No. PRX026

AN EXAMINATION REPORT:

Date: 28th July, 2014.

The inactivating performance evaluation examination of the virus with the chlorine dioxide generating agent [AirDoctor (portable type)]. (40L space)

By General incorporated foundation, the Kitasato Research Center for Environmental science.

PRX026

267013／26_0013

株式会社プロテックス 様

試 験 報 告 書

二酸化塩素発生剤「AirDoctor portable」

によるウイルスの不活化性能評価試験（40L 空間）

北環発 26_0013 号
平成 26 年 7 月 28 日

神奈川県相模原市南区北里 1 丁目 15 番 1 号
一般財団法人 北里環境科学センター
理 事 長　伊 藤　俊 洋

1． An examination purpose:

It installed a chlorine dioxide generating agent[AirDoctor(portable type)] in the examination chamber of 40L and evaluated the inactivating effect of the type A influenza virus which It installed in the same examination space.

2． A client:
Protex Co., Ltd.

3． A testing institution:
General incorporated foundation, the Kitasato Research Center for Environmental science, virus division of virus section

4． A study time: From May 26, 2014 to June 2

5． An examination product:
Chlorine dioxide generating agent [AirDoctor (portable type)] (photograph 1)

※It assumed it 6g at the time of the prior radiation before the examination start, and did the quantity of the examination product with 1.6g after examination start.

From examination start, It added one examination product (6g) after progress for approximately 23 hours and installed it.

6． An examination condition:

Action time: 0 (prophase), 24 hours

Action temperature: 25 degrees Celsius

7． A preparation method of a test virus and the virus liquid:

The type A influenza virus (Influenza A Virus, H1N1, A/PR/8/34, ATCC cVR-95TM) virus inoculated it into urine membranae of the growth chicken egg and gathered urine after culture with a artificial incubator device and did the virus liquid which was refined by density gradient centrifugation method with test virus liquid.

8． Test method

1) A virus is impossible, and examine it:

The inactivating examination of the virus reached by the following procedures.

It installed an examination product in the center in the examination chamber of 40L and radiated it for approximately 16 hours and prepared chlorine dioxide gas density to approximately 0.04 ppm of the aim density.

It located it in the state that opened the cover of the laboratory dish of 60mm in diameter that put 4 ml of examination virus liquid in the distance of approximately 10cm from an examination product. (photograph .1)

It sealed up a chamber and gathered virus liquid from a laboratory dish after setting at room temperature (position 25 degrees Celsius) for 24 hours and assumed it a sample undiluted solution for the infection value measurement.

In addition, It operated it equally in the space not to install an examination product in as examination contrast.

※It installed one examination product, and because chlorine dioxide gas density became 4times density higher than it of the target value after the approximately 16 hours radiation, the quantity of the solidity agent in the examination product reduce to 0.16 g from 6g and started action.

Because density fell with 0.01 ppm action 23 hours later, It added one solid agent (6 g) and behaved it for remainder one hour.

2) The measurement of the viral infection value:

After having diluted a sample undiluted solution for the viral infection value measurement with a phosphate-buffered normal saline (PBS: Phosphate buffered saline) for a 10 times stage (write it down with dilution virus liquid), It planted dog kidney origin cell strain (MDCK: Medin-Darby canine kidney) 50μL which I suspended in sample undiluted solution for the infection value measurement or dilution virus liquid 50μL and 5% of fetal bovine serum (FBS: fetal bovine serum) addition Dulbecco's modified Eagle's Medium (EMEM) to 96 well plates.

It cultured it in a carbon dioxide artificial incubator device of 37 degrees Celsius afterwards for four days.

After incubations, It observed the cytopathic effect (CPE: cytopathic effect) by the increase of the virus with an inverted microscope and found a viral infection value (TCID 50/mL) using the Reed-Muench method.

3) The measurement of the chlorine dioxide density:

With a portable gas density measuring instrument (carry-on product), It measured the chlorine dioxide density in the examination chamber.

9. A test result:

It showed a test result in table - 1.

It showed the chlorine dioxide density in the chamber during the examination in table - 2.

The initial viral infection value was 3.9×10^7 TCID50/mL.

The infection value after a standstill became 2.9×10^6 50/mL of for 24 hours of [(comparison) that there is no examination product in].

On the other hand, the infection value of 【chlorine dioxide generating agent, Air Doctor portable type】 for 24 hours, which installed in an examination chamber of 40L become $6.3 \times 10_2$ TCID 50/ml.

When It compared the infection value logarithm decrease value (LRV: log reduction value) after the action with the comparison for 24 hours, it was 3.7log10.

The rate of decline that It calculated from LRV became 99.98%.

As reference data, It showed the chlorine dioxide gas density at the time of the examination.

The chlorine dioxide gas density examining fluctuated in the range of 0.01-0.13 ppm for target value 0.04 ppm.

10. Comment:

In this examination, It established "chlorine dioxide generating agent Air Doctor" (portable type) of the offer in an examination chamber of 40L and evaluated the removal effect on type A influenza virus.

As a result of this examination, a decrease in 3.ylog10 (99.98% of rates of decline) was accepted after a still standing for 24 hours.

the inactivating effect of the virus with the chlorine dioxide gas, it is reported one being affected by humidity (water) and organic existence.

In true use, appropriate usage is necessary in consideration of possibility to be affected by humidity and organic matter.

References:

1) Morino H et aol., Inactivation of feline calici-virus by chlorine dioxide gas-generating gel. Yakugaku Zasshi, 133 (9): 1017.22, 2013.

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Table-2: The chlorine dioxide gas density in the examination chamber of 40L at the time of the examination:

Measurement item:	Action time (hours)	
	0 (prophase)	24
Chlorine dioxide gas density:	0.040	0.024

※ A measuring instrument: Portable gas degree measuring instrument.(JMS, carry on product)

※ A unit: ppm

※ The result of a measurement of the chlorine dioxide gas density at the time of the examination, please refer the reference data.
A measuring instrument: A chlorine dioxide gas-detecting tube.(No.23L, Gas tech. center)

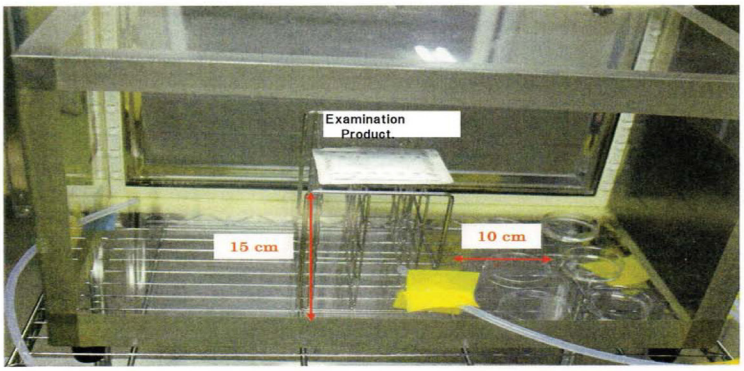

Photo-1: The examination situation in the examination chamber of 40L.

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Reference Date:

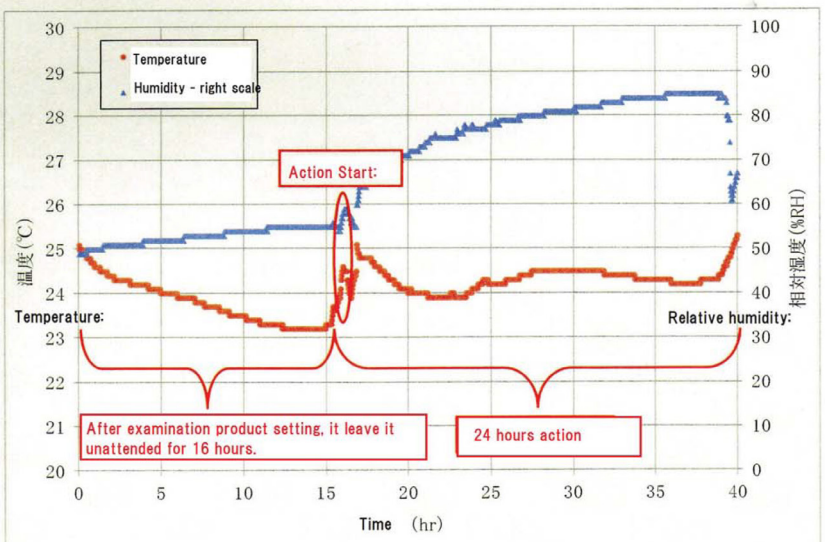
It showed the chlorine dioxide gas density in the examinaion chamber at he time of the examination and temperature-humidity:

Table-3: A chlorine dioxide gas concerntration measurement result:

Date:	Time:	Chlorine dioxide density (ppm)	Remarks:
May, 27	9:00	0.160	
	Examination start ⇒9:50	0.040	Reduce a solid agent 6g to 1.6g.
	14:30	0.057→0.041	Ventilated and assumed 0.057～0.041ppm.
	17:00	0.037	
	18:00	0.035	
May, 28	9:00	0.01	Add one solid agent (6g)
	9:20	0.13→0.04	Ventilated and assumed it 0.04ppm.
	Examination end ⇒9:50	0.024	

※ A measuring instrument: A portable gas density measuring instrument. (JMS, carry on product).

※ Examination start: May, 27. 9:50 (action time 0 hours).
Examination end: May, 28, 9:50 (action time 24 hours)



Temperature-humidity change in the chamber at the time of examination.(2014.5.26 17:50-2014.5.28 9:50)

Figure - 1: Temperature-humidity change in the examination chamber at the time of examination:

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株式会社 プロテックス 様

試 験 報 告 書

二酸化塩素発生剤「Air Doctor portable type」による

スギ花粉アレルゲンの不活化性能評価試験（40 L 空間）

北生発 26_4053 号
平成 26 年 7 月 23 日

神奈川県相模原市南区北里 1 丁目 15 番 1 号
一般財団法人 北里環境科学センター
理 事 長　伊 藤　俊 洋

1． A purpose:

When It installed a chlorine dioxide generating agent[Air Doctor(portable type)] in the examination space of 40L and radiated chlorine dioxide gas, It evaluated an effect for the cedar pollen allergen liquid which It installed in the examination space (Cry j1).

2． A client:
Protex Co. Ltd.

3． A testing institution:
A name: General Incorporated foundation, The Kitasato Research Center for Environmental science , biotechnology division of microscopic organism department.

4． A implementation period:
From June 23, 2014 to June 24

5． An examination product:
Chlorine dioxide generating agent "Air Doctor" (portable type). . . . .
Photograph -1:

※It installed one examination product (6 g) and acted it.

6． Examination condition

Action time: 0 (prophase), 24 hours
Action temperature: Approximately 25 degrees Celsius

7． Examination pollen:
Cedar pollen antigen liquid. (Cry j1)

Acquisition: Nichinichi medicine manufacture Co., Ltd.

8． A reagent and instrument, equipment.

1) Main reagent

●Buffer solution for the cedar pollen. (Nichinichi medicine manufacture Co., Ltd.)

●Sodium thiosulfate (Wako, the first grade)

2) Main Instrument, equipment.

●Examination chamber of 40L (special order product)
● Thirmo-hygrograph: (T&D, TR-72Ui)

9． A test method:

1) A preparation of the pollen liquid.

It diluted cedar pollen antigen liquid with buffer solution for the pollen and It prepared it in about 80ng/mL and offered it for an examination.

2) Operation

It installed an examination product in the center in the examination chamber of 40L and installed it in the state that opened the cover of the laboratory dish of φφ60mm that put 2 ml of examination pollen liquid in the distance of approximately 10cm from an examination product (photograph 1).

It sealed up a chamber and harvested pollen liquid from a laboratory dish after preservation at room temperature (approximately 25 degrees Celsius) for 24 hours.

In addition, It put the laboratory dish which poured examination pollen liquid into the space not to install an examination product in as examination comparison and operated it likewise.

※I installed one examination product (6 g) and behaved it.

3) The fixed-quantity of the cedar pollen allergen (Cry j1):

It sent it to the measurement organization by a refrigeration service, and the pollen liquid after the examination assayed a cedar pollen allergen (Cry j1) by the ELISA method (a measurement organization: Nichinichi medicine manufacture Co., Ltd, central laboratory).

4) The measurement of the chlorine dioxide gas density

It aspirated the air in the examination chamber with a gas-detecting tube after action at scheduled time and measured the chlorine dioxide density in the chamber.

10. Result

It showed quantity of cedar pollen allergen in table 1.

It showed the chlorine dioxide gas density in the chamber at the time of setting and the collection of pollen liquid in table 2.

As reference data, It showed the temperature-humidity in the chamber.

The quantity of cedar pollen allergen at the time of the examination start was 81.0ng/mL.

The quantity of cedar pollen allergen after the action became 82.4ng/mL for 24 hours of [(comparison) that there is no examination in] and I did not pass or did not do the allergenic quantity.

As for the quantity of cedar pollen allergen after the action for 24hours of 【examination product setting】 was 64.5ng/mL, the inactivating rate were 21%.

On this examination condition, most of the inactivating effects on pollen allergen were not provided.

The chlorine dioxide gas density was 0.12ppm until 2-8hours action, but, it was 0.18 ppm after 24hours action.

Table-1: The inactivation effect of the cedar pollen allergen:

Examination condition:	Action time. (h)	
	0	24
No examination product.(comprison)	81.0	(A) 82.4
Examination product setting.		(B) 64.5(21%*)

※ An examination product: Chlorine dioxide generating agent "AirDoctor (Portable type)"

※ Examination pollen: Cedar pollen allergen. (Cryj1)

※ An allergenic quantity unit: ng/mL.

※ Examination space: 40L.

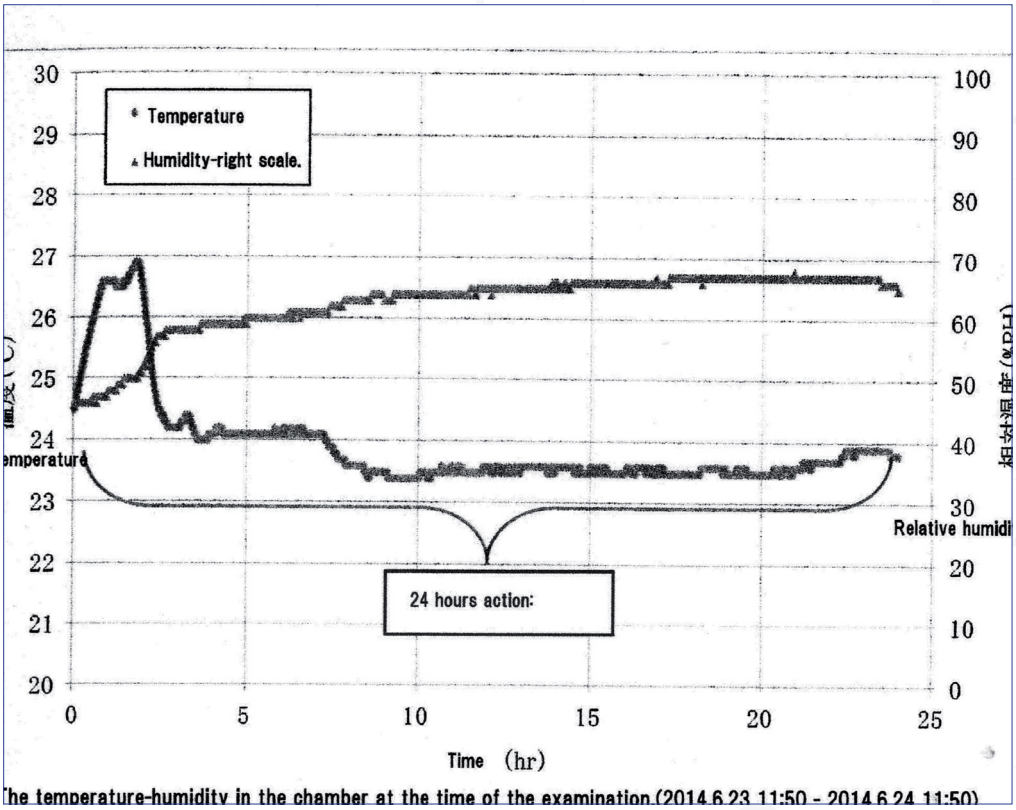
*: Inactivating rate = (1-(B)/(A) x 100%

Table-2: The chlorine dioxide gas density in the 40L chamber at the time of the examination:

Examination condition:	Time (h)					
	0	2	4	6	8	24
Examination product setting:	0	0.12	0.12	0.12	0.12	0.18

※ A measuring instrument: A gas detecting tube.(chlorine dioxide No. 23L, gas technical center)

※ A unit: ppm.



The temperature-humidity in the chamber at the time of the examination (2014.6.23 11:50 - 2014.6.24 11:50)

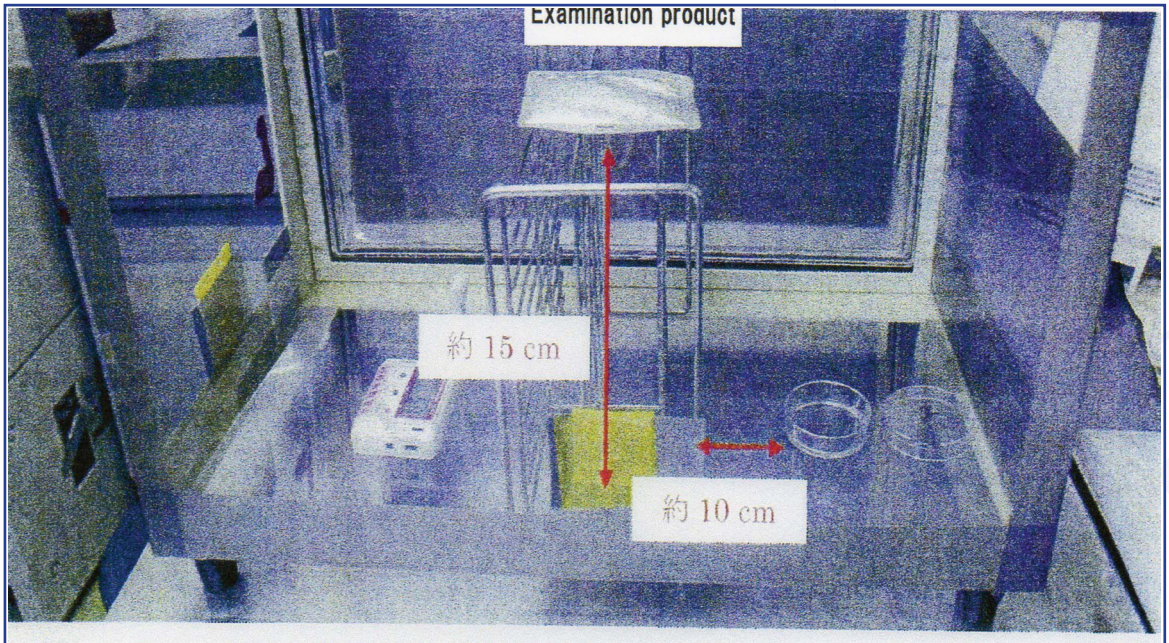


Photo-1: The examination situation in the 40L of examination chamber.

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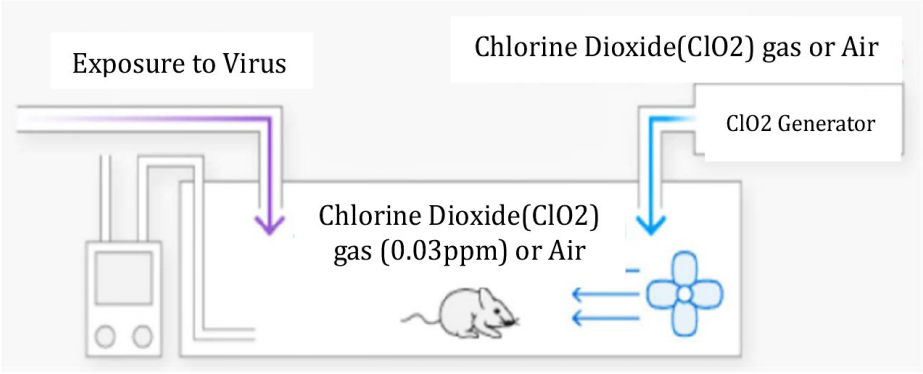
Quality Control Division

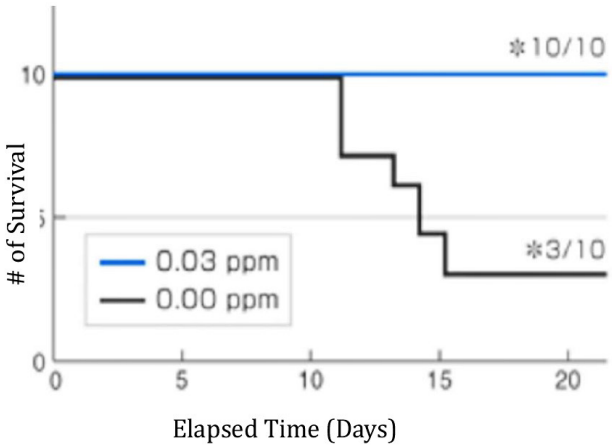
Test Data on Viruses

Ten (10) mice were exposed to either Air Doctor, or Chlorine Dioxide gas (0.03ppm) for 15 minutes and mortality rate was monitored for each case for 21 days.



<Test Result-1>

Under the exposure to the Chlorine Dioxide gas (0.03ppm), death of mice from infection by the Virus I was inhibited. (p=0.002)
(Long-term permissible level of Chlorine Dioxide gas concentration (TLV) to human is 0.1ppm for 8 hour weighed average (TLV-TWA))



Chlorine Dioxide gas Concentration: 0.03ppm
Virus titer: 1 LD50 , Exposure time: 15 min., N=10

*:p=0.002 (Comparison of 20 days)

Efficacy of measures which are currently available for infection prevention by influenza viruses is limited and not satisfactory. Safe and effective measures for pandemic influenza are now desired.

We are proud to report that the infection of mouse, which is induced by aerosol of influenza type-A virus, was effectively prevented through the exposure to extremely low concentration of Chlorin Dioxide gas (ClO_2), which is namely less than 0.1ppm, the long-term permissible level of Chlorine Dioxide gas concentration (TLV) to human.

Mice were put in a half-closed cage and let them expose to either the influenza type-A aerosol (1LD50) only or together with the Chlorin Dioxide(ClO_2) gas (0.03ppm) or for 15 minutes.

3 days later, it was observed that a viral titer in the lung of 5 mice that were exposed to the Chlorin Dioxide gas was 102.6±1.5, whereas that of the other 5 mice that were not was 106.7±
0.2 (p=0.003).

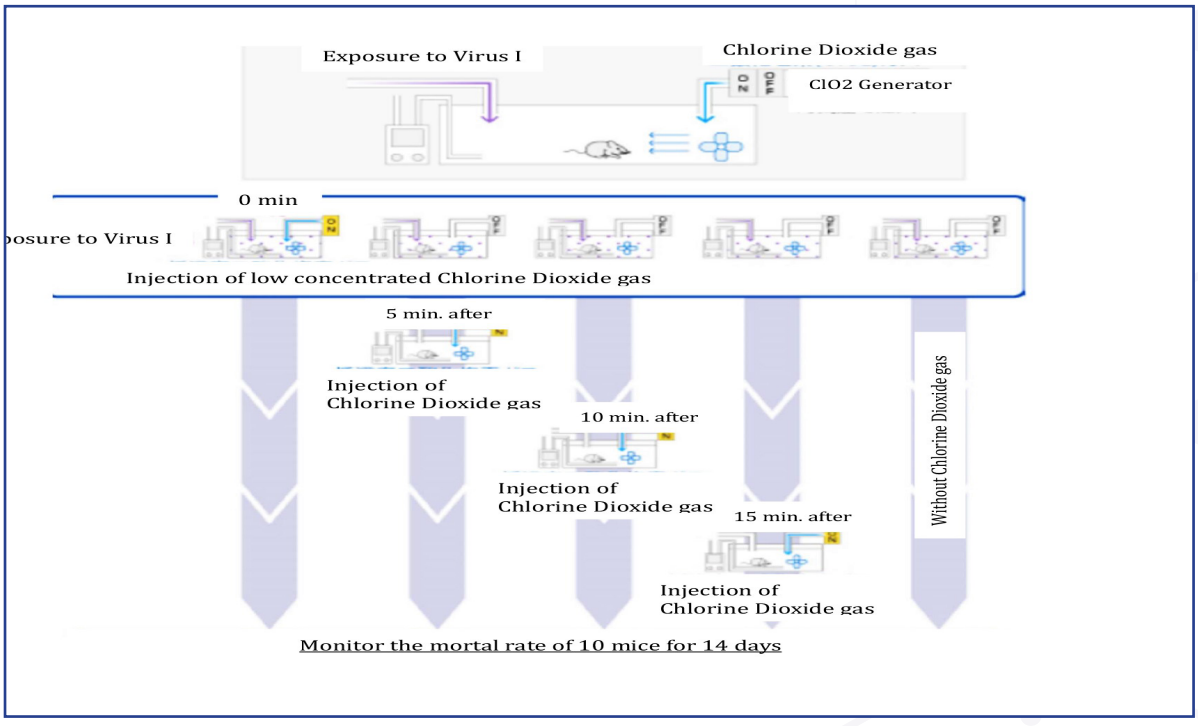
16 days later, accumulated fatal rate of mice that were exposed to $ClO_2$was 0/10, whereas that of those that were not exposed was 7/10 (p=002). In vitro experiment, ClO_2has disabled the infection by denaturing the viral membrane proteins (hemagglutinin and neuraminidase), which are indispensable for a virus infection.

Therefore, we conclude that, as far as mice is concerned, less-than the permissible level of Chlorine Dioxide gas concentration to human is effective for the prevention of aerosol influenza viruses by denaturing the viral membrane proteins.

From the results above, it can be said that the ClO_2gas is also significantly effective for the prevention of influenza even in the area where human activity resides without leaving.

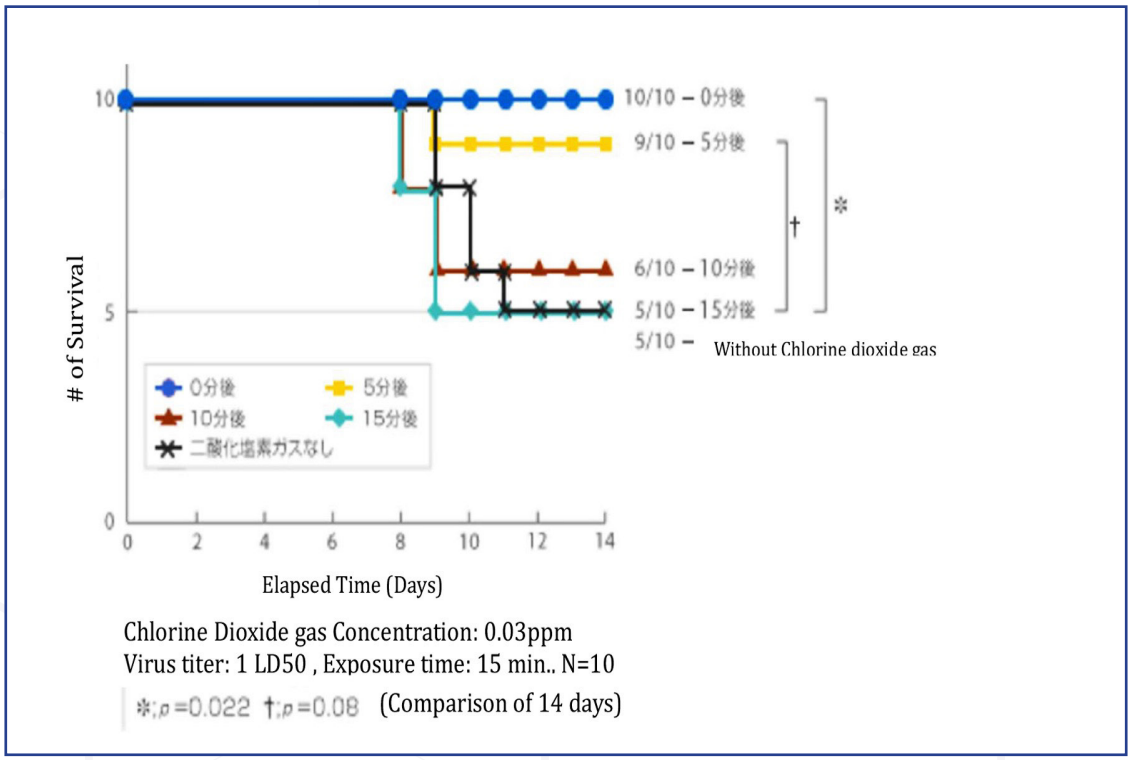
<Method of Experiment>

10 mice were exposed to the virus I($1LD_{50}$)and the mortal rate of the mice was monitored by having them exposed also to the Chlorin Dioxide gas (0.03ppm)in 0, 5, 10 and 15 minutes after the start of exposure.



<Results of Experiment>

Death of 5 mice was observed when exposed to the Chlorine Dioxide gas in 15 minutes after the start of exposure to the virus I, which is the same rate as the case without exposure to the Chlorine Dioxide gas. On the other hand, no death of mice was observed when the mice were exposure to the Chlorine Dioxide gas at the same time as to the virus I. Although it was not statistically confirmed (p=0.081), the death of only one mouse was observed when the exposure to the Chlorine Dioxide gas was started 5 minuets after.



Chlorine Dioxide gas Concentration: 0.03ppm
Virus titer: 1 LD50 , Exposure time: 15 min.. N=10

※;p =0.022 †;p =0.08 (Comparison of 14 days)

US005567405A

United States Patent [19]

Klatte et al.

[11] **Patent Number: 5,567,405**

[45] **Date of Patent: Oct. 22, 1996**

[54] **METHOD FOR PRODUCING CHLORINE DIOXIDE USING CHEMICALLY IMPREGNATED ZEOLITE**

[75] Inventors: **Fred Klatte**, San Francisco, Calif.; **James Aamodt**, Wilsonville, Oreg.; **David Biswell**, Kings Bang, Calif.

[73] Assignee: **Klatte Inc.**, Petaluma, Calif.; a part interest

[21] Appl. No.: **445,025**

[22] Filed: **May 19, 1995**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 382,601, Feb. 2, 1995, which is a continuation-in-part of Ser. No. 150,438, Nov. 10, 1993, Pat. No. 5,464,598, which is a continuation-in-part of Ser. No. 975,680, Nov. 13, 1992, Pat. No. 5,278,112.

[51] **Int. Cl.**[6] **C01B 11/02**

[52] **U.S. Cl.** ..... **423/477**; 423/240 R; 422/4; 422/29; 422/30; 422/37

[58] **Field of Search** ..... 423/477, 478, 423/240 R; 422/4, 29, 30, 37

[56] **References Cited**

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Primary Examiner—Steven Bos
Assistant Examiner—Thomas G. Dunn, Jr.
Attorney, Agent, or Firm—Limbach & Limbach L.L.P.

[57] **ABSTRACT**

A method for producing chlorine dioxide by moving fluid (such as air) relative to a first bed of zeolite crystals impregnated with sodium chlorite and/or zeolite crystals impregnated with chlorine, and by moving the fluid relative to a second bed of zeolite crystals impregnated with at least one of the following: phosphoric acid, acetic acid and citric acid. The first and second beds may be physically mixed together.

15 Claims, 1 Drawing Sheet

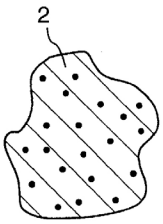


FIG. 1

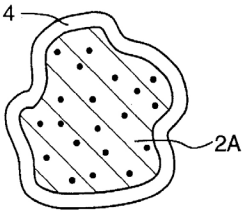


FIG. 2

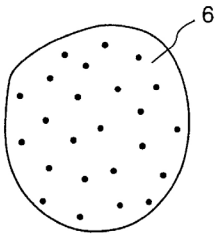


FIG. 3

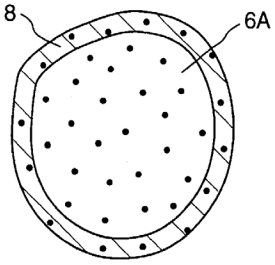


FIG. 4

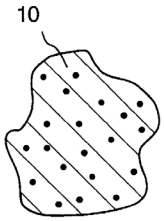


FIG. 5

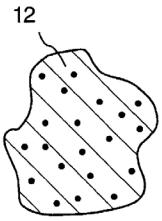


FIG. 6

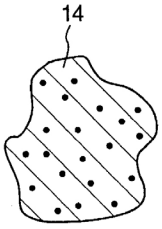


FIG. 7

METHOD FOR PRODUCING CHLORINE DIOXIDE USING CHEMICALLY IMPREGNATED ZEOLITE

CROSS-REFERENCE TO RELATED APPLICATION

The present application is a continuation-in-part of U.S. patent application Ser. No. 08/382,601, filed Feb. 2, 1995 which is a continuation-in-part of pending U.S. patent application Ser. No. 08/150,438 filed Nov. 10, 1993 now U.S. Pat. No. 5,464,598, which is a continuation-in-part of U.S. patent application Ser. No. 07/975,680, filed Nov. 13, 1992 issued as a U.S. Pat. No. 5,278,112 on Jan. 11, 1994.

FIELD OF THE INVENTION

The invention relates to processes for producing chemically impregnated zeolite and coated, chemically impregnated zeolite, to the products of such processes, and to use of such products for absorbing a contaminant from a fluid. A preferred embodiment of the invention using chemically impregnating zeolite crystals to produce chlorine dioxide.

BACKGROUND OF THE INVENTION

Zeolites are hydrated metal aluminosilicate compounds with well-defined (tetrahedral) crystalline structures. Because zeolite crystals (both natural and synthetic) have a porous structure with connected channels extending through them, they have been employed as molecular sieves for selectively absorbing molecules on the basis of size, shape, and polarity.

Volumes packed with zeolite crystals (for example, small zeolite crystals chosen to have size in the range from 0.2 mm to several millimeters) have been employed in water and air (or other gas) filtration systems to selectively absorb contaminants from a flowing stream of water or gas.

It has been proposed to treat zeolite crystals by impregnating them with quaternary ammonium cations (such as tetramethylammonium, tetraethylammonium, hexadecyltrimethylammonium, dibenzyldimethylammonium, benzyltriethylammonium, and cetyltrimethylammonium), to enhance the zeolite's capacity to absorb heavy metal, benzene, toluene, and xylene contaminants from water. See, for example, Cadena, et al., "Treatment of Waters Contaminated with BTX and Heavy Metals Using Tailored Zeolites," New Mexico Waste-management Education and Research Consortium Technical Completion Report for Project No. WERC-91-41 (February 1992). If not impregnated with a quaternary ammonium cation (QAC), zeolite does not function adequately as a molecular sieve for organic chemicals such as benzene, toluene, and xylene.

It has also been proposed to impregnate an aqueous solution of permanganate (such as permanganate of potassium, sodium, magnesium, calcium, barium, or lithium) into pores of substrates such as silica gel, alumina, silica-alumina, activated bauxite, and activated clay. The resulting impregnated porous substrates have been employed for filtering and deodorizing air. See, for example, U.S. Pat. No. 3,049,399, issued Aug. 14, 1962, to Gamson, et al.

However, above-mentioned U.S. Pat. No. 5,278,112 represents the first teaching of how to impregnate zeolite crystals (throughout their volume) with permanganate.

Further, because permanganates are strong oxidizing agents, those skilled in the art have avoided exposing quaternary ammonium cations or salts to permanganates (to avoid violent reactions of the type predicted in the literature). For this reason, until U.S. Pat. No. 5,278,112, it had not been proposed to treat a permanganate-impregnated substrate (such as permanganate-impregnated zeolite) with a quaternary ammonium cation or salt, nor to treat a substrate impregnated with a QAC (quaternary ammonium cation) to permanganate.

One of the inventors has found that zeolite crystals can readily be impregnated with a usefully high concentration of potassium permanganate. However, this inventor has recognized that, under certain conditions, such permanganate-impregnated zeolite reacts too rapidly to be practically useful for some air filtration applications. For example, when air contaminated with 50 ppm of hydrogen sulfide is caused to flow (at a rate of 15 liters per minute) through a bed of the inventive permanganate-impregnated zeolite crystals (where the crystals have size about 0.25 inch×0.125 inch, and the bed has volume of 75 cubic centimeters, and dimensions 1" (ld)×6"), the crystals typically become saturated with hydrogen sulfide within about 48 hours. Although the impregnated zeolite crystals usefully absorb hydrogen sulfide from air, the hydrogen sulfide absorption rate is significantly higher than can be achieved using conventional permanganate-impregnated alumina products, and is undesirably high for some applications.

For both air (and other gas) and water filtration applications, it would be desirable to reduce the rate at which permanganate-impregnated zeolite absorbs selected contaminants, and to control such absorption rate. Similarly, it would be desirable to reduce the rate at which QAC-impregnated zeolite absorbs selected contaminants, and to control such absorption rate. However, until the present invention, it was not known how to achieve either of these objectives.

Zeolite coated (but not impregnated) with manganese dioxide has been employed in water filtration systems to selectively absorb contaminants from a flowing stream of water, as described in U.S. Pat. No. 4,581,219, issued Apr. 8, 1986 to Imada, et al. However, until the present invention, it was not known how to impregnate zeolite with manganese dioxide, or to employ zeolite impregnated with manganese dioxide in water or gas filtration systems to selectively absorb contaminants from a flowing stream of water or gas.

SUMMARY OF THE INVENTION

In one class of embodiments, the invention is a process for producing zeolite crystals impregnated with one or more of sodium chlorite, acetic acid, citric acid, chlorine, sodium sulfite, and sodium bisulfite. The product of each such process is another class of embodiments of the invention.

Throughout the specification, including in the claims, the term "permanganate" used alone is intended to refer to any permanganate, including permanganate of potassium, sodium, magnesium, calcium, barium, or lithium.

A further aspect of the present invention relates to production of chlorine dioxide by moving fluid (such as air) relative to a first bed of zeolite crystals impregnated with sodium chlorite and/or zeolite crystals impregnated with chlorine, and by moving the fluid relative to a second bed of zeolite crystals impregnated with one of the following: phosphoric acid, acetic acid and citric acid. The first and second beds can be physically mixed together, or the fluid can flow sequentially through distinct first and second beds.

A further aspect of the present invention relates to removing chlorine dioxide from a fluid by moving the fluid relative

to a bed of zeolite crystals impregnated with one of the following: potassium hydroxide, sodium sulfite, sodium bisulfate and ferrous sulfate. This method may be used to remove chlorine dioxide produced using the method for producing chlorine dioxide described above.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a cross-sectional view of a zeolite crystal impregnated with permanganate.

FIG. **2** is a cross-sectional view of the impregnated zeolite crystal of FIG. **1**, after it has been coated with a QAC in accordance with the invention.

FIG. **3** is a cross-sectional view of a zeolite crystal impregnated with manganese dioxide.

FIG. **4** is a cross-sectional view of the impregnated zeolite crystal of FIG. **3**, after it has been coated with a QAC in accordance with the invention.

FIG. **5** is a cross-sectional view of a zeolite crystal impregnated with phosphoric acid.

FIG. **6** is a cross-sectional view of a zeolite crystal impregnated with one of the following impregnating agents: sodium chlorite, acetic acid, citric acid, and chlorine.

FIG. **7** is a cross-sectional view of a zeolite crystal impregnated with one of the following impregnating agents: sodium sulfite, sodium bisulfite, and ferrous sulfate.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In one class of embodiments, the invention is a process for impregnating zeolite crystals (for example, crystals having size 0.125 inch×0.10 inch, 0.25 inch×0.125 inch, 0.125 inch×0.50 inch, or 0.50 inch×0.75 inch) with manganese dioxide, and the product of such process. Preferred embodiments of such process employ, as input material, zeolite crystals uniformly impregnated with potassium permanganate, with a 4% potassium permanganate content and a 15% moisture content. Such input material is preferably produced by a method including the steps of initially dehydrating the zeolite crystals to have about 5% moisture content, then mixing the dehydrated zeolite crystals with potassium permanganate crystals (preferably with a weight ratio P/T substantially equal to 4%, where P is the potassium permanganate weight and T is the total weight of the final product of the process), then immersing the crystal mixture in (or spraying the mixture with) water at about 190° F., thoroughly mixing the resulting slurry, and then air drying the mixed slurry to produce potassium permanganate-impregnated zeolite crystals having about 15% moisture content. Typically, the process employs four pounds of potassium permanganate and fifteen pounds of water for every 86 pounds of dehydrated (5% moisture) zeolite crystals, and this mixture (105 pounds) is dried to produce 100 pounds of permanganate-impregnated zeolite crystals having about 15% moisture content. FIG. **1** represents one such impregnated crystal, having channels uniformly impregnated with potassium permanganate **2**.

Variations on the method described above produce zeolite crystals uniformly impregnated with potassium permanganate, having a potassium permanganate content of X%, where X is greater than 4, and is preferably in the range from 8 to 10. In such variations, the dehydrated zeolite crystals are mixed with solid potassium permanganate with a weight ratio P/T substantially equal to X%, where P is the potassium permanganate weight and T is the total weight of the final product of the process.

In variations on any of the above-described methods, permanganate other than potassium permanganate (such as permanganate of sodium, magnesium, calcium, barium, or lithium) is employed to impregnate the zeolite crystals.

In another variation on the described methods, zeolite crystals are immersed in (or sprayed with) aqueous potassium permanganate (having permanganate concentration in the range from about 10% to about 20%), where the weight of aqueous potassium permanganate is about 10% of the weight of the final product of the process. The crystals (after they are dried) will be uniformly impregnated with about a 1% concentration of potassium permanganate.

In yet another variation on the described methods, zeolite crystals are immersed in (or sprayed with) supersaturated aqueous potassium permanganate (having permanganate concentration of 20% or higher) at 190° F., where the weight of aqueous potassium permanganate is about 10% of the weight of the final product of the process. The zeolite crystals (after they are dried) are uniformly impregnated with a concentration of potassium permanganate greater than 1%.

For many applications (including air and water filtration applications), the desired concentration of potassium permanganate impregnated in zeolite crystals is in the range from about 1% to about 4% (or from about 1% to about 8% or 10%).

However, as explained above, permanganate-impregnated zeolite may have an activity rate too high or too low for some useful applications (i.e., its rate of absorption of contaminants may be too high, or too low, for some air or water filtration applications). One of the inventors has found that the rate at which permanganate-impregnated zeolite absorbs (or reacts with, or both absorbs and reacts with) selected contaminants can be controlled (and reduced or increased to a desired level) by applying a quaternary ammonium cation (QAC) coating to the permanganate-impregnated zeolite. This inventor has also found that the rate at which QAC-impregnated zeolite absorbs selected contaminants can be controlled (and reduced or increased to a desired level) by applying a permanganate coating to the QAC-impregnated zeolite.

Thus, in a first class of preferred embodiments, the inventive method uses zeolite which has first been impregnated with permanganate (preferably, potassium permanganate) and then coated with a QAC (preferably, cetyltrimethylammonium, although other QACs are suitable for certain applications). FIG. **2** represents one such impregnated crystal, whose channels contain QAC **4** in the region near the crystal's surface, and whose channels are impregnated with potassium permanganate **2**A throughout the volume of the crystal inside the region containing QAC **4**.

In a second class of preferred embodiments, the invention uses zeolite which has been impregnated with a QAC (preferably, cetyltrimethylammonium) and then coated with permanganate (preferably, potassium permanganate). Either type of coated, impregnated zeolite (or a mixture of both types of coated, impregnated zeolite, or a mixture of uncoated impregnated zeolite with coated, impregnated zeolite of either type) is useful for a variety of molecular sieving applications (such as filtration of contaminants from air or water).

Development of the first class of preferred embodiments began with our unexpected observation that no obvious reaction resulted from immersion of potassium permanga-

nate-impregnated zeolite in (or spraying of such impregnated zeolite with) liquid cetyltrimethylammonium chloride (with a weight ratio Q/T in the range from 0.1% to 5%, where Q is the cetyltrimethylammonium chloride weight and T is the total weight of the final product of the process). As a result of such immersion (or spraying), a QAC coating was applied to each permanganate-impregnated zeolite crystal in the sense that the QAC (cetyltrimethylammonium) entered the channels near each crystal's outer surface but the QAC did not penetrate farther into the interior of each crystal. From a practical point of view, one of the inventors has found that the weight ratio of liquid cetyltrimethylammonium chloride employed for coating permanganate-impregnated zeolite crystals should preferably (at least for most air filtration applications) satisfy the following relation: $0.1\%<Q/T<0.5\%$, where Q is the cetyltrimethylammonium chloride weight and T is the total weight of the final product of the process.

As a result of permanganate leaching studies on the inventive QAC-coated, potassium permanganate-impregnated zeolite crystals (in which the coated, permanganate-impregnated zeolite crystals were immersed in, or sprayed with, water and the permanganate concentration in the water measured over time), one of the inventors determined that the QAC coating substantially slowed the permanganate leaching rate (and thus would substantially slow the expected activity rate, i.e., the rate at which the impregnated zeolite would absorb and/or react with contaminants such as organic chemicals). This result was highly unexpected in view of the conventional belief that the presence of QAC would increase zeolite's absorption of organic chemicals (such as toluene).

One of the inventors found that the activity rate of QAC-coated, potassium permanganate-impregnated zeolite depends on the concentration of the QAC solution with which the permanganate-impregnated zeolite is coated. Increasing the QAC concentration will decrease the activity rate. This inventor found that the leaching rate of permanganate from within QAC-coated, impregnated zeolite (and hence the expected activity rate) is negligible if the weight ratio of the QAC coating is in the range from 1% to 2% (i.e., if the weight of liquid cetyltrimethylammonium chloride employed for coating permanganate-impregnated zeolite crystals satisfies the relation $1\%<Q/T<2\%$, where Q is the cetyltrimethylammonium chloride weight and T is the total weight of the final product of the process). To produce QAC-coated, potassium permanganate-impregnated zeolite for most air filtration applications, the optimum QAC coating weight ratio is in the range from 0.1% to 0.5% (i.e., the weight of liquid cetyltrimethylammonium chloride employed for coating the permanganate-impregnated zeolite crystals satisfies the relation $0.1\%<Q/T<0.5\%$, where Q is the cetyltrimethylammonium chloride weight and T is the total weight of the final product of the process). However, for permanganate-impregnated zeolite crystals with a permanganate concentration greater than 4%, it may be desirable to employ a greater amount of QAC for the coating (i.e., the weight of liquid cetyltrimethylammonium chloride employed for the coating should satisfy the relation $1\%<Q/T<2\%$, where Q is the cetyltrimethylammonium chloride weight and T is the total weight of the final product of the process).

An optimal permanganate-impregnated zeolite product for absorbing (and/or reacting with) any of a wide variety of contaminants (or contaminant groups) from a fluid (such as air or water) can be determined experimentally in the following manner. Uncoated, QAC-impregnated zeolite crystals (preferably produced in the manner described below) are mixed in various ratios with QAC-coated, permanganate-impregnated zeolite crystals, and the contaminant absorption and/or reaction characteristics of each mixture studied. The mixture producing the best absorption and/or reaction characteristics is identified as the optimal mixture.

Since the QAC known as cetyltrimethylammonium is commercially available in aqueous form, impregnation of zeolite with this aqueous QAC product can be accomplished more easily than can impregnation of zeolite with potassium permanganate. A preferred method for impregnating zeolite crystals with QAC to produce zeolite crystals uniformly impregnated with cetyltrimethylammonium cations includes the following steps: dehydrating the zeolite crystals to have about 5% moisture content, then immersing the dehydrated zeolite crystals in (or spraying the dehydrated crystals with) liquid cetyltrimethylammonium chloride (the cetyltrimethylammonium chloride weight is preferably in the range from 5% to 15% of the total weight of the final product of the process) and thoroughly mixing the resulting slurry, and finally air drying the mixed slurry to produce the cetyltrimethylammonium-impregnated zeolite crystals. Typically, fifteen pounds of liquid QAC and 90 pounds of dehydrated (5% moisture) zeolite crystals are employed to produce each 100 pounds of such cetyltrimethylammonium-impregnated zeolite crystals.

Although the QAC in preferred embodiments of the invention is cetyltrimethylammonium, other QACs can be substituted for cetyltrimethylammonium in alternative embodiments.

One of the inventors has also unexpectedly observed that no obvious reaction resulted from immersion of cetyltrimethylammonium-impregnated zeolite in (or spraying of such impregnated zeolite with) aqueous potassium permanganate (where the weight of the potassium permanganate is in the range from 0.1% to 2% of the weight of the impregnated zeolite). Where the weight of the potassium permanganate in the immersing (or spraying) solution is in the range from 0.1% to 1% of the weight of the impregnated zeolite, the immersion (or spraying) results in application of a permanganate coating to each QAC-impregnated zeolite crystal (in the sense that permanganate enters the channels near each crystal's outer surface but permanganate does not penetrate farther into the interior of each crystal).

Where the weight of the permanganate in the immersing (or spraying) solution is above 1% of the weight of the impregnated zeolite, this inventor has found that immersion of QAC-impregnated zeolite crystals in (or spraying of QAC-impregnated zeolite with) aqueous permanganate results in penetration of permanganate throughout the channels of each crystal (with permanganate displacing QAC from channels not only near each crystal's outer surface but also from channels deep within the interior of each crystal). From a practical point of view, potassium permanganate solution for coating QAC-impregnated zeolite crystals, preferably (at least for many air filtration applications) includes a total weight of permanganate in the range from 0.1% to 0.5% of the weight of the final weight of the permanganate-coated, QAC-impregnated product of the process.

As a result of permanganate leaching studies on potassium permanganate-coated, QAC-impregnated zeolite crystals (in which the coated, QAC-impregnated zeolite crystals were immersed in water and the QAC concentration in the water measured over time), it has been determined that the permanganate coating substantially slowed the QAC leach-

ing rate (and thus would substantially slow the expected activity rate, i.e., the rate at which the impregnated zeolite would absorb contaminants such as organic chemicals).

The activity rate of permanganate-coated, QAC-impregnated zeolite depends on the concentration of the permanganate solution with which the QAC-impregnated zeolite is coated. Increasing the permanganate concentration of the coating solution will decrease the activity rate (until the concentration is reached at which the permanganate penetrates through the entire volume of each zeolite crystal, displacing QAC impregnated throughout such volume). To produce potassium permanganate-coated, QAC-impregnated zeolite for most air filtration applications, the optimum weight of permanganate in the coating solution is in the range from 0.1% to 0.5% of the final weight of the permanganate-coated, QAC-impregnated product of the process.

An optimal QAC-impregnated zeolite product for absorbing any of a wide variety of contaminants (or contaminant groups) from a fluid (such as air or water) can be determined experimentally in the following manner. Uncoated, permanganate-impregnated zeolite crystals are mixed in various ratios with permanganate-coated, QAC-impregnated zeolite crystals, and the contaminant absorption characteristics of each mixture studied. The mixture producing the best absorption characteristics is identified as the optimal mixture.

It may also be useful to mix permanganate-coated, QAC-impregnated zeolite crystals with QAC-coated, permanganate-impregnated zeolite crystals.

The characteristics of a QAC (or permanganate) coating on a zeolite crystal impregnated with permanganate (or QAC) can be varied to control the reaction rate of the substance impregnated within the zeolite. Such characteristics can be varied by changing the concentration of the coating solution in which (or with which) the impregnated zeolite crystal is immersed (or sprayed) to form the coating.

Important aspects of the invention are methods for producing zeolite crystals impregnated with manganese dioxide, the product of such methods, and methods for using such manganese dioxide-impregnated zeolite crystals to absorb contaminants from fluid (especially liquids).

One preferred technique for producing the inventive manganese dioxide-impregnated crystals is to flow a gas comprising one or more of hydrogen, nitrogen, ethylene, and formaldehyde through a bed of permanganate-impregnated zeolite crystals (preferably, with the crystals enclosed in a vessel or other container having a gas inlet and a gas outlet). Alternatively, the permanganate-impregnated zeolite crystals are caused to flow through a non-flowing volume of such gas. Also alternatively, the gas which flows through the permanganate-impregnated zeolite crystals comprises one or more of hydrogen, nitrogen, ethylene, formaldehyde, and other gases similar to these gases (but not H_2S gas).

In another preferred embodiment, the invention produces manganese dioxide-impregnated zeolite crystals from zeolite crystals impregnated with permanganate (with or without a QAC coating) in the following manner. The permanganate-impregnated zeolite crystals (e.g., crystals having a potassium permanganate content of about 4% and a moisture content of about 15%) are employed to filter fluid (such as air or liquid water) containing a gas (e.g., a contaminant gas) comprising one or more of hydrogen, nitrogen, ethylene, and formaldehyde. The filtration can be performed either by flowing the fluid through the crystals or by flowing the crystals through the fluid. During the filtration step, the crystals eventually become "spent" due to chemical reaction with the fluid (including one or more of the listed gases in the fluid). One of the inventors has recognized that each of the "spent" zeolite crystals is substantially uniformly impregnated with manganese dioxide throughout its volume.

One mechanism by which permanganate-impregnated zeolite becomes impregnated with manganese dioxide (as it becomes "spent" when employed to filter air) is believed to be as follows. This example assumes that the zeolite is initially impregnated with potassium permanganate ($KMnO_4$), and that the potassium permanganate-zeolite is employed to filter air contaminated with ethylene (C_2H_4). The following reaction is believed to explain the result that manganese dioxide forms in the pores throughout the volume of each zeolite crystal as it becomes "spent" (activated to MnO_2):

$$KMnO_4+C_2H_4 \rightarrow KMnO_2+CO_2+H_2O.$$

In a variation on the previous example, the air is contaminated with another oxidizable gas similar to ethylene, such as formaldehyde (HCHO). In the latter case, the following reaction is believed to explain the result that manganese dioxide forms in the pores throughout the volume of each zeolite crystal as it becomes "spent" (activated to MnO_2):

$$KMnO_4+HCHO+H_2O \rightarrow KOH+CO_2+MnO_2+H_2O.$$

FIG. **3** represents a "spent" zeolite crystal produced according to the invention, having channels substantially uniformly impregnated with manganese dioxide **6** throughout the crystal's volume.

The manganese dioxide-impregnated zeolite crystals of the invention can be coated with a QAC (or with a permanganate), e.g., as a result of any of the above-described coating operations. FIG. **4** represents one such coated, impregnated crystal, whose channels contain QAC **8** in the region near the crystal's surface, and whose channels are impregnated with manganese dioxide **6**A throughout the volume of the crystal inside the region containing QAC **8**. The presence of such a QAC coating allows regulated time release control of the impregnating manganese dioxide **6**A (which is an oxidizing filtering agent), and thus permits a controlled diffusion (or absorption) rate in applications in which QAC-coated, manganese dioxide-impregnated zeolite crystals are employed to absorb contaminants from a fluid (especially a liquid such as water). The characteristics of the QAC coating can be varied to control the reaction rate of the impregnating substance (manganese dioxide) within the zeolite crystals. Such characteristics can be varied by changing the concentration of the coating solution employed to coat the impregnated zeolite crystals.

The manganese dioxide-impregnated zeolite crystals, or QAC-coated, manganese dioxide-impregnated zeolite crystals of the invention, can be used for a variety of molecular sieving applications, such as filtration of contaminants from fluid (especially liquid). Various combinations of such coated and uncoated crystals can be employed to match specific environmental circumstances which can be calculated by analysis of the fluid to be treated.

To perform fluid filtration, the fluid is caused to flow through a bed of the inventive manganese dioxide-impregnated zeolite crystals (coated or uncoated), or the crystals are caused to flow through the fluid.

Other embodiments of the invention are a process for producing zeolite crystals impregnated with phosphoric acid, phosphoric acid-impregnated zeolite crystals produced by such process, and methods for using phosphoric acid-impregnated crystals to absorb contaminants from fluid.

Zeolite crystals have some capacity to absorb NH_3 due to their cation exchange capacity. By impregnating zeolite crystals uniformly throughout their volume with phosphoric acid (to cause the impregnated zeolite crystals to include from 1% to 10% phosphoric acid by weight), the NH_3 absorption capacity is increased greatly (up to five times the NH_3 absorption capacity of non-impregnated zeolite crystals).

Preferably, the impregnation step is performed by immersing the zeolite in (or spraying the zeolite with) aqueous phosphoric acid. The inventive method preferably includes the steps of: dehydrating the zeolite crystals until they have moisture content substantially below their initial moisture content (preferably until their moisture content is about 5%), then immersing the dehydrated zeolite crystals in (or spraying the dehydrated crystals with) an aqueous solution of phosphoric acid at high temperature and thoroughly mixing the resulting slurry, and finally air drying the mixed slurry to produce impregnated zeolite crystals. FIG. **5** represents one such impregnated crystal, having channels uniformly impregnated with phosphoric acid **10**.

Phosphoric acid-impregnated zeolite crystals can be used to control NH_3 odor in fluids such as air (or liquid manure). The reaction for neutralizing NH_3 gas in such fluids is believed to be

$$2NH_3+H_3PO_4 \rightarrow (NH_4)_2HPO_4,$$

where $(NH_4)_2HPO_4$ has no odor.

We contemplate that beds of phosphoric acid-impregnated zeolite crystals can be used in animal confinement facilities to receive liquid animal wastes. Similarly, phosphoric acid-impregnated zeolite crystals can be used for such applications as in cat litter boxes and in stable "freshener" products for filtering air (or liquids).

Other embodiments of the invention are a process for producing zeolite crystals impregnated with one of the following: (1) sodium chlorite, (2) acetic acid, (3) citric acid, and (4) chlorine solution. Other embodiments of the invention are directed to zeolite crystals impregnated with one of the following: (1) sodium chlorite, (2) acetic acid, (3) citric acid, and (4) chlorine solution. Other embodiments of the invention are directed to using zeolite crystals impregnated with one of the chemicals listed directly above (i.e., (1) sodium chlorite, (2) acetic acid, (3) citric acid, and (4) chlorine solution) to absorb contaminants from fluid.

The impregnation step is performed by immersing the zeolite in (or spraying the zeolite with) an aqueous solution of one or more of the following: (1) sodium chlorite, (2) acetic acid, (3) citric acid, and (4) chlorine. The inventive method preferably includes the steps of: dehydrating the zeolite crystals until they have moisture content substantially below their initial moisture content (preferably until their moisture content is about 5%), then immersing the dehydrated zeolite crystals in (or spraying the dehydrated crystals with) one or more of the aqueous solutions listed above (i.e., (1) sodium chlorite, (2) acetic acid, (3) citric acid, and (4) chlorine) at high temperature and thoroughly mixing the resulting slurry, and finally air drying the mixed slurry to produce impregnated zeolite crystals. FIG. **6** represents one such impregnated crystal, having channels uniformly impregnated with a chemical **12** chosen from the following group: (1) sodium chlorite, (2) acetic acid, (3) citric acid, and (4) chlorine solution. Chemical **12** is alternatively a mixture of two or more of these substances.

Other embodiments of the invention are a process for producing zeolite crystals impregnated with one of the following: (1) sodium sulfite, (2) sodium bisulfite (also called sodium metabisulfite), and (3) ferrous sulfate. Other embodiments of the invention are directed to zeolite crystals impregnated with one of the following: (1) sodium sulfite, (2) sodium bisulfite, and (3) ferrous sulfate. Other embodiments of the invention are directed to using zeolite crystals impregnated with one of the chemicals listed directly above (i.e., (1) sodium sulfite, (2) sodium bisulfite, and (3) ferrous sulfate) to absorb contaminants from fluid.

The impregnation step is performed by immersing the zeolite in (or spraying the zeolite with) an aqueous solution of one or more of the following: (1) sodium sulfite, (2) sodium bisulfite, and (3) ferrous sulfate. The inventive method preferably includes the steps of: dehydrating the zeolite crystals until they have moisture content substantially below their initial moisture content (preferably until their moisture content is about 5%), then immersing the dehydrated zeolite crystals in (or spraying the dehydrated crystals with) one or more of the aqueous solutions listed above (i.e., (1) sodium sulfite, (2) sodium bisulfite, and (3) ferrous sulfate) at high temperature and thoroughly mixing the resulting slurry, and finally air drying the mixed slurry to produce impregnated zeolite crystals. FIG. **7** represents one such impregnated crystal, having channels uniformly impregnated with a chemical **14** chosen from the following group: (1) sodium sulfite, (2) sodium bisulfite, and (3) ferrous sulfate. Chemical **14** is alternatively a mixture of two or more of these substances.

Some of the impregnated zeolite crystals described above can be used in a process to produce Chlorine dioxide (ClO_2). Chlorine dioxide is useful for killing biological contaminants such as microorganisms, mold, fungi, yeast and bacteria.

First, a fluid containing oxygen (typically, but not necessarily air) is caused to move relative to a first bed of: (1) zeolite crystals which are impregnated with sodium chlorite ($NaClO_2$) or (2) a mixture of zeolite crystals impregnated with sodium chlorite and zeolite crystals impregnated with chlorine. The inclusion of zeolite crystals impregnated with chlorine is thought to enhance sodium dioxide production. Then, the fluid is caused to move relative to a second bed of zeolite crystals impregnated with: (1) phosphoric acid (H_3PO_4), (2) acetic acid (CH_3COOH), or (3) citric acid. Upon moving the fluid (containing oxygen) relative to the second bed, chlorine dioxide is released by one or more of the following equations.

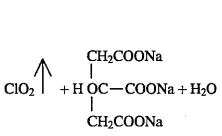
For a phosphoric acid impregnated second bed:

$$O_2+H_3PO_4+NaClO_2 \rightarrow ClO_2\uparrow+NaHPO_4+H_2O$$

For an acetic acid impregnated second bed:

$$O_2+CH_3COOH+NaClO_2 \rightarrow ClO_2\uparrow+CH_3COONa \text{ (sodium acetate)}+H_2O$$

For a citric acid impregnated second bed:



While the foregoing process for producing ClO_2 has been described with reference two distinct (first and second) beds of impregnated zeolite crystals, a single bed containing a mixture of crystals can be used as long as the mixed bed contains both impregnated zeolite crystals from the first bed described above and zeolite crystals from the second bed described above. As an illustrative example, a mixture bed of zeolite crystals impregnated with sodium chlorite, mixed with zeolite crystals impregnated with phosphoric acid can be used to produce chlorine dioxide (by flowing a fluid containing oxygen through it).

While chlorine dioxide can kill microorganisms as described above, chlorine dioxide itself is a contaminant. Therefore, it is sometimes desirable to remove chlorine dioxide from the fluid stream after the chlorine dioxide has performed biological purification of the fluid stream. Another aspect of the present invention relates to a multi-step filtration process in which chlorine dioxide is first produced in a fluid stream and, subsequently, removed from the fluid stream.

First, a fluid is cased to be moved relative to primary bed(s) of zeolite crystals which will cause chlorine dioxide to be released, as described above. These primary bed(s) of zeolite crystals may include a first and second bed, or a mixture bed, as described above. Upon moving relative to the primary bed(s), chlorine dioxide is released (generally as a gas) and biological contaminants are killed in the fluid.

Then, the fluid is moved relative to a secondary bed (filter) of zeolite crystals impregnated with one of the following: (1) potassium hydroxide (KOH), (2) sodium sulfite, (3) sodium bisulfite, and (4) ferrous sulfate. The zeolite crystals of the secondary bed react with the chlorine dioxide to remove the chlorine dioxide from the fluid. Some chemical equations describing possible reactions in the secondary bed follow.

For a secondary bed of potassium hydroxide:

$$2KOH+2ClO_2 \rightarrow KClO_2+KCLO_4+H_2O$$

For a secondary bed of sodium sulfite:

$$ClO_2+ Na_2SO_3 \rightarrow H_2O+S_2O_5+ H^+_3ClO_3$$

Note that H^{+++} from the acids involved in the previous reactions cancel this reaction.

For a secondary bed of sodium bisulfite:

$$ClO_2+Na_2SO_5 \rightarrow H_2O+S_2O_5+ H^+_3ClO_3$$

Note that H^{+++} from the acids involved in the previous reactions cancel this reaction.

The preferred composition of the secondary bed is ferrous sulfate. For a secondary bed of ferrous sulfate:

$$ClO_2 + Fe^{++}SO_4 \longrightarrow$$

$$Fe^{+++} + Cl^- + ClO_2^- \longrightarrow FeCl_3 \text{ (primarily).}$$

When using a secondary bed of ferrous sulfate a color change, from white to brown, takes place. This is an indicator of neutralization.

Various modifications and variations of the described method of the invention will be apparent to those skilled in the art without departing from the scope and spirit of the invention. Although the invention has been described in connection with specific preferred embodiments, it should be understood that the invention as claimed should not be unduly limited to such specific embodiments.

What is claimed is:

1. A method for producing chlorine dioxide, including the steps of:

(a) moving a fluid containing oxygen through a first bed of impregnated zeolite crystals, which are impregnated with at least sodium chlorite; and

(b) moving the fluid through a second bed of impregnated zeolite crystals, which are impregnated with at least one of the following impregnating agents: phosphoric acid, acetic acid, and citric acid, thereby producing the chlorine dioxide as a result of chemical reaction of the fluid and said sodium chlorite and said at least one of the impregnating agents.

2. The method of claim **1** wherein the fluid is moved first through the first bed and then through the second bed.

3. The method of claim **1** wherein the first bed consists essentially of zeolite crystals impregnated with sodium chlorite.

4. The method of claim **1** wherein the first bed consists essentially of a mixture of zeolite crystals impregnated with sodium chlorite and zeolite crystals impregnated with chlorine.

5. The method of claim **1** wherein the chlorine dioxide is produced as a gas.

6. The method of claim **1** wherein the fluid is air.

7. The method of claim **1**, wherein the fluid includes microorganisms, and further including the step of:

(c) exposing the microorganisms to the chlorine dioxide thereby killing at least some of said microorganisms.

8. The method of claim **1**, wherein the first bed of impregnated zeolite crystals comprises zeolite crystals impregnated with sodium chlorite and zeolite crystals impregnated with chlorine.

9. The method of claim **1**, also including the steps of:

(c) before step (a), dehydrating zeolite crystals to substantially decrease their moisture content below their initial moisture content, thereby producing dehydrated zeolite crystals;

(d) after step (c) but before step (a), adding to the dehydrated zeolite crystals an aqueous solution of sodium chlorite, thereby producing wet impregnated zeolite crystals;

(e) after step (d) but before step (a), drying the wet impregnated zeolite crystals to produce the impregnated zeolite crystals, wherein said impregnated zeolite crystals have channels uniformly impregnated with sodium chlorite; and

(f) after step (e) but before step (a), providing the first bed of said impregnated zeolite crystals.

10. The method of claim **6**, wherein the fluid includes microorganisms, and further including the step of:

(c) exposing the microorganisms to the chlorine dioxide thereby killing at least some of said microorganisms.

11. A method for producing chlorine dioxide, including the step of:

moving a fluid containing oxygen through a mixture bed comprising a mixture of a first type of impregnated zeolite crystals and a second type of impregnated zeolite crystals, thereby producing the chlorine dioxide, with the first type of impregnated zeolite crystals comprising zeolite crystals impregnated with at least sodium chlorite, and with the second type of impregnated zeolite crystals comprising zeolite crystals impregnated with one of the following impregnating agents: phosphoric acid, acetic acid, and citric acid, whereby the chlorine dioxide is produced as a result of chemical reaction of the fluid and said sodium chlorite and said at least one of the impregnating agents.

12. The method of claim **11**, wherein the first type of impregnated zeolite crystals comprise zeolite crystals impregnated with sodium chlorite and zeolite crystals impregnated with chlorine.

13. The method of claim **11**, wherein the chlorine dioxide is produced as a gas.

14. The method of claim **11** wherein the fluid is air.

15. The method of claim **11**, wherein the fluid includes microorganisms, and further including the step of:

(c) exposing the microorganisms to the chlorine dioxide thereby killing at least some of said microorganisms.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 5,567,405
DATED : October 22, 1996
INVENTOR(S) : Fred Klatte, et. al.

It is certified that error appears in the above-indentified patent and that said Letters Patent is hereby corrected as shown below:

On the cover page, under Inventors, "David Biswell, Kings Bang, Calif." should read -- David Biswell, Kingsburg, Calif. --;

In Col. 10, line 30, "sodium" should be replaced by -- chlorine --; and

In Col. 11, line 9, "cased" should be replaced by -- caused --.

Signed and Sealed this

Eighteenth Day of February, 1997

Attest:

Attesting Officer

BRUCE LEHMAN

Commissioner of Patents and Trademarks

Method of controlling floating virus infection

Nov 27, 2006 - Taiko Pharmaