems. Hydrogen sulfide H_2S , is naturally generated, when organic matters in the wastewater treatment process are degraded through anaerobic digestion by bacteria. In typical domestic wastewater, microbial reduction of the sulfate ion is the dominant mechanism for sulfide formation.

20

25

Bacteria in wastewater treatment system may respire soluble oxygen, soluble nitrate, or soluble sulfate as sources for terminal electron acceptors to generate energy depending on the type of environment they live in. Soluble oxygen is usually present in fresh wastewater, but is rapidly depleted by biological activity. There is typically very little nitrate present in wastewater, while sulfate is typically abundant. Since little or no nitrate is available, in the absence of soluble oxygen and in the presence of soluble biological oxygen demand, the bacteria begin respiring sulfate to generate energy. To obtain energy, the bacteria must transfer the electron from the electron donor to sulfate, effectively reducing the sulfate to sulfide. The dissolved sulfide combines with hydrogen ions to form hydrogen sulfide, causing odor problems. The rate of sulfide production is dependent upon the concentrations of sulfate ions, organic matter, as well as other factors such as pH, temperature, retention time and stream velocity. Sulfides exist in wastewater in three forms: H_2S gas, non-volatile bisulfate HS^- and sulfide S^{2-} .

35

Hydrogen sulfide is a dense, colorless and strongly odorous gas. It is naturally converted to sulfuric acid by certain bacteria in aerobic conditions. Sulfuric acid is corrosive towards steel and concrete used in the equipment of the wastewater or wastewater sludge collection and treatment systems.

5 Thus, dissolved sulfides in wastewater may also cause corrosion problems.

The amount of hydrogen sulfide may be controlled by preventing sulfide formation or removing sulfide after it has formed by precipitation and/or oxidation. Liquid phase control is a method of odor and corrosion prevention,
10 by which chemicals are introduced into the wastewater to react with dissolved sulfides effectively oxidizing them, thereby preventing the release of H_2S into the vapor phase. Liquid phase treatment of wastewater to remove soluble/dissolved sulfides usually involves adding significant quantities of chemicals, several classes of chemicals are used. One of the commonly
15 used methods is chemical oxidation of sulfides to sulfate or sulfur by chlorine, chlorine-based chemicals or hydrogen peroxide (H_2O_2). However, the reaction between hydrogen peroxide and sulfide is relative slow and thus adequate mixing and contact time must be provided in the wastewater treatment. Further to this, hydrogen peroxide is very reactive, and it is very
20 difficult to maintain a residual through the system to maintain an effective odor control system. Also, other chemicals used in liquid phase treatment of wastewaters may have side-effects on the downstream treatment plant and receiving waters. For example, chlorine used to oxidize sulfide may have a residual disinfectant effect on activated sludge processes, and iron salts may
25 increase in sludge production.

Although a number of sulfide control strategies are available, no preferable technology is identified. There is still need for an efficient and preferably environmentally friendly method for controlling odors in wastewater treatment
30 processes.

Summary of the Invention

It is an object of the present invention to reduce or even eliminate the
35 disadvantages existing in prior art.

It is an object of the present invention to provide a novel method for treating wastewater and/or wastewater sludge for preventing bad odors. Especially, it is an object of the present invention to provide a method for controlling dissolved sulfide levels in wastewater. It is also an object of the invention to provide an effective and more economical and environmentally friendly alternative to the applications using chemical oxidants.

In order to achieve among others, the objects presented above, the invention is characterized by what is presented in the enclosed independent claims.

Some preferred embodiments of the invention will be described in the other claims.

The embodiments and advantages mentioned in this text relate, where applicable, both to the method as well as to the uses according to the invention, even though it is not always specifically mentioned.

Typical method according to the present invention for treating wastewater or wastewater sludge uses a treating chemical comprising percarboxylic acid as an odor controlling agent and/or a corrosion controlling agent. Typically, the method according to the invention for treating of wastewater or wastewater sludge comprises

- obtaining a wastewater or wastewater sludge stream, and
- adding a treating chemical comprising percarboxylic acid to the wastewater or wastewater sludge stream.

In typical method according to the invention a level of dissolved sulfides is controlled by adding a treating chemical comprising percarboxylic acid to the wastewater or wastewater sludge stream, wherein an amount of the dissolved sulfides is reduced in wastewater or wastewater sludge stream. This may be observed by reduced odor and corrosion problems. In the present application dissolved sulfides means also soluble sulfides which are capable of dissolve into wastewater or wastewater sludge. The present invention is concerned to affect a level of dissolved sulfides and/or soluble sulfides.

