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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
08 November 2018 (08.11.2018)

WIPO | PCT

(10) International Publication Number
WO 2018/203158 A1

(51) International Patent Classification:
C01B 11/02 (2006.01)

(21) International Application Number:
PCT/IB2018/052482

(22) International Filing Date:
10 April 2018 (10.04.2018)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
106114742 04 May 2017 (04.05.2017) TW

(71) Applicant: **UNIQUE BIOTECH CO., LTD.** [CN/CN]; 22F.-1, No. 56, Minsheng 1st Rd., Xinxing Dist., Kaohsiung, 80045 (TW).

(72) Inventors: **HUANG, Bin-Syuan**; 3F.-1, No. 346, Dafong 2nd Rd., Sanmin Dist., Kaohsiung, 80774 (TW). **YIN, Hao-Chang**; No. 3-3, Ln. 208, Jhuangjing Rd., Banciao Dist., New Taipei, 22042 (TW). **MA, Jui-Wen**; No. 6, Aly. 43, Ln. 100, Fujhih Rd., Shalu Dist., Taichung, 43354 (TW). **WANG, Shan-Shue**; No. 10, Ln. 292, Sec. 2, Linan Rd., North Dist., Tainan, 70450 (TW). **CHENG, Ming-Long**; No. 143, Chengjhang 4th St., Jhongli Dist., Taoyuan, 70450 (TW). **HSU, Chu-Wei**; No. 21-2, Aly. 1, Ln. 301, Dachang 1st Rd., Sanmin Dist., Kaohsiung, 80794 (TW). **PENG, Chun-Wei**; 9F.-1, No. 145, Jianguo 4th Rd., Yancheng Dist., Kaohsiung, 80346 (TW).

(74) Agent: **XU AND PARTNERS, LLC.**; Room 106, Building No. 1, Universal High-Tech Plaza, 958 Zhen Bei Road, Putuo District, Shanghai 200333 (CN).

