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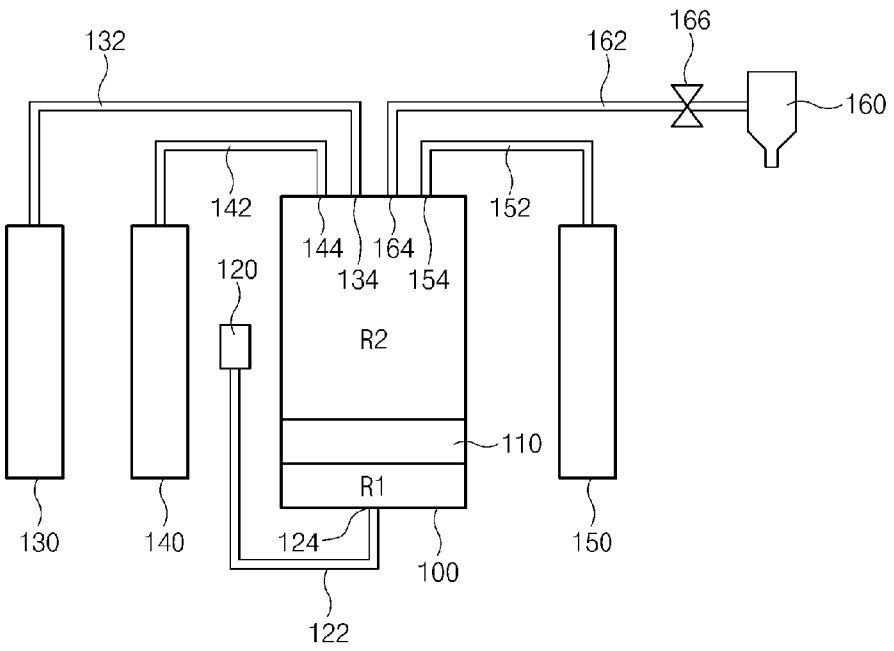
(54) **Title:** APPARATUS FOR THE PRODUCTION OF CHLORINE DIOXIDE

[Fig. 1]



(57) **Abstract:** Provided is an apparatus for production of chlorine dioxide. In the apparatus, raw-material chemicals necessary for producing chlorine dioxide are quantitatively supplied to a reaction bath using solenoid valves so that necessary amounts of raw-material chemicals can be exactly supplied to the reaction bath from outside storage vessels through pipes by decompressing the reaction bath without having to use a flow meter or a metering pump.

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Description

APPARATUS FOR THE PRODUCTION OF CHLORINE DIOXIDE

Technical Field

[1] The present invention disclosed herein relates to an apparatus for producing chlorine dioxide.

Background Art

[2] Chlorine dioxide was discovered in 1811 by Sir Humphrey Dary. Chlorine dioxide has a melting point of -59℃, a boiling point of 11℃ and is in a greenish yellow gas state at room temperature. Chlorine dioxide gives off a slight smell of chlorine and dissolves easily in water, ether and so on.

[3] In a storage, chlorine dioxide decomposes gradually into chlorous acid, chloric acid, chlorine ions, etc., and chlorine dioxide is germicide owing to its strong oxidizing power (oxidation state: +4).

[4] Chlorine dioxide is useful because it does not oxidize organic substances. Particularly, carcinogenic chlorinated organic substances such as trihalomethane (THM), haloacetic acids (HAAs), and haloacetonitrile are not generated from chlorine dioxide. Furthermore, chlorine dioxide is germicide over a wide range of pH. In addition, chlorine dioxide does not produce carcinogenic byproducts and decomposes easily by light, and owing to these ecological characteristics, the use of chlorine dioxide as a replacement of chlorine disinfectants is rapidly increased.

[5] Owing to the above-described characteristics, chlorine dioxide was first used in 1944 at water treatment equipment of Niagara Falls (New York, USA), and currently, chlorine dioxide is widely used as a disinfectant all over the world including about nine hundreds of sites in USA and several thousands of sites in Europe.

[6] In Korea, chlorine dioxide has also been used as a disinfectant at a concentration of 1 ppm or less. In addition, chlorine dioxide can be used for sterilizing foods such as vegetables and fruits.

[7] However, chlorine dioxide is time-variable and difficult to produce, store, and analyze. Moreover, although daily production of several hundreds of tons of chlorine dioxide is possible through a process of reducing a chlorate (a raw material) in a liquid-state acid such as sulfurous acid, hydrochloric acid, or hydrogen peroxide as expressed by Chemical Formula 1 through 3 below, this mass production of chlorine dioxide requires large equipment. Therefore, such mass production is not normally used except for a bleaching process.

[8] [Chemical Formula 1]

[9] $2NaClO_3 + H_2S0_3 \rightarrow 2Cl0_2 + Na_2S0_4 + H_20$

[10] [Chemical Formula 2]

[11] $2NaClO_3 + 4HCl \rightarrow 2ClO_2 + 2NaCl + Cl_2 + 2H_2O$

[12] [Chemical Formula 3]

[13] $2NaCl0_3 + H_20_2 + 2HCl \rightarrow 2Cl0_2 + 2NaCl + O_2 + 2H_20$

[14] Besides, since chlorine dioxide is unstable at room temperature, chlorine dioxide should be prepared just prior to use at a workplace, and the transportation and distribution of chlorine dioxide are not easy.

[15] Therefore, a simple method for preparing pure chlorine dioxide water not containing chlorite (ClO_2^-), chlorate (ClO_3^-), and salts thereof is necessary to make it practical to use chlorine dioxide water as, for example, a food sterilant.

Disclosure of Invention

Technical Problem

[16] The present invention provides an apparatus for quantitatively producing pure chlorine dioxide gas not containing a chlorous acid, a chloric acid, and salts thereof.

[17] The present invention also provides an apparatus for rapidly producing high-concentration chlorine dioxide gas without the possibility of explosion of the high-concentration chlorine dioxide gas.

Technical Solution

[18] Exemplary embodiments of the present invention provide apparatuses for producing chlorine dioxide, the apparatuses including: a reaction bath in which a chlorine dioxide producing reaction occurs; and a porous glass filter dividing the reaction bath into a first region and a second region.

[19] At least one gas supply unit is connected to the first region of the reaction bath in order to supply chlorine gas and inert (non-active) gas to the reaction bath.

[20] At least one raw material supply unit is connected to the second region of the reaction bath in order to supply hypochlorite, chlorite, or acid to the reaction bath.

[21] A pressure adjustment unit is connected to at least one of the first and second regions of the reaction bath in order to keep the second region at a pressure level lower than that of the first region.

[22] The reaction bath has a discharge hole which is connected to the reaction bath to discharge chlorine dioxide gas generated in the second region of the reaction bath.

[23] In one exemplary embodiment of the present invention, the porous glass filter may have a pore size in range of from about 10 μm to about 100 μm.

[24] In other exemplary embodiment of the present invention, the pressure adjustment unit may be a compression pump connected to the first region for compressing the first region, or a decompressor or a vacuum pump connected to the second region for de-

compressing the second region.

[25] In still other exemplary embodiments, if the pressure adjustment unit is a de-compressor, the decompressor may be an aspirator operated by using decompression water or gas, and the chlorine dioxide gas generated in the second region may be absorbed in the compression water passing through the aspirator or is mixed with the compression gas passing through the aspirator.

[26] In even other exemplary embodiments, the inert gas may be at least one of nitrogen gas, carbon dioxide gas, and air.

[27] In further exemplary embodiments, the raw material supply unit may be connected to the second region of the reaction bath through a solenoid valve. The solenoid valve may be controlled by a control unit. The control unit may adjust the amount of the hypochlorite, the chlorite, or the acid supplied to the reaction bath by controlling the solenoid valve.

[28] In still further exemplary embodiments, the apparatus may further include a pressure detection unit disposed at the reaction bath for detecting a pressure inside the reaction bath. A signal of the pressure detection unit may be transmitted to the control unit.

[29] In even further exemplary embodiments, the discharge hole may be connected to an adsorption tower. The adsorption tower may contain an organic solvent and an adsorption material, which are used to dissolve and adsorb the inert gas and the generated chlorine dioxide gas. The organic solvent may be one of n-hexane, methylene chloride, ethyl ether, tert-butyl methyl ether, and petroleum ether. The adsorption material may be zeolite or silica gel.

[30] In yet further exemplary embodiments, a chlorine dioxide gas removing tower may be connected to the adsorption tower in order to remove the chlorine dioxide gas remained after the chlorine dioxide gas passes through the adsorption tower. The chlorine dioxide gas removing tower may contain hydrogen peroxide or sodium thiosulfate to remove the remaining chlorine dioxide gas.

Advantageous Effects

[31] According to the present invention, in the chlorine dioxide producing apparatus, reactants are uniformly agitated owing to gas bubbles generated from gas passing through the porous glass filter, so that chlorine dioxide can be produced with high yield.

[32] Since the inside of the reaction bath is decompressed and gas bubbles are generated in the reaction bath from a lower part of the reaction bath, chlorine dioxide can be easily vaporized without the possibility of explosion. Pure chlorine dioxide gas obtained in this way can be easily dissolved in decompression water, and thus a pure chlorine dioxide solution can be obtained.

[33] Furthermore, according to the present invention, small or large amounts of raw materials can be quantitatively supplied for a desired time by using a solenoid valve, and thus reactants and the resulting products can be easily controlled with low costs.

Brief Description of Drawings

[34] FIG. 1 is a schematic sectional view illustrating an apparatus for producing chlorine dioxide according to a first embodiment of the present invention.

[35] FIG. 2 is a schematic sectional view illustrating an apparatus for producing chlorine dioxide according to a second embodiment of the present invention.

[36] FIG. 3 is a schematic sectional view illustrating an apparatus for producing chlorine dioxide according to a third embodiment of the present invention.

Best Mode for Carrying out the Invention

[37] Preferred embodiments of the present invention will be described below in more detail with reference to the accompanying drawings. The present invention may, however, be embodied in different forms and should not be construed as limited to the embodiments set forth herein. Rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the present invention to those skilled in the art.

[38] FIG. 1 is a schematic sectional view illustrating an apparatus for producing chlorine dioxide according to a first embodiment of the present invention.

[39] Referring to FIG. 1, the chlorine dioxide producing apparatus of the current embodiment includes a reaction bath 100 to produce chlorine dioxide through a pre-determined reaction.

[40] In the reaction bath 100, the reaction bath 100 is is provided with a porous glass filter 110 to divide the inside of the reaction bath 100 into two regions. Specifically, the porous glass filter 110 divides the inside of the reaction bath 100 into a first region R1 and a second region R2.

[41] The porous glass filter 110 may divide the inside of the reaction bath 100 into upper and lower regions, left and right regions, or the like. For example, in the current embodiment, the porous glass filter 110 divides the inside of the reaction bath 100 into upper and lower regions (the second region R2 and the first region R1). In this case, gas is generated by a liquid-state reaction and moved upward, resulting in the gas being easily exhausted through an exhaust port.

[42] The first region R1 is connected to at least one gas supply unit 120 to supply chlorine gas, which is used for chlorine dioxide producing reaction, and inert gas which is used for adjusting a concentration of the chlorine gas by diluting the chlorine gas. The gas supply unit 120 may be connected to the first region R1 of the reaction bath 100 through a gas supply line 122, and a gas injection hole 124 is formed at an end of the

gas supply line 122 connected to the first region R1.

[43] In the current embodiment, inert gas and chlorine gas may be supplied through the same gas injection hole 124. In another embodiment, however, inert gas and chlorine gas may be stored in separate gas supply units and supplied through separate gas injection holes simultaneously or non-simultaneously. For example, an additional gas injection hole may be provided to supply inert gas for controlling the concentration of chlorine gas and for having the chlorine gas moved from the first region R1 to the second region R2 through the porous glass filter 110. In the current embodiment shown in FIG. 1, a single gas injection hole 124 is illustrated.

[44] Gas that does not affect a chlorine dioxide producing reaction is supplied to the reaction bath 100. For example, inert gas such as helium, neon, and argon, and stable gas such as carbon dioxide and air may be supplied.

[45] At least one raw material supply unit is connected to the second region R2 of the reaction bath 100 to supply a chlorite or a hypochlorite, and an acid such as sulfuric acid, hydrochloric acid, or nitric acid, which are used for performing a chlorine dioxide producing reaction. In the current embodiment, a first raw material supply unit 130, a second raw material supply unit 140, and a third raw material supply unit 150 are connected to the second region R2 of the reaction bath 100 for the convenience of explanation.

[46] The first to third raw material supply units 130, 140, and 150 are connected to the second region R2 of the reaction bath 100 through first to third raw material supply lines 132, 142, and 152, respectively. First to third raw material injection holes 134, 144, and 154 are formed at ends of the first to third raw material supply lines 132, 142, and 152 connected to the second region R2 of the reaction bath 100.

[47] The first to third raw material supply units 130, 140, and 150 may include raw material supply tanks (not shown). Raw materials are supplied from the first to third raw material supply units 130, 140, and 150 to the second region R2 of the reaction bath 100 through the first to third raw material supply lines 132, 142, and 152 and the first to third raw material injection holes 134, 144, and 154, respectively.

[48] As shown in FIG. 1, in the current embodiment, a plurality of raw material supply units are provided for supplying raw materials individually. However, the present invention is not limited thereto. For example, in another embodiment of the present invention, two or more materials may be supplied through the same raw material injection hole. That is, the numbers of raw material supply lines and raw material injection holes can be varied according to the raw material supply configuration. In addition, although a plurality of raw material injection holes are separately formed in the current embodiment, a Y-shaped raw material supply line may be used to supply two raw materials through the same raw material injection hole.

[49] A pressure adjust unit is provided for at least one of the first and second regions R1 and R2 of the reaction bath 100. The pressure adjustment unit makes a pressure different between the first and second regions R1 and R2 to generate a flow between the first and second regions R1 and R2 through the porous glass filter 110.

[50] In the current embodiment, a decompressor 160 is connected to the second region R2 of the reaction bath 100 as a pressure adjustment unit for adjusting the pressure inside the reaction bath 100. The decompressor 160 is connected to the second region R2 through a discharge line 162. The decompressor 160 may be an aspirator or a vacuum pump. In the current embodiment, an aspirator is used as the decompressor 160.

[51] A cutoff valve 166 may be disposed between the reaction bath 100 and the decompressor 160. The decompressor 160 sucks gas from the inside of the reaction bath 100 to lower the inside pressure of the reaction bath 100, particularly, the second region R2. Various decompressors such as a gas decompressor and an air pump may be used as the decompressor 160. For example, an aspirator operated by using decompression liquid or gas may be used as the decompressor 160.

[52] A discharge hole 164 of the reaction bath 100 is connected to the decompressor 160.

[53] An exemplary mechanism for producing chlorine dioxide using the above-described chlorine dioxide producing apparatus will now be explained.

[54] First, explanations will be given on three methods of preparing chlorine dioxide according to raw materials. In a first method, a chlorite and an acid such as sulfuric acid or hydrochloric acid are used; in a second method, a chlorite, a hypochlorite, and an acid such as sulfuric acid or hydrochloric acid are used; and in a third method, a chloride and chlorine are used.

[55] The three methods can be expressed by Chemical Formulas below. In detail, the first method using a chlorite and an acid such as hydrochloric acid or sulfuric acid can be expressed by Chemical Formulae 4 and 5; the second method using a chlorite, an inorganic acid (hydrochloric acid or sulfuric acid), and a hypochlorite can be expressed by Chemical Formulae 6 and 7; and the third method using a chlorite and chlorine can be expressed by Chemical Formula 8.

[56] [Chemical Formula 4]

[57] $5NaClO_2 + 4HCl \rightarrow 4ClO_2 + 5NaCl + 2H_2O$

[58] [Chemical Formula 5]

[59] $5NaClO_2 + 2H_2SO_4 \rightarrow 4ClO_2 + 2Na_2SO_4 + NaCl + 2H_2O$

[60] [Chemical Formula 6]

[61] $2NaClO_2 + NaClO + 2HCl \rightarrow 2ClO_2 + 3NaCl + H_2O$

[62] [Chemical Formula 7]

[63] $2NaClO_2 + NaClO + H_2SO_4 \rightarrow 2ClO_2 + Na_2SO_4 + NaCl + H_2O$

[64] [Chemical Formula 8]

[65] $2NaClO_2 + Cl_2 \rightarrow 2ClO_2 + 2NaCl$

[66] The above-described raw materials are supplied to the inside of the reaction bath 100 through the gas injection hole 124 provided at the first region R1 and the first to third raw material injection holes 134, 144, and 154 provided at the second region R2.

[67] For example, in the first method, an acid such as sulfuric acid or hydrochloric acid, and a chlorite are supplied to the second region R2. In the second method, a chlorite, a hypochlorite, and an acid (sulfuric acid or hydrochloric acid) are supplied to the second region R2. In the third method, chlorine gas is supplied to the first region R1, and a chlorite is supplied to the second region R2.

[68] Before, after, or at the time when such raw materials are supplied to the reaction bath 100, the decompressor 160 sucks gas from the inside of the reaction bath 100 to reduce the inside pressure of the reaction bath 100.

[69] When decompression water is allowed to pass through the aspirator (decompressor 160), the pressure of the second region R2 becomes lower than the pressure of the first region R1. Then, inert gas (nitrogen gas, carbon dioxide gas, or air) is sucked into the reaction bath 100 through the gas injection hole 122.

[70] The sucked inert gas passes through the porous glass filter 110 disposed across a lower side of the reaction bath 100 due to the pressure difference between the first and second regions R1 and R2, so that fine bubbles are generated in the second region R2. Owing to the fine bubbles, reactants supplied into the second region R2 through the raw material injection holes 134, 144, and 154 can be uniformly agitated, and thus high-concentration chlorine dioxide can be obtained with high process yield.

[71] The chlorine dioxide can be easily vaporized owing to the fine bubbles and the lower pressure inside the reaction bath 100.

[72] The chlorine dioxide gas is sucked toward the decompressor 160 and dissolves in decompression water. Therefore, a pure chlorine dioxide solution can be obtained.

[73] As explained above, according to the present invention, although the same raw materials as those used in a conventional chlorine dioxide producing method are used, the raw materials can be reacted more rapidly at higher concentrations as compared with the case of a conventional method. Thus, high-concentration chlorine dioxide gas can be obtained without increasing the process time as compared with a conventional method.

[74] High-concentration chlorine dioxide can be obtained with high process yield and kept without explosion because reactants (raw materials) are continuously and quantitatively supplied to the second region of the reaction bath, and fine bubbles are continuously generated in the second region by using inert gas supplied to the lower first region of the reaction bath. For this, the reaction bath is kept at a decompressed state by using the decompressor connected to the upper second region of the reaction bath.

[75] Reactants can be agitated rapidly and uniformly owing to fine bubbles, and generated high-concentration chlorine dioxide can be extracted from a solution containing the reactants and reaction byproducts by vaporizing the chlorine dioxide using the fine bubbles.

[76] In other words, owing to fine inert gas bubbles, reactants can be ideally agitated, and generated chlorine dioxide can be easily extracted from the solution containing the reactants and reaction byproducts by vaporizing the chlorine dioxide using the fine bubbles. In addition, since the extracted chlorine dioxide gas is diluted by the fine bubbles, explosion of the chlorine dioxide gas can be prevented.

[77] A pure chlorine dioxide solution can be obtained by dissolving the extracted pure chlorine dioxide gas in decompression water at the decompressor.

[78] The pressure inside of the reaction bath, the inert gas supplied to the inside of the reaction bath, and the porous glass filter are important factors in producing a pure chlorine dioxide solution. The size of pores of the porous glass filter may be in the range from about 10 μm to 100 μm. For example, the pore size of the porous glass filter may be in the range from about 10 μm to 40 μm . If the pore size is smaller than about 10 μm, it is difficult to transfer a reactant between the first and second regions of the reaction bath. If the pore size is greater than about 100 μm, relatively large bubbles are generated, and thus reaction decreases.

[79] When the inside of the reaction bath is decompressed using the decompressor, the inside pressure of the reaction bath may be reduced from atmospheric pressure to a pressure in the range from about 200 mmHg to 400 mmHg, for example, about 210 mmHg to 240 mmHg. If the inside pressure of the reaction bath is smaller than about 200 mmHg, relatively large bubbles are generated, and fine bubbles are not generated. If the inside pressure of the reaction bath is greater than about 400 mmHg, the generation rate of bubble is reduced, and thus, the possibility of explosion increases.

[80] Although parts of the reaction bath are not described in detail, it will be easily understood that parts of the reaction bath may be connected to each other directly or through various connection members such as conduits and pipes according to situations.

[81] [Example 1-1]

[82] 25 wt% of sodium chlorite aqueous solution and 30 wt% of sulfuric acid aqueous solution were injected into an upper part of a reaction bath at a rate of 6.5 mL/minute and a rate of 2 mL/minute respectively by using a metering pump.

[83] An aspirator connected to compression water was operated at range of 3- to 3.5-atm to decompress the reaction bath to suck outside air into the reaction bath and pass the sucked air through a porous glass filter disposed at a lower part of the reaction bath at a rate of 400 mL/minute so as to generate fine air bubbles. As the fine air bubbles were

generated, the two compounds injected into the upper part of the reaction bath were rapidly mixed to generate chlorine dioxide, and at the same time, the generated chlorine dioxide was easily vaporized from the mixture containing byproducts. The vaporized chlorine dioxide was dissolved in decompression water discharged from the aspirator. In this way, a pure chlorine dioxide solution was obtained at a rate of 5.8 L/minute from the decompression water in which the chlorine dioxide was dissolved.

[84] In Example 1-1, a chlorine dioxide solution having a concentration of about 172 mg/L was obtained with about 85% yield.

[85] [Example 1-2]

[86] 25 wt% of sodium chlorite, 12 wt% of sodium hypochlorite, and 30 wt% of sulfuric acid were injected into an upper part of a reaction bath at rates of 4.8 mL/minute, 4 mL/minute, and 2 mL/minute, respectively, by using a metering pump.

[87] An aspirator connected to compression water was operated at range of 3- to 3.5-atm to evacuate the reaction bath to suck nitrogen gas into the reaction bath and pass the sucked nitrogen gas through a porous glass filter disposed at a lower part of the reaction bath at a rate of 400 mL/minute so as to generate fine bubbles. As the fine bubbles were generated, the three compounds injected into the upper part of the reaction bath were rapidly mixed to generate chlorine dioxide, and at the same time, the generated chlorine dioxide was easily vaporized from the mixture containing byproducts and impurities. The vaporized chlorine dioxide was dissolved in decompression water discharged from the aspirator. In this way, a pure chlorine dioxide solution was obtained at a rate of 5.8 L/minute.

[88] In Example 1-2, a chlorine dioxide solution having a concentration of about 185 mg/L was obtained with about 95% yield.

[89] [Example 1-3]

[90] While supplying 25 wt% of sodium chlorite solution to an upper part of a reaction bath at a rate of 4.9 mL/minute by using a metering pump, an aspirator connected to compression water was operated at range of 3- to 3.5-atm. As the reaction bath was decompressed by the operation of the aspirator, carbon dioxide gas and chlorine gas were sucked into the reaction bath and passed through a porous glass filter disposed at a lower part of the reaction bath at a rate of 400 mL/minute and a rate of 170 mL/minute, and thus fine bubbles of the carbon dioxide gas and the chlorine gas were generated. The fine bubbles were intermediately mixed with the sodium chlorite solution to generate pure chlorine dioxide gas. The generated chlorine dioxide gas was dissolved in decompression water discharged from the aspirator. In this way, a pure chlorine dioxide solution was obtained at a rate of 5.8 L/minute.

[91] In Example 1-3, a chlorine dioxide solution having a concentration of about 180 mg/L was obtained with about 98% yield.

[92] [Example 1-4]

[93] The same reaction bath and reagents as those used in Examples 1-1 to 1-3 were used but a gas decompressor was used instead of a liquid decompressor to suck inert compressing gas such as nitrogen, carbon dioxide, and air. In this way, a mixture of chlorine dioxide and inert gas was obtained at a rate of 16 L/minute.

[94] In Example 1-4, a chlorine dioxide solution having a concentration of about 69 mg/L was obtained with about 90% yield.

Mode for the Invention

[95] FIG. 2 is a schematic sectional view illustrating an apparatus for producing chlorine dioxide according to a second embodiment of the present invention. In the following description of the second embodiment, the difference between the first and second embodiments will be mainly explained, and non-described features are the same as those described in the first embodiment. In the drawings, like reference numerals denote like elements.

[96] In the current embodiment, the chlorine dioxide producing apparatus includes: a reaction bath 200; a porous glass filter 220 to divide the inside of the reaction bath 200 into a first region R1 and a second region R2; at least one gas supply unit 220 connected to the first region R1 of the reaction bath 200 for supplying chlorine gas and inert gas; at least one raw material supply unit 230, 240 and 250 connected to the second region R2 of the reaction bath 200 for supplying a hypochlorous acid, a chlorous acid, or an acid to the inside of the reaction bath 200; a pressure adjustment unit connected to at least one of the first and second regions R1 and R2 for making the pressure of the second region R2 lower than the pressure of the first region R1; and a discharge hole 264 formed at the reaction bath 200 for discharging chlorine dioxide gas generated in the second region R2.

[97] A compression pump 260 is used as the pressure adjustment unit, and an adsorption tower 270 is further provided to obtain a chlorine dioxide solution from generated chlorine dioxide gas.

[98] The compression pump 260 is disposed between the first region R1 of the reaction bath 200 and the gas supply unit 220. The compression pump 260 may be disposed at a supply line 222 used to supply inert gas for supplying inert gas to the region R1 at a high pressure.

[99] If inert gas and chlorine gas are supplied to the first region R1 of the reaction bath 200 at a high pressure by the compression pump 260, the pressure of the first region R1 of the reaction bath 200 becomes higher than the pressure of the second region R2 of the reaction bath 200. Owing to this pressure difference, gas is transferred from the first region R1 to the second region R2. That is, the inert gas and the chlorine gas are

moved from the first region R1 to the second region R2 through the porous glass filter 210. When the inert gas and the chlorine gas pass through the porous glass filter 210, fine bubbles are generated in the second region R2. Reactants (raw materials) injected into the second region R2 through raw material injection holes 234, 244, and 254 are uniformly agitated by the fine bubbles, and thus high-concentration chlorine dioxide gas can be generated with high process yield. The generated chlorine dioxide gas is discharged through the discharge hole 164.

[100] The adsorption tower 270 is connected to the discharge hole 164. A single adsorption tower 270 may be used or a plurality of adsorption towers 270 connected in series may be used.

[101] The adsorption tower 270 contains an organic solvent and an adsorption material for dissolving and adsorbing the inert gas and the chlorine dioxide gas. That is, the chlorine dioxide gas is absorbed in the adsorption tower 270, and thus a pure chlorine dioxide organic solution can be obtained.

[102] Examples of the organic solvent include water-soluble solvents and non-water-soluble organic solvents that may form layers separate from water. Examples of the water-soluble solvents include methanol, ethanol, propanol, isopropanol, tetrahydrofuran, acetone, and ethyl acetate. Examples of the non-water-soluble organic solvents include n-hexane, methylene chloride, ethyl ether, tert-butyl methyl ether, and petroleum ether.

[103] Among the organic solvent, a volatile organic solvent, which does not dissolve in water but forms a layer separate from water, may be extracted directly from a chlorine dioxide solution by using a separator.

[104] The organic solvent adsorption tower may further include zeolite or silica gel to collect chlorine dioxide gas by adsorbing the chlorine dioxide gas to the zeolite or silica gel. Later, the chlorine dioxide can be desorbed from the zeolite or silica gel by supplying a large amount of inert gas to the zeolite or silica gel.

[105] [Example 2-1]

[106] Ethyl alcohol was filled in three organic solvent adsorption towers connected in series; 25 wt% of sodium chlorite and 30 wt% of sulfuric acid were injected into a second region of a reaction bath at a rate of 6.5 mL/minute and a rate of 2 mL/minute respectively through injection holes; and inert nitrogen gas was supplied to a first region of the reaction bath at a rate of 350 mL/minute for 15 minutes.

[107] Finally, a chlorine dioxide-ethyl alcohol solution having a concentration of about 2,125 mg/L was obtained with about 85% yield.

[108] In the same manner, chlorine dioxide-methanol, chlorine dioxide-isobutyl alcohol, and chlorine dioxide-acetone solutions having a concentration in the range from about 2,000 mg/L to 2,200 mg/L can be obtained.

[109] [Example 2-2]

[110] N-hexane was filled in three organic solvent adsorption towers connected in parallel to each other; 25 wt% of sodium chlorite and 30 wt% of sulfuric acid were injected into a second region of a reaction bath at a rate of 6.5 mL/minute and a rate of 2 mL/minute respectively through injection holes; and inert carbon dioxide gas was supplied to a first region of the reaction bath at a rate of 300 mL/minute for 15 minutes.

[111] Finally, a solution of chlorine dioxide and n-hexane having a concentration of about 2,250 mg/L was obtained with about 90% yield.

[112] In the same manner, a solution of chlorine dioxide-ethyl ether having a concentration of about 2370 mL/L, and a solution of chlorine dioxide and tert-butyl methyl ether having a concentration of about 2,320 mg/L were obtained.

[113] [Example 2-3]

[114] Zeolite or silica gel was filled in three organic solvent adsorption towers connected in parallel to each other; 25 wt% of sodium chlorite was injected into a second region of a reaction bath at a rate of 6.5 mL/minute through an injection hole; and air and chlorine gas were simultaneously supplied to a first region of the reaction bath at a rate of 360 mL/minute and a rate of 946 mL/minute respectively.

[115] Generated chlorine dioxide gas was adsorbed to the zeolite or silica gel, and finally, chlorine dioxide was obtained with about 95% yield.

[116] FIG. 3 is a schematic sectional view illustrating an apparatus for producing chlorine dioxide according to a third embodiment of the present invention. In the following description of the third embodiment, the difference between the first and third embodiments will be mainly explained, and non-described features are the same as those described in the first embodiment. In the drawings, like reference numerals denote like elements.

[117] During a chlorine dioxide generating reaction, a chlorite decomposes disproportionately by an acid, resulting in products such as a hypochlorous acid, a chloric acid, and chlorine. Therefore, the reactants should be rapidly agitated and mixed while supplying exact amounts of raw-material compounds so as to produce pure chlorine dioxide with high yield. Thus, in the current embodiment, solenoid valves are used for reacting exact amounts of reactants for a proper time.

[118] Referring to FIG. 3, the chlorine dioxide producing apparatus of the current embodiment includes: a reaction bath 300; a porous glass filter 320 configured to divide the inside of the reaction bath 300 into a first region R1 and a second region R2; at least one gas supply unit 320 connected to the first region R1 of the reaction bath 300 for supplying chlorine gas and inert gas; at least one raw material supply unit (330, 340, 350) connected to the second region R2 of the reaction bath 300 for supplying a hypochlorous acid, a chlorous acid, or an acid to the inside of the reaction bath 300; a

pressure adjustment unit connected to at least one of the first and second regions R1 and R2 for making the pressure of the second region R2 lower than the pressure of the first region R1; and a discharge hole 364 formed at the reaction bath 300 for discharging chlorine dioxide gas generated in the second region R2.

[119] First to third solenoid valves S1, S2, and S3 are respectively disposed at first to third raw material supply units 330, 340, and 350 connected to the first and second regions R1 and R2 for opening first to third raw material injection holes 334, 344, and 354 when raw materials are supplied to the reaction bath 300. Each of the first to third solenoid valves S1, S2, and S3 is configured by a solenoid having a magnetic core, and one or more orifices. When a current is applied to the core or not applied to the core, the core is positioned to block or allow a flow.

[120] The first to third solenoid valves S1, S2, and S3 may be configured to be opened for about 0.5 to about 10 seconds and closed for about 1 to about 60 seconds. Therefore, the amounts of raw-material chemicals supplied to the reaction bath 300 can be adjusted. If necessary, a solenoid valve may be additionally provided between the reaction bath 300 and a decompressor 360 to adjust the pressure inside of the reaction bath 300 for generating fine bubbles using the porous glass filter 310 disposed in the reaction bath 300.

[121] A pressure detection unit 312 is disposed at the reaction bath 300 for measuring the pressure of the first region R1 or the second region R2. For example, the pressure detection unit 312 may be disposed at the second region R2 to measure the pressure of the second region R2 and send a detected pressure signal to a control unit 370 (described later).

[122] The decompressor 360 may be connected to the reaction bath 300 through a discharge line 362, and a solenoid valve S4 may be disposed at an end of the discharge line 362 adjoining the reaction bath 300. A switch 372 is provided at the decompressor 360, and the switch 372 is electrically connected to the control unit 370. The switch 372 is for operating or stopping the decompressor 360 using an electric signall. The decompressor 360 decompresses the inside of the reaction bath 300 by sucking gas from the inside of the reaction bath 300.

[123] A discharge hole 364 is connected to the decompressor 360 for discharging gas from the reaction bath 300, and in the case where the decompressor 600 is an aspirator, a discharge hole through which decompression water or gas is discharged may be used as the discharge hole 364. Pure chlorine dioxide gas may be easily absorbed in decompression water to form a pure chlorine dioxide solution.

[124] The control unit 370 is electrically connected to the solenoid valves S1, S2, and S3 of the first to third raw material supply units 330, 340, and 350, and the decompressor 360; the switch 372 of the decompressor 360; and the pressure detection unit 312. The

control unit 370 controls the solenoid valves S1, S2, and S3, the decompressor 360, and the reaction bath 300.

[125] The control unit 370 may be an electric control device mounted on a printed circuit board (PCB). The control unit 370 controls opening/closing operations or other operations of the components of the chlorine dioxide producing apparatus.

[126] Chlorine dioxide may be produced using the chlorine dioxide producing apparatus of the current embodiment as follows.

[127] First, the inside of the reaction bath 300 is decompressed by operating the decompressor 360 such a vacuum pump or an aspirator connected to the reaction bath 300 through a pipe. In the current embodiment, an aspirator is used as the decompressor 360; however, the decompressor 360 is not limited thereto. For example, the decompressor 360 may be a vacuum pump.

[128] First, the control unit 370 turns on the switch 372 of the decompressor 360. Then, the decompressor 360 is operated, and the solenoid valve S4 connected to the decompressor 360 is opened to discharge gas from the inside of the reaction bath 300. As the inside of the reaction bath 300 is decompressed, the pressure of the second region R2 becomes lower than the pressure of the first region R1, and thus a gas flow is generated from the first region R1 to the second region R2. Therefore, fine bubbles are formed from the porous glass filter 310.

[129] If it is determined by using the pressure detection unit 312 that the inside of the reaction bath 300 is sufficiently and stably decompressed, the control unit 370 controls opening and closing operations of the solenoid valves S1, S2, and S3 connected to the first to third raw material supply units 300 to 500 according to a predetermined time sequence. Therefore, necessary raw materials can be quantitatively supplied to the reaction bath 300.

[130] The supplied raw materials are mixed by the fine bubbles generated from the porous glass filter 310 and react with each other as expressed by Chemical Formulas 4 to 8, so that chlorine dioxide can be produced.

[131] That is, the inert gas and chlorine gas are transferred from the first region R1 to the second region R2 through the porous glass filter 310, and thus fine bubbles are generated at the second region R2 from the gases passing through the porous glass filter 310. Then, the reactants (raw materials) injected into the second region R2 through raw material injection holes are uniformly agitated by the fine bubbles, so that high-concentration chlorine dioxide can be produced with high yield.

[132] Chlorine dioxide contained in the mixture solution of the reactants and byproducts can be easily vaporized and extracted owing to the decompressed state of the reaction bath 300 and the fine bubbles, and thus pure chlorine dioxide gas can be obtained.

[133] The chlorine dioxide gas is sucked by the decompressor 360 and is absorbed in de-

compression water discharged from the decompressor 360. Therefore, a pure chlorine dioxide solution can be obtained.

[134] As described above, according to the current embodiment, the amounts of raw material supplies can be finely controlled by controlling the solenoid valves using the electric control device, so that necessary reaction can be effectively controlled, and generation of byproducts can be effectively suppressed.

[135] In a typical apparatus, raw materials are supplied using a metering pump or a flow meter. This is possible since the raw materials (chemicals) are liquid or gas such as chlorine gas; however, desired amounts of raw materials cannot be exactly supplied, and the amounts of supplied raw materials cannot be precisely measured. Thus, the amounts of reactants and the degree of reaction cannot be finely controlled. Thus, the present invention is provided to obviate such limitations. Furthermore, although the same raw materials as those used in a typical chlorine dioxide producing method are used in the present invention, the raw materials can be supplied with high concentrations, and the raw materials can be rapidly reacted. Moreover, high-concentration chlorine dioxide can be obtained within the same process time as that of a typical chlorine dioxide producing process.

[136] [Example 3-1]

[137] 12.5 wt% of sodium chlorite was prepared in a first raw material storage vessel, and 15 wt% of sulfuric acid was prepared in a second raw material storage vessel. Then, an aspirator was switched on, and then a solenoid valve of a reaction bath was opened to decompress the reaction bath. Thereafter, the sodium chlorite was supplied to the reaction bath through a solenoid valve at a rate of 1,104 mL/minute, and at the same time, the sulfuric acid was supplied to the reaction bath at a rate of 0.4 mL/minute.

[138] Finally, 5.8 L of chlorine dioxide solution having a concentration of 17 ppm was obtained with 92% yield.

[139] [Example 3-2]

[140] 12.5 wt% of sodium chlorite was prepared in a first raw material storage vessel; 6 wt% of sodium hypochlorite was prepared in a second raw material storage vessel; and 12.5 wt% of sulfuric acid was prepared in a third raw material storage vessel. Then, an aspirator was switched on, and then a solenoid valve of a reaction bath was opened to decompress the reaction bath. Thereafter, the sodium chlorite, the sodium hypochlorite, and the sulfuric acid were supplied to the reaction bath at rates of 2.66 mL/minute, 2.18 mL/min, and 1.45 mL/min, respectively.

[141] Then, generated chlorine dioxide gas is dissolved in water at the aspirator. In this way, 5.8 L of chlorine dioxide solution having a concentration of 53 ppm was obtained with 95% yield.

Claims

[1] An apparatus for producing chlorine dioxide, the apparatus comprising:
a reaction bath;
a porous glass filter dividing the reaction bath into a first region and a second region;
at least one gas supply unit connected to the first region of the reaction bath for supplying chlorine gas and inert gas to the reaction bath;
at least one raw material supply unit connected to the second region of the reaction bath for supplying a hypochlorite, a chlorite, or an acid to the reaction bath;
a pressure adjustment unit connected to at least one of the first and second regions of the reaction bath to keep the second region at a pressure level lower than that of the first region; and
a discharge hole connected to the reaction bath for discharging chlorine dioxide gas generated in the second region of the reaction bath.

[2] The apparatus of claim 1, wherein the porous glass filter has a pore size in a range from about 10 μm to about 100 μm.

[3] The apparatus of claim 1, wherein the pressure adjustment unit is a compression pump connected to the first region for compressing the first region.

[4] The apparatus of claim 1, wherein the pressure adjustment unit is a decompressor connected to the second region for decompressing the second region.

[5] The apparatus of claim 4, wherein the decompressor is an aspirator operated by using decompression water or gas, so that the chlorine dioxide gas generated in the second region is absorbed in the compression water passing through the aspirator or is mixed with the compression gas passing through the aspirator.

[6] The apparatus of claim 4, wherein the decompressor is a vacuum pump.

[7] The apparatus of claim 1, wherein the inert gas is at least one of nitrogen gas, carbon dioxide gas, and air.

[8] The apparatus of claim 1, wherein the raw material supply unit is connected to the second region of the reaction bath through a solenoid valve.

[9] The apparatus of claim 8, further comprising a control unit to control the solenoid valve,
wherein the control unit adjusts the amount of the hypochlorite, the chlorite, or the acid supplied to the reaction bath by controlling the solenoid valve.

[10] The apparatus of claim 9, further comprising a pressure detection unit disposed at the reaction bath for detecting a pressure inside the reaction bath, wherein a signal of the pressure detection unit is transmitted to the control unit.

[11] The apparatus of claim 1, further comprising an adsorption tower connected to the discharge hole, wherein the adsorption tower contains an organic solvent and an adsorption material to dissolve and adsorb the inert gas and the generated chlorine dioxide gas.

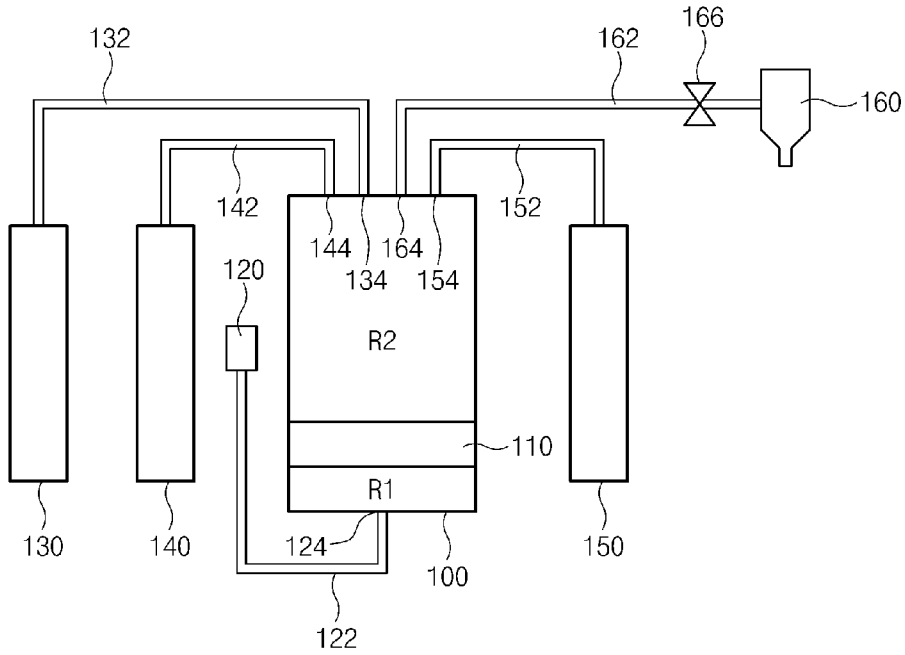
[12] The apparatus of claim 11, wherein the organic solvent is one of n-hexane, methylene chloride, ethyl ether, tert-butyl methyl ether, and petroleum ether.

[13] The apparatus of claim 11, wherein the adsorption material is zeolite or silica gel.

[14] The apparatus of claim 11, further comprising a chlorine dioxide gas removing tower connected to the adsorption tower to remove the chlorine dioxide gas remained after the chlorine dioxide gas passes through the adsorption tower.

[15] The apparatus of claim 14, wherein the chlorine dioxide gas removing tower contains hydrogen peroxide or sodium thiosulfate to remove the remaining chlorine dioxide gas.

[Fig. 1]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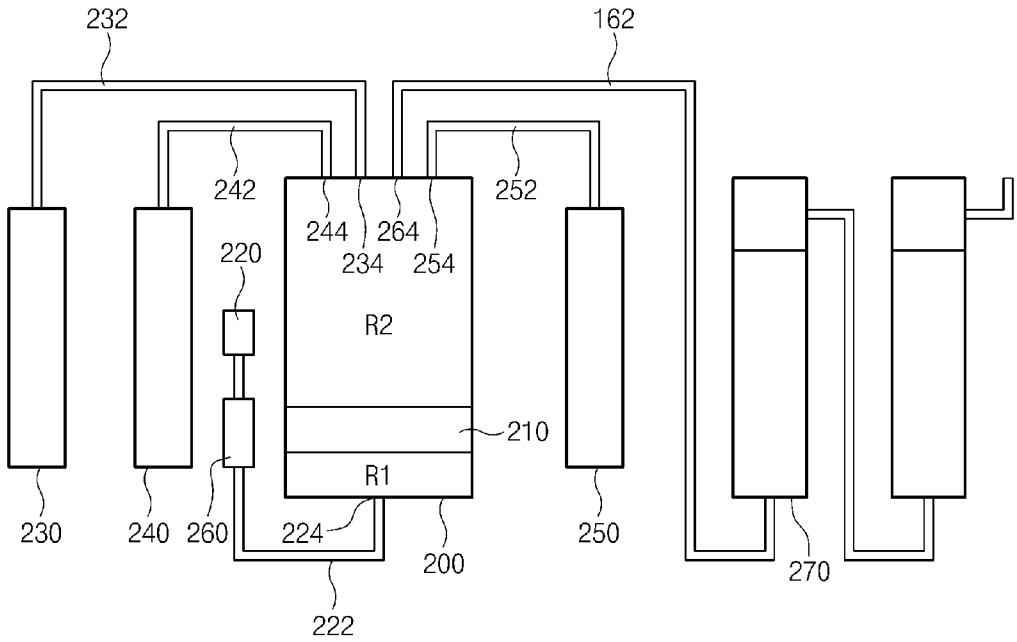
[Fig. 2]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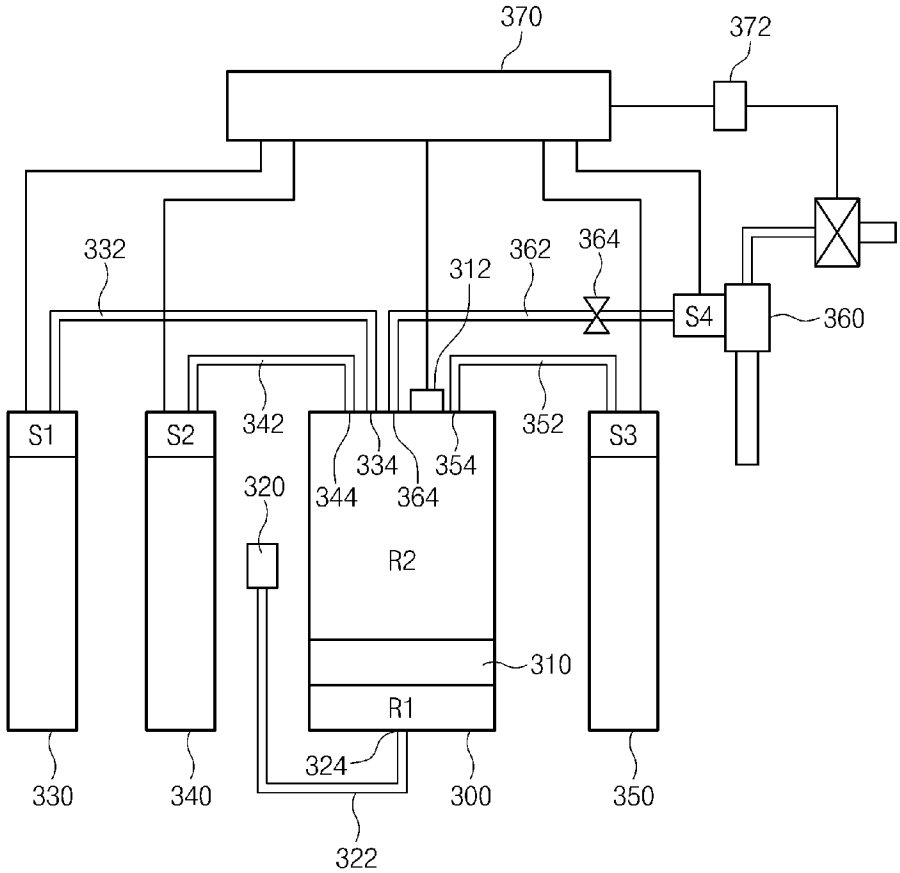
[Fig. 3]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