Typically, the percarboxylic acid is selected from the group consisting of performic acid (PFA), peracetic acid and a combination of thereof. Thus, the invention relates also to the use of the percarboxylic acid, preferably performic acid, peracetic acid or a combination thereof, in odor control of the wastewater and/or wastewater sludge. In addition, the invention relates the use of the percarboxylic acid, preferably performic acid, peracetic acid or a combination thereof, as a corrosion control in wastewater or wastewater sludge collection and treatment processes. In one preferred embodiment, performic acid (PFA) is used as a treating chemical comprising for odor and/or corrosion controlling.

It has been surprisingly found that a treating chemical comprising percarboxylic acid may effectively oxidize dissolved sulfides to sulfate in wastewater and/or wastewater sludge, and preventing the formation of H_2S under favorable conditions that is mal-odorous and corrosion causing, whereas the sulfate remains in wastewater or wastewater sludge. Thus, the odor and corrosion can be remarkably decreased. A treating chemical according to the invention comprising percarboxylic acid, such as performic acid, reduces a concentration of gaseous sulfides in air above the wastewater by significantly reducing the dissolved sulfide in the wastewater that can volatilize into the air, and thus eliminating bad odors.

The method according to the invention is based on liquid phase control method for odor and corrosion prevention, by which a treating chemical is introduced into the wastewater and/or wastewater sludge to react with dissolved sulfides, thereby preventing the release of H_2S into the vapor phase. The present invention is based on liquid-phase H_2S control method by using a treating chemical comprising percarboxylic acid. The percarboxylic acid may be performic acid, peracetic acid or a combination of thereof.

According to a preferred embodiment of the invention, a treating chemical comprising performic acid is used as an odor controlling agent and/or corrosion controlling agent. Performic acid (CH_2O_3) is a reaction product of formic acid and hydrogen peroxide. It is fully biodegradable since it degrades to water and carbon dioxide. Thus, a treating chemical comprising performic acid is environmentally friendly. Ultimately, its use as odor controlling agent and/or corrosion controlling agent is advantageous, as it does not harm the

environment. Performic acid also has strong oxidizing properties, and thus, small dosing amount of PFA as active concentration may achieve significant reduction of dissolved sulfides.

- 5 It has been also observed that the addition of percarboxylic acid, such as performic acid, effectively prevents, or at least decreases, corrosion of process surfaces in wastewater or sludge treatment and collection systems.

10 In a preferred embodiment of the invention, performic acid is used as the treating chemical. The performic acid generated to be added to wastewater and/or wastewater sludge may have an active concentration at least 8 %, preferably at least 9 % or preferably at least 10 %, calculated as weight to volume. In an embodiment of the invention, the performic acid generated to be added to wastewater and/or wastewater sludge may have an active
15 concentration in the range of 8 – 14 % or 10 - 14 %, calculated as weight to volume. According to one typical embodiment of the invention, the performic acid generated to treat the wastewater and/or wastewater sludge may have an active concentration around 13.5 %, calculated as weight to volume. In some embodiments, an active concentration of performic acid may be about
20 9 % or 9.5 %, calculated as weight to volume. Above mentioned active concentrations are preferred used concentrations but the invention is not limited to these, but also lower concentrations may be used. Preferably the performic acid is used as an equilibrium solution comprising performic acid and hydrogen peroxide.

25

A treating chemical may be added to wastewater stream and/or wastewater sludge in at least one process location. It is also possible to add a treating chemical to wastewater stream and/or wastewater sludge in several different locations. This may include but is not limited to any location along the
30 wastewater collection system where odors or corrosion are believed to occur. Preferably, a treating chemical is added one, two or more process locations that are close to locations where soluble/dissolved sulfides are supposed to exist or be generated. The treating chemical may be added to the headworks of the wastewater treatment plant to eliminate odors and corrosion caused by
35 the change in flow dynamics, temperature, pH causing a release of H₂S gas. Depending on conditions, the addition point may be at the influent or effluent of the primary or secondary treatment sections to reduce H₂S levels for odor,

corrosion or safety concerns. The treating chemical may also be added to any of the wastewater treatment plant solids applications or piping leading to or from any wastewater treatment solids applications such as anaerobic digesters, solids collection tanks and holding tanks. Dewatering equipment including, but not limited to filter presses, centrifuges and belts presses along with areas where solids may be collected, stored, conveyed, or moved from any one location to another. In an embodiment of the invention, the treating chemical may be added into a mixing sleeve in the wastewater sludge line. The treating chemical, such as percarboxylic acid would also apply to any solids that were being created or used for land application, reuse, fertilization, sterilization, composting or any other process whereby wastewater solids may be converted from one form to another.

In one preferred embodiment of the invention, a treating chemical comprising percarboxylic acid, preferably performic acid may be added to at least the influent of the wastewater treatment plant, since there might be observed significant amounts of dissolved sulfides.

According to an embodiment of the invention, performic acid to be used as a treating chemical may be prepared in the immediate vicinity of the process location where it is added to the wastewater or wastewater sludge. This guarantees the high chemical efficiency of the performic acid. Performic acid or other treating chemical according to the invention may be led to the process location through suitable connections and fed to a desired flow of wastewater or wastewater sludge by using suitable feeding means. The addition of the treating chemical may be continuous, i.e. the treating chemical is continuously added to the wastewater or wastewater sludge at least one process location during wastewater and sludge treatment. Alternatively, the treating chemical may be added to the wastewater or sludge under specified time period at predetermined time intervals.

According to an embodiment of the invention, the performic acid to be used as a treating chemical may be applied into the wastewater stream or wastewater sludge prior to addition of iron salts for dewatering.

The addition of the treating chemical may be fully automated. It is possible that there is at least one sensor which detects a concentration of dissolved

sulfides in the wastewater or wastewater sludge stream, and the addition of the treating chemical may be automatically adjusted according to the information obtained from the at least one sensor. According to one embodiment a concentration of dissolved sulfides in the wastewater or wastewater sludge stream is detected, either continuously or at predetermined intervals, and the addition of the treating chemical is automatically adjusted according to the information obtained about the concentration. This kind of system improves the control of the added amount and guarantees the proper effective concentration of performic acid in the wastewater stream or wastewater sludge.

According to an embodiment of the invention a concentration of dissolved sulfides in the wastewater or wastewater sludge stream may be measured prior to the addition of the treating chemical and the addition of the treating chemical may be automatically adjusted according to the information obtained about the concentration. According to another embodiment of the invention, a concentration of dissolved sulfides in the wastewater or wastewater sludge stream may be measured at a point to which the wastewater stream is flowed after the addition of the treating chemical. Thus, the concentration may be measured prior to the addition point and/or after the addition point of the treating chemical. The control system for measuring a concentration of dissolved sulfides may comprise at least one sensor or it may comprise several sensors in different locations for providing information of the changes in dissolved sulfide concentrations. According to an embodiment of the invention, the method may further comprise modifying a rate of the addition of the treating chemical to the wastewater stream or wastewater sludge based on the measurement of the concentration of dissolved sulfides.

According to an embodiment of the invention, the treating chemical is added into the wastewater stream or wastewater sludge so as to bring the level of soluble sulfides, in particular H_2S , to a level of less than 5 ppm, in particular less than 2 ppm or even less than 1 ppm in the wastewater stream or wastewater sludge at the point where odor, corrosion or environmental issues are a concern. At 2 ppm or less, soluble sulfides are below the nuisance level. Therefore, in an embodiment of the present invention a

treating chemical is added into the wastewater or wastewater sludge in an amount that reduces the sulfides below the nuisance level, i.e. below 2 ppm.

5 The amount of the treating chemical desired to dose into wastewater stream or wastewater sludge depends on the concentration of dissolved sulfides, but it may also depend on the volume of wastewater flow or a desired level of sulfides in the wastewater. The measurement of the concentration of dissolved sulfides and the dosing of the treating chemical on the basis on the measurements may be important since the amount of soluble sulfides may
10 vary by time of day or time of year. In an embodiment of the present invention, the performic acid used as a treating chemical may be added in amount of 1 – 12 ppm, preferably 5 – 10 ppm calculated as an active concentration of PFA, since PFA has strong oxidizing properties and thus already small dosing amount of PFA as active concentration may achieve
15 significant reduction of dissolved sulfides. A suitable amount may also be dependent on the active concentration of PFA. Due to strong oxidizing properties of PFA, it may also react rapidly with sulfides present in wastewater or wastewater sludge. Thus, it may not require long residence time in the wastewater or wastewater sludge and it may be added close to
20 locations where dissolved sulfides are supposed to exist or be generated.

The method according to the invention may be used to treat any kind of wastewater streams and/or wastewater sludge. A treating chemical according to the invention is suitable for use in treating wastewater or wastewater
25 sludge regardless of solid content and thus a method according to the invention is applicable for different kind of wastewater treatment processes. According to an embodiment of the invention the wastewater or wastewater sludge is treated in municipal wastewater collection or treatment application, municipal sludge collection or treatment application or industrial wastewater
30 treatment applications. The wastewater stream refers in the present disclosure broadly to wastewater or wastewater sludge processed in wastewater treatment process regardless of the processing step or process flow of the wastewater treatment. These systems may range from vary simple processes to advanced treatment facilities designed to go from
35 wastewater to drinking water quality. These can be used for public and private utilities as well as treatment facilities own by private industry.

EXPERIMENTAL

Example: Odor control laboratory testing utilizing

- 5 A sample from influent wastewater is grabbed at an influent channel of a municipal wastewater treatment plant. The samples are grabbed in a 1000 ml polypropylene bottle and filled completely to the top to prevent any volatilization of sulfide out of the sample.
- 10 A treating chemical formulation comprising performic acid (PFA) as an active odor controlling agent and all other reagents are prepared just prior to be used.
- PFA 13.5 % formulation is made of mixing stabilized formic acid with 50
- 15 weight-% hydrogen peroxide.

Separation of Soluble Sulfide from Insoluble Sulfide

20 The Standard Methods 4500-S²⁻ for waters and wastewaters: Section B procedure is used to determine soluble sulfides with a DR2800 spectrophotometer for the Methylene Blue analysis. The procedure comprises the following steps:

- 25 1. In a 15 ml glass tube, place approximately 10 drops of 6N Sodium Hydroxide (NaOH).
2. Obtain 15 ml of sample from the middle of the water column in the sample bottle and place the pipetter in the glass tube and gently dispense the sample into the NaOH solution.
- 30 3. Add approximately 7 drops of Aluminum Chloride (AlCl₃) into the glass tube ensuring that the tube is full to the top at this point.
4. Mix the tube 4 times by inverting and let stand until the flocculant settles out yielding a fairly clear supernatant at the top of the glass tube.
- 35 5. Analyze immediately using DR2800 spectrophotometer for the Methylene Blue analysis.

PFA tests to determine soluble sulfides

Multiple samples were taken as describe above. For the test, 3 sample bottles are taken and labelled accordingly to: Control, 5 ppm PFA, and 10 ppm PFA. These test concentrations are within a recommended range of 1 – 10 ppm PFA active concentration. Samples are taken from the test bottles to establish a time 0 sulfide concentration within the bottles. No PFA was added to the test bottle labelled as control. To the 5 ppm PFA test bottle, 37 ppm of 13.5% PFA is added to the bottle. To the 10 ppm PFA test bottle, 74 ppm of 13.5% PFA is added to the bottle. All the bottles are gently mixed over 5 min. After 5 min, a 15 ml sample from each test bottle is collected as described standard method from mid-water column and placed gently in glass tubes respectively labeled as described above to separate the soluble sulfides from insoluble sulfides. After 10 min, another 15 ml sample is collected from the test bottles as collected from mid-water column and placed gently in glass tubes respectively labeled as described above.

Results

Test results are presented in Table 1. Time 0 samples taken just prior to the addition of PFA chemical. The time 0 Samples were taken to set the baseline of soluble sulfide in the samples collected.

Table 1: An amount of soluble sulfides (ppm) in different treatment times of the samples and different dosage amounts of PFA.

PFA (as active conc.)	Treatment Time (min.)		
	0*	5	10
Control (0 ppm PFA)	6.44	7.66	8.88**
5 ppm PFA	6.44	2.66	2.03
10 ppm PFA	6.44	2.12	1.72

The increase in sulphide in the control could be a result of non-soluble sulfides being converted to soluble sulfides due to mixing and sampling.

As shown in the results, the addition of PFA reduces the soluble sulfides and so dissolved sulfides in wastewater treatment plant influent significantly with dosages from 5 ppm to 10 ppm. At 2 ppm or less, sulfide is below the nuisance level. Therefore, as PFA reduces the sulfide below the nuisance

level, PFA may be used to control odor in wastewater and wastewater sludge. The 5 minutes and 10 minutes residence times are evaluated for this study as the PFA chemistry is very effective at short times, and the time required to neutralize sulfide would occur very quickly. The results of this study demonstrate that greater than 90 % reduction of the soluble sulfide concentration occurred within 5 minutes as compared to the untreated control which demonstrated no loss of soluble sulfide over the 5 minutes residence time or the 10 minutes residence time. This study also demonstrates that PFA is capable of removing soluble sulfide from wastewaters with suspended solids proved to reduce soluble sulfides further in contrast to the control with increased sulfide generation.

Claims

1. Method for treating wastewater and/or wastewater sludge, wherein using a treating chemical comprising percarboxylic acid as an odor controlling agent
5 and/or corrosion controlling agent.
2. The method according to claim 1, wherein the percarboxylic acid is selected from the group consisting of performic acid, peracetic acid and a combination of thereof, preferably performic acid.
10
3. The method according to claim 1 or 2, wherein performic acid is used as the treating chemical.
4. The method according to claim 4, wherein an active concentration of
15 performic acid is at least 8 %, preferably at least 9 % or at least 10 %, even more preferably in the range of 8 – 14 % calculated as weight to volume.
5. The method according to any of the preceding claims, wherein the method comprises
20 - obtaining a wastewater or wastewater sludge stream, and
- adding a treating chemical comprising percarboxylic acid to the wastewater or wastewater sludge stream.
6. The method according to claim 5, wherein the wastewater or wastewater
25 sludge stream is a stream in municipal wastewater collection or treatment application, municipal sludge collection or treatment application or industrial wastewater application.
7. The method according to claim 5 or 6, wherein a concentration of
30 dissolved sulfides in the wastewater or wastewater sludge stream is measured prior to the addition of the treating chemical and the addition of the treating chemical is adjusted according to the information obtained about the concentration.
8. The method according to any of the preceding claims 5 to 7, wherein a
35 concentration of dissolved sulfides in the wastewater or wastewater sludge

stream is measured at a point to which the wastewater or wastewater sludge stream is flowed after the addition of the treating chemical.

5 9. The method according to any of the preceding claims 5 to 8, wherein modifying a rate of the addition of the treating chemical to the wastewater or wastewater sludge stream based on the measurement of the concentration of dissolved sulfides.

10 10. The method according to any of the preceding claims 5 to 9, wherein adding the treating chemical continuously to the wastewater or wastewater sludge stream at least one process location.

15 11. The method according to any of the preceding claims 5 to 10, wherein the treating chemical is added into the wastewater or wastewater sludge stream so as to bring the level of dissolved sulfides, in particular H_2S , to a level of less than 5 ppm, in particular less than 2 ppm, or even less than 1 ppm in the wastewater stream.

20 12. Use of a treating chemical comprising percarboxylic acid, preferably performic acid, peracetic acid or a combination thereof, in odor control of the wastewater or wastewater sludge.

25 13. Use of a treating chemical comprising percarboxylic acid, preferably performic acid, peracetic acid or a combination thereof, in corrosion control of wastewater or wastewater sludge collection and treatment processes.

14. Use according to claim 12 or 13, wherein treating chemical is performic acid.

30 15. Use according to claim 13, wherein an active concentration of performic acid is at least 8 %, preferably at least 9 % or at least 10 %, even more preferably in the range of 8 – 14 % calculated as weight to volume.

INTERNATIONAL SEARCH REPORT

International application No

PCT/FI2017/050791

A. CLASSIFICATION OF SUBJECT MATTER

INV. C02F1/72
ADD. C02F11/00

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

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 practicable, 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.
X	US 4 595 577 A (STAS GEORGES [BE] ET AL) 17 June 1986 (1986-06-17) column 1, lines 8-23 column 1, lines 55-62 column 2, lines 30-59 column 4, lines 29-51	1-15
X	JP 3 712018 B2 (MITSUBISHI GAS CHEMICAL CO) 2 November 2005 (2005-11-02) paragraphs [0007], [0009], [0016], [0019] paragraph [0037]; table 1	1-15
X	WO 2014/182561 A1 (ECOLAB USA INC [US]) 13 November 2014 (2014-11-13) page 1, lines 5-12 page 3, line 10 - page 4, line 18 page 14, line 2 - page 15, line 13	1-15
	-/--	



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

17 January 2018

Date of mailing of the international search report

29/01/2018

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

OneI Inda, Santiago

INTERNATIONAL SEARCH REPORT

International application No

PCT/FI2017/050791

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2016/100700 A1 (ECOLAB USA INC [US]) 23 June 2016 (2016-06-23) page 1, lines 10-22 page 48, lines 9-11 page 49, lines 18-25 -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/FI2017/050791

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4595577	A	17-06-1986	BR 8201802 A 01-03-1983
			CA 1202765 A 08-04-1986
			DE 3260816 D1 31-10-1984
			EP 0063829 A1 03-11-1982
			FR 2503130 A1 08-10-1982
			US 4443342 A 17-04-1984
			US 4595577 A 17-06-1986
JP 3712018	B2	02-11-2005	JP 3712018 B2 02-11-2005
			JP H0994583 A 08-04-1997
WO 2014182561	A1	13-11-2014	US 2014332463 A1 13-11-2014
			WO 2014182561 A1 13-11-2014
WO 2016100700	A1	23-06-2016	AU 2015364492 A1 13-07-2017
			CA 2971416 A1 23-06-2016
			EP 3232781 A1 25-10-2017
			US 2016176814 A1 23-06-2016
			WO 2016100700 A1 23-06-2016