(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,

(54) Title: CHLORINE DIOXIDE AQUEOUS SOLUTION PRODUCTION SYSTEM

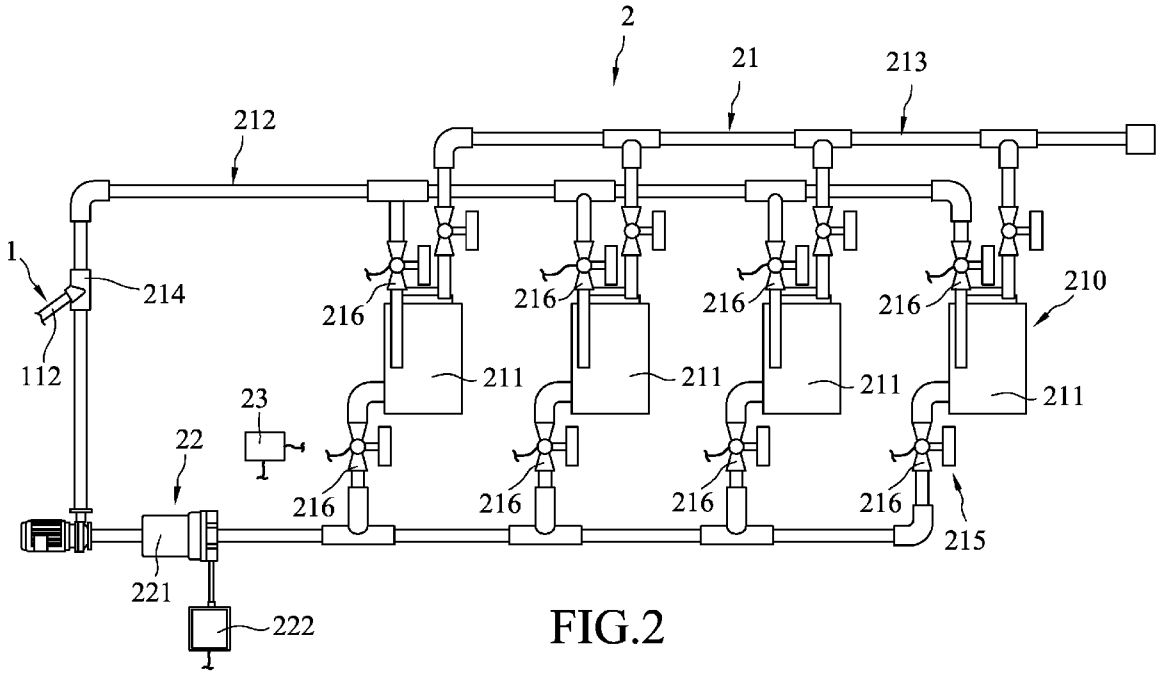

FIG.2

(57) Abstract: A chlorine dioxide aqueous solution production system includes an electrolysis unit, and a mixing and measuring device including a mixing unit, a measuring unit, and a control unit. Water flowing from a container set of the mixing unit into a chlorine dioxide aqueous solution mixer of the mixing unit and gaseous chlorine dioxide advanced from the electrolysis unit are mixed to form chlorine dioxide aqueous solution circulating through the transporting pipe and the container set. The control unit compares the measured redox potential valve from the measuring unit with a predetermined value to control operation of a control valve set of the mixing unit for permitting and blocking the circulation of water and the chlorine dioxide aqueous solution.

WO 2018/203158 A1

[Continued on next page]

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).

Published:

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

CHLORINE DIOXIDE AQUEOUS SOLUTION PRODUCTION SYSTEM

FIELD

The disclosure relates to a chemical production system, and more particularly to a chlorine dioxide aqueous solution production system.

BACKGROUND

Chlorine dioxide aqueous solution is used for bleaching of wood pulp and the disinfection of municipal drinking water. Chlorine dioxide, when dissolved in water, is able to kill off bacteria and virus at a concentration of 2 to 10 ppm. As chlorine dioxide is less corrosive than chlorine, it is commonly used in many industrial water treatment applications as a biocide.

Under economical circumstances, such as avoiding product recall, the concentration of the chlorine dioxide aqueous solution from a production plant is usually higher than average, in order to ensure that it meets minimum quality standard. However, human inspection with spectrophotometry is required to conduct quality control effectively, which is not efficient for automated mass production process.

SUMMARY

Therefore, an object of the disclosure is to provide a chlorine dioxide aqueous solution production system that can alleviate the drawback of the prior art.

According to the disclosure, the chlorine dioxide aqueous solution production system includes a chlorine dioxide generating device, and a mixing and measuring device. The chlorine dioxide generating device includes an electrolysis unit that is adapted for generating gaseous chlorine dioxide by electrolysis. The mixing and measuring device includes a mixing unit, a measuring unit, and a control unit.

The mixing unit has a chlorine dioxide aqueous solution mixer that is connected to the electrolysis unit, a transporting pipe that is connected to the chlorine dioxide aqueous solution mixer, a container set and a control valve set. The container set is connected to the transporting pipe such that water flowing from the container set into the chlorine dioxide aqueous solution mixer and the gaseous chlorine dioxide advanced from the electrolysis unit are mixed together to form chlorine dioxide aqueous solution which circulates through the transporting pipe and the container set. The control valve set is mounted on one of the container set and the transporting pipe, and is operable for permitting and blocking the circulation of water and the chlorine dioxide aqueous solution. The measuring unit is mounted on the transporting pipe of the mixing unit for measuring redox potential of the chlorine dioxide aqueous solution passing therethrough. The control unit is electronically connected to the

control valve set of the mixing unit and the measuring unit, and compares the measured redox potential value from the measuring unit with a predetermined value for actuating and terminating operation of the control valve set.

BRIEF DESCRIPTION OF THE DRAWINGS

Other features and advantages of the disclosure will become apparent in the following detailed description of the embodiment with reference to the accompanying drawings, of which:

FIG. 1 is a partly schematic side view of a chlorine dioxide generating device of an embodiment of a chlorine dioxide aqueous solution production system according to the disclosure;

FIG. 2 is a partly schematic side view of a mixing and measuring device of the embodiment; and

FIG. 3 is a graph of relationship between redox potential and concentration of chlorine dioxide aqueous solution.

DETAILED DESCRIPTION

Referring to FIGS. 1 to 3, an embodiment of a chlorine dioxide aqueous solution production system according to the disclosure has a chlorine dioxide generating device 1 and a mixing and measuring device 2. The chlorine dioxide aqueous solution production system is adapted for producing chlorine dioxide aqueous solution from an electrolytic solution and water.

The chlorine dioxide generating device 1 includes an electrolysis unit 11. The chlorine dioxide generating device 1 also includes a feeding unit 12, a cleaning unit 13, and a thermostat unit 14, each of which is connected to the electrolysis unit 11.

The electrolysis unit 11 includes an electrolytic cell 111 adapted for performing electrolysis of the electrolytic solution, a gas transporting pipe 112 that interconnects the electrolytic cell 111 with the mixing and measuring device 2, and a waste exhaust pipe 113 that is connected to the electrolytic cell 111. After gaseous chlorine dioxide is generated from the electrolytic solution in the electrolytic cell 111, it is collected by the gas transporting pipe 112 for further uses in the mixing and measuring device 2. Byproducts of the electrolysis, primarily liquid substances, are removed from the electrolytic cell 111 through the waste exhaust pipe 113. The electrolytic cell 111 mentioned in this disclosure is a known technology and will not be discussed in further detail.

The feeding unit 12 is operable for feeding electrolytic solution to the electrolysis unit 11. The feeding unit 12 includes a raw material tank 121 that dissolves raw salt with solvent to form the electrolytic solution, and an electrolytic solution tank 122 that interconnects the raw material tank 121 and the electrolytic cell 111 through connecting pipes. The

abovementioned raw salt may be sodium chloride or sodium chlorite, the solvent may be water, and the electrolytic solution may consequently be aqueous solution of sodium chloride or sodium chlorite. After filtration of solid particles, the electrolytic solution from the raw material tank 121 is transported to and stored in the electrolytic solution tank 122. The electrolytic solution is further fed to the electrolytic cell 111 to undergo electrolysis.

The cleaning unit 13 is operable for water-flushing the electrolysis unit 11 when it is not in use. In this embodiment, the cleaning unit 13 is a pipe that transports tap water into the electrolytic cell 111 for water-flushing. After cleaning, the tap water is also removed from the electrolytic cell 111 through the waste exhaust pipe 113.

The thermostat unit 14 is operable for controlling temperature of the electrolysis unit 11 through the process of heat exchange utilizing refrigerant. The thermostat unit 14 includes a cooler 141 that cools temperature of refrigerant, and a cooling pipe 142 that allows the refrigerant to circulate between the electrolytic cell 111 and the cooling 141. The process of heat exchange utilizing refrigerant as a working fluid is a known mechanical process and will not be discussed in details.

The mixing and measuring device 2 includes a mixing

unit 21 that mixes the gaseous chlorine dioxide advanced from the electrolysis unit 11 with water to form chlorine dioxide aqueous solution, a measuring unit 22 that is mounted on the mixing unit 21, and a control unit 23 that is electronically connected to the measuring unit 22.

In this embodiment, the mixing unit 21 has a container set 210 that includes four containers 211, a transporting pipe 212 that is connected to and surrounds the container set 210 and that aligns the containers 211 in parallel, a water inlet 213 that has a plurality of branch pipes connected respectively to the containers 211, a chlorine dioxide aqueous solution mixer 214 that is mounted on the transporting pipe 212 and that is connected to gas transporting pipe 112 of the electrolysis unit 11, and a control valve set 215 that is mounted on the transporting pipe 212.

Each of the containers 211 stores the chlorine dioxide aqueous solution of varying concentration, ranging from zero, containing only the water from the water inlet 213, to an amount satisfactory to meet minimum standard. The transporting pipe 212 circulates the flowing fluid (chlorine dioxide aqueous solution or water) through the containers 211 and the chlorine dioxide aqueous solution mixer 214. The chlorine dioxide aqueous solution mixer 214 is operable to mix the gaseous chlorine dioxide advanced from the electrolysis unit

11 with the flowing fluid, increasing its chlorine dioxide concentration. The chlorine dioxide aqueous solution mixer 214 is a prior art disclosed in PCT publication number WO/2017/113111, and will not be discussed in further details in this disclosure. The control valve set 215 includes a plurality of control valves 216 that are mounted on the transporting pipe 212 and that are electronically connected to the control unit 23. In this embodiment, the control valves 216 are grouped into pairs, each pair being respectively located at opposite sides of a respective one of the containers 211, being operable for permitting and blocking the circulation of the water and the chlorine dioxide aqueous solution via the respective one of the containers 211, and being able to be manually controlled when not electronically connected.

The measuring unit 22 includes an ORP (Oxidation-Reduction Potential) meter 221 mounted on the transporting pipe 212 between the chlorine dioxide aqueous solution mixer 214 and one of the containers 211 which is closest to the chlorine dioxide aqueous solution mixer 214, and a display monitor 222 digitally connected to the ORP meter 221. The ORP meter 221 of the measuring unit 22 is operable to measure redox potential of the chlorine dioxide aqueous solution passing therethrough and to process a digital signal to be sent to the display monitor 222 and the control

unit 23. The display monitor 222 simply displays the redox potential value measured.

The control unit 23, which is a computer in this embodiment, receives and compares the measured redox potential value from the ORP meter 221 with a predetermined value for actuating and terminating operation of the control valve set 215.

To determine the predetermined value for the control unit 23, it is recommended to make a graph establishing relationship between redox potential and concentration of the chlorine dioxide aqueous solution, similar to the one shown in FIG. 3, by sampling a set amount of data to plot a best-fit curve. In this embodiment, By assigning variable y as the redox potential (mV) and variable x as the concentration of the chlorine dioxide aqueous solution (ppm), an equation of the best-fit curve with $y = 74.868\ln(x) + 670.95$ (eq.1) is established with $R^2 = 0.9764$, representing an almost perfect fit. The abovementioned formula (eq.1) may also be expressed in terms of x as well: $x = \exp[(y-670.95)/74.868]$ (eq. 2). One may simply utilize interpolation and exterpolation, or use professional data processing applications such as Origin or SigmaPlot to determine the abovementioned relationship. With the graph and the equation on hand, it is easier to build a chart (shown below) to select the predetermined value for the control unit 23.

ClO_2 Concentration (ppm)	Redox Potential (mV)

2000	1211
1500	1206
1000	1192
750	1178
500	1154
250	1113
100	1049
50	915
25	902
10	846
5	794

To begin the operation of the disclosure, one is ought to initiate the mixing unit 21 by filling the containers 211 with water from the water inlet 213 first, which in turns circulate the water throughout the transporting pipe 212 and the chlorine dioxide aqueous solution mixer 214. Then, the chlorine dioxide generating device 1 is initiated, such that the feeding unit 12 feeds electrolytic solution to the electrolytic cell 111, which in turns generates gaseous chlorine dioxide by electrolysis. The gaseous chlorine dioxide is collected by the gas transporting pipe 112 and is transported to the chlorine dioxide aqueous solution mixer 214 of the mixing unit 21, while the byproducts of the electrolysis is transported out of the system through the waste exhaust pipe 113. The gaseous chlorine dioxide is mixed together with the water in the chlorine dioxide aqueous solution mixer 214 to form chlorine dioxide aqueous solution, which circulates into the containers 211. The chlorine dioxide aqueous solution in the container 211, driven by the ongoing fluid circulation throughout the

transporting pipe 212, is then driven back into the chlorine dioxide aqueous solution mixer 214 yet again, mixing with more gaseous chlorine dioxide to increase its concentration. The process repeats.

The measuring unit 22 constantly measures the redox potential passing therethrough and sends the signal to the control unit 23 for value comparison. Once the measured value exceeds or equals to the predetermined value, the concentration of the chlorine dioxide solution has reached minimal standard, in which the control unit 23 is operable to send signals to terminate operation of the control valves 216 and to stop the circulation of fluid in the mixing and measuring device 2. The containers 211 would have the finished products ready for shipping, and may be replaced with a new set of containers 211 for the next production. The automated measurement of the measuring unit 22 and the control unit 23 alleviate the need for human sampling.

When setting up a predetermined value, one may assign the redox potential value that corresponds to the desired concentration value. It is also possible to assign the value in concentration value, by having the control unit 23 convert the redox potential value into the equivalent concentration value when it compares values. In other embodiments, the measuring unit 22 may be assigned to directly convert the redox potential value into the equivalent concentration instead when sending signals

to the display monitor 222 and the control unit 23.

In addition, the number of containers 211 is subject to change, and is not restricted to the four containers 211 mentioned in this embodiment. Likewise, the number of control valves 216 should corresponds to the number of the containers 211. Lastly, it should be mentioned that, while the electronic communication in this embodiment is connected directly by wires, it may also be wireless in other embodiments.

In the description above, for the purposes of explanation, numerous specific details have been set forth in order to provide a thorough understanding of the embodiment. It will be apparent, however, to one skilled in the art, that one or more other embodiments may be practiced without some of these specific details. It should also be appreciated that reference throughout this specification to "one embodiment," "an embodiment," an embodiment with an indication of an ordinal number and so forth means that a particular feature, structure, or characteristic may be included in the practice of the disclosure. It should be further appreciated that in the description, various features are sometimes grouped together in a single embodiment, figure, or description thereof for the purpose of streamlining the disclosure and aiding in the understanding of various inventive aspects.

While the disclosure has been described in connection

with what is considered the exemplary embodiment, it is understood that this disclosure is not limited to the disclosed embodiment but is intended to cover various arrangements included within the spirit and scope of the broadest interpretation so as to encompass all such modifications and equivalent arrangements.

What is claimed is:

1. A chlorine dioxide aqueous solution production system comprising:

a chlorine dioxide generating device (1) that includes an electrolysis unit (11) adapted for generating gaseous chlorine dioxide by electrolysis; and

a mixing and measuring device (2) that includes

a mixing unit (21) having

a chlorine dioxide aqueous solution mixer (214) that is connected to said electrolysis unit (11),

a transporting pipe (212) that is connected to said chlorine dioxide aqueous solution mixer (214),

a container set (210) that is connected to said transporting pipe (212) such that water flowing from said container set (210) into said chlorine dioxide aqueous solution mixer (214) and the gaseous chlorine dioxide advanced from said electrolysis unit (11) are mixed together to form chlorine dioxide aqueous solution which circulates through said transporting pipe (212) and said container set (210), and

a control valve set (215) that is mounted on one of said container set (210) and said transporting pipe (212), and that is operable for permitting and blocking the circulation of water and the chlorine dioxide aqueous solution,

a measuring unit (22) mounted on said transporting

pipe (212) of said mixing unit (21) for measuring redox potential of the chlorine dioxide aqueous solution passing therethrough, and

a control unit (23) that is electronically connected to said control valve set (215) of said mixing unit (21) and said measuring unit (22), and that compares the measured redox potential value from said measuring unit (22) with a predetermined value for actuating and terminating operation of said control valve set (215).

2. The chlorine dioxide aqueous solution production system as claimed in claim 1, wherein said container set (210) includes a plurality of containers (211), said control valve set (215) including a plurality of control valves (216) that are operable for permitting and blocking the circulation of the water and the chlorine dioxide aqueous solution via said containers (211).

3. The chlorine dioxide aqueous solution production system as claimed in claim 1, wherein said chlorine dioxide generating device (1) further includes a thermostat unit (14) that is connected to said electrolysis unit (11) and that is operable for controlling temperature of said electrolysis unit (11).

4. The chlorine dioxide aqueous solution production system as claimed in claim 1, wherein said chlorine

dioxide generating device (1) further includes a feeding unit (12) that is connected to said electrolysis unit (11) and that is operable for feeding electrolytic solution to said electrolysis unit (11).

5. The chlorine dioxide aqueous solution production system as claimed in claim 1, wherein said chlorine dioxide generating device (1) further includes a cleaning unit (13) that is connecting to said electrolysis unit (11) and that is operable for water-flushing said electrolysis unit (11).

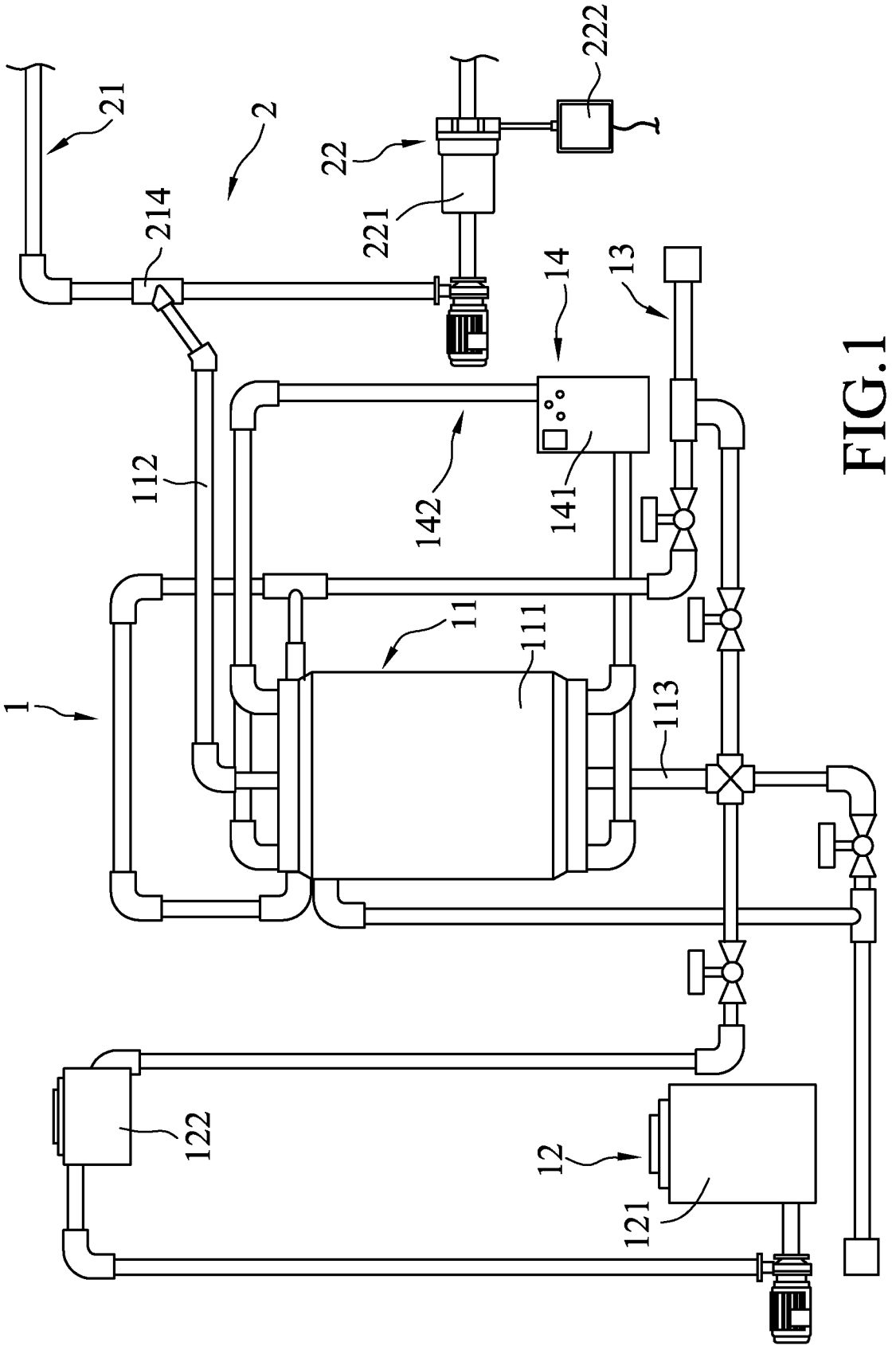

FIG.1

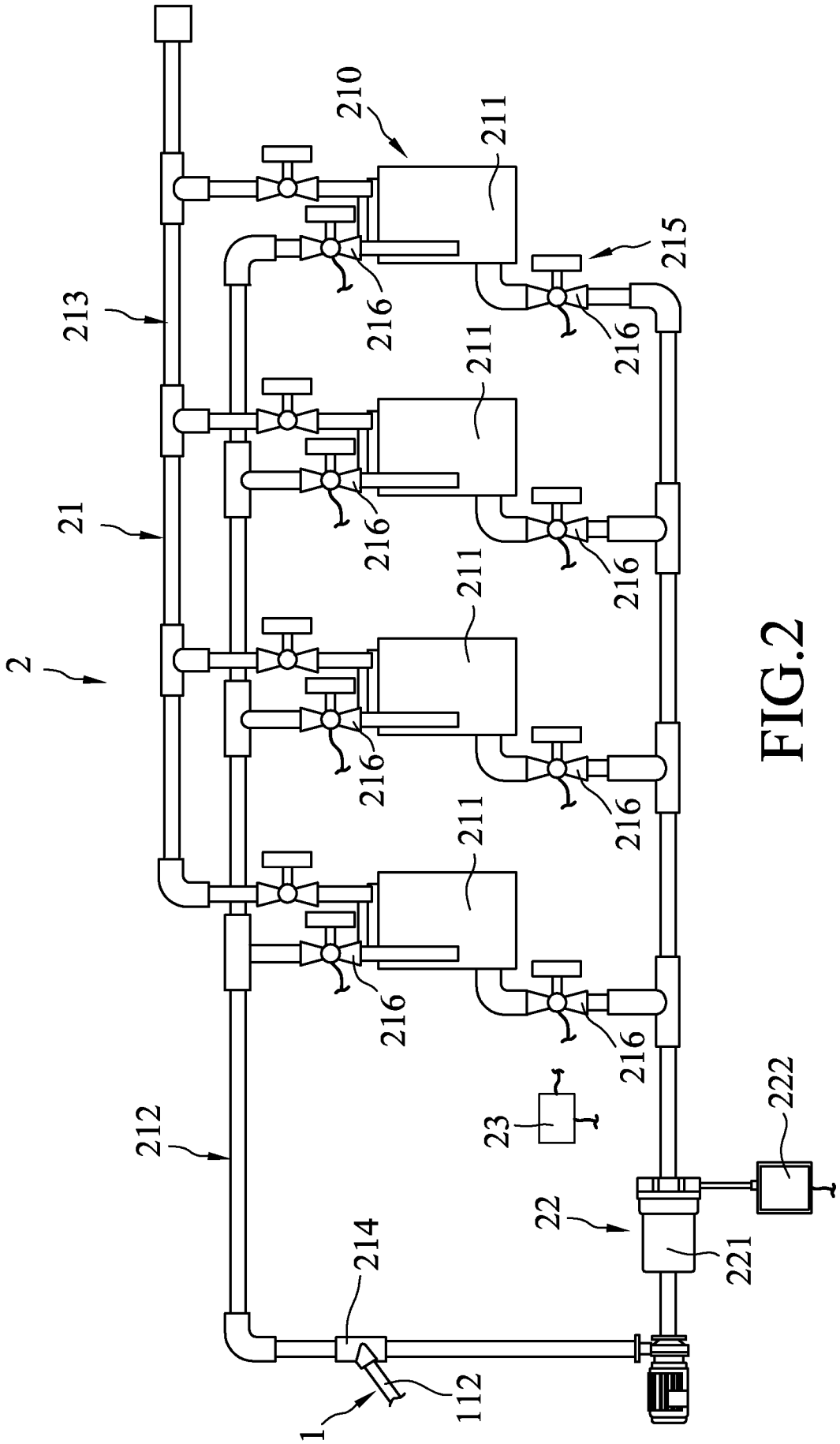

FIG.2

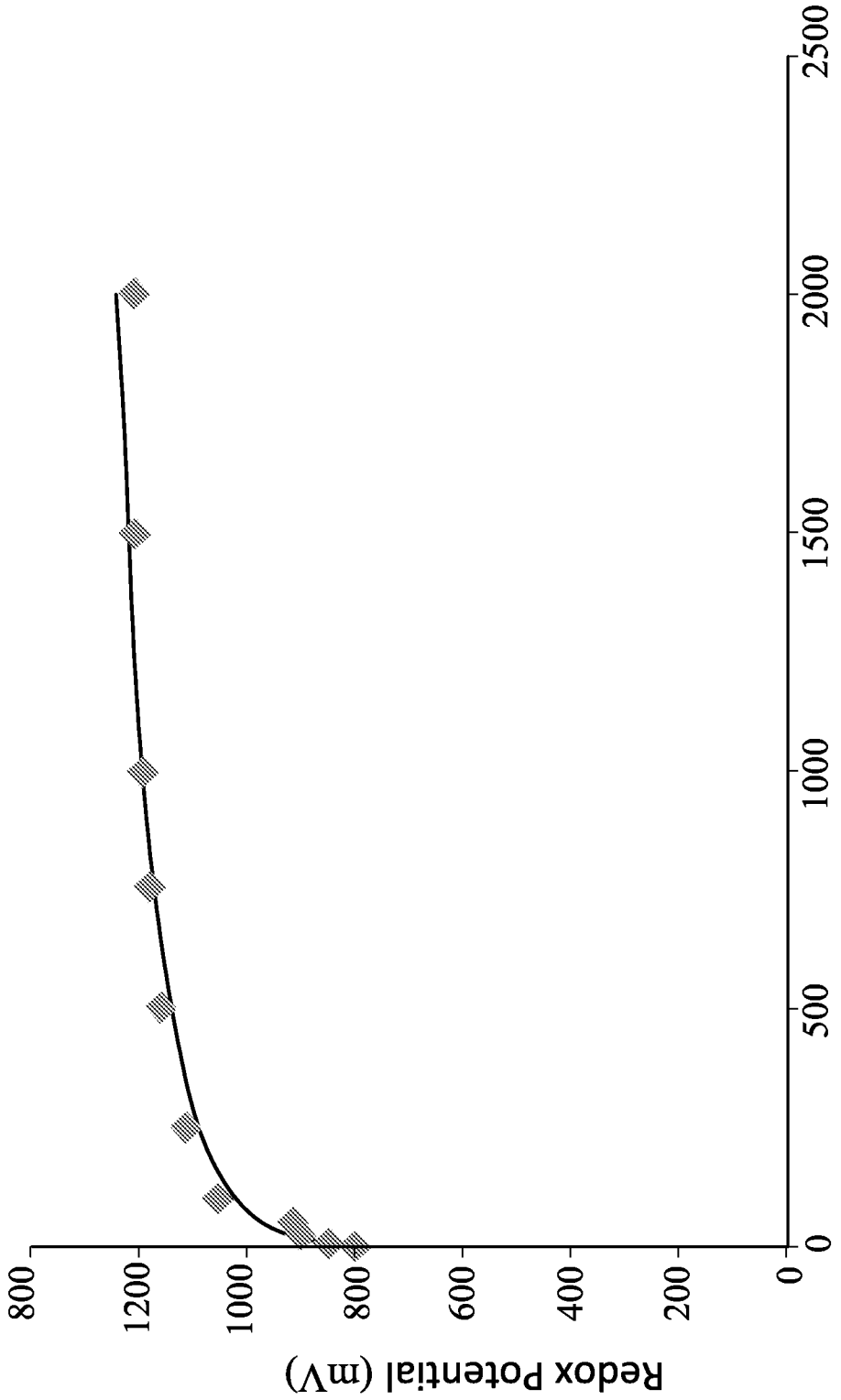
Redox Potential (mV)
800
1200
1000
800
600
400
200
0
0
500
1000
1500
2000
2500
Concentration of ClO2 (ppm)

FIG.3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2018/052482

A. CLASSIFICATION OF SUBJECT MATTER

C01B 11/02(2006.01)i

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)

C01B

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)

WPI, EPODOC, CNPAT, CNKI: chlorine dioxide, clo2, gas+, liquid, solution, concentration, water, sterile, measure+, control

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2006015071 A1 (PURELINE TREAT SYSTEMS LLC ET AL.) 09 February 2006 (2006-02-09) see claims 1, 11-13; description, paragraphs 0047-0048, 0035; Figs. 1-2	1-5
Y	JP 2015217334 A (CENTRAL FILTER MFG CO LD ET AL.) 07 December 2015 (2015-12-07) see description, paragraphs 0026, 0049; Fig. 1	1-5
A	JP 2016182590 A (CENTRAL FILTER MFG CO LD) 20 October 2016 (2016-10-20) see the whole document	1-5
A	WO 2006062456 A1 (AKZO NOBEL NV ET AL.) 15 June 2006 (2006-06-15) see the whole document	1-5
A	CN 204958389 U (QINGDAO JUCHUAN ENV PROT TECH CO LTD) 13 January 2016 (2016-01-13) see the whole document	1-5

☐ 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	Date of mailing of the international search report
18 July 2018	**13 August 2018**

Name and mailing address of the ISA/CN	Authorized officer
STATE INTELLECTUAL PROPERTY OFFICE OF THE P.R.CHINA **6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing 100088** **China**	**CHEN,Ning**
Facsimile No. **(86-10)62019451**	Telephone No. **86-(10)-53962316**

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/IB2018/052482

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
WO	2006015071	A1	09 February 2006	US	2006113196	A1	01 June 2006
				US	2006022360	A1	02 February 2006
				AU	2005269289	B2	18 November 2010
				DE	112005001836	T5	14 June 2007
				GB	2432831	A	06 June 2007
				US	7914659	B2	29 March 2011
				CA	2574618	A1	09 February 2006
				GB	2432831	B	23 September 2009
				AU	2005269289	A1	09 February 2006
				GB	0701629	D0	14 March 2007
				EP	1809572	A1	25 July 2007
				BR	PI0513931	A	20 May 2008
				US	7799198	B2	21 September 2010
JP	2015217334	A	07 December 2015	JP	6317623	B2	25 April 2018
JP	2016182590	A	20 October 2016		None		
WO	2006062456	A1	15 June 2006	AU	2005312379	A1	15 June 2006
				EP	1819635	B1	03 March 2010
				MX	2007003242	A	23 May 2007
				ES	2341980	T3	30 June 2010
				CA	2589721	A1	15 June 2006
				AU	2005312379	B2	19 February 2009
				AT	459574	T	15 March 2010
				EP	1819635	A1	22 August 2007
				BR	PI0518029	A	04 November 2008
				JP	2008522941	A	03 July 2008
				JP	4637916	B2	23 February 2011
				BR	PI0518029	B1	22 November 2016
				CA	2589721	C	04 May 2010
CN	204958389	U	13 January 2016		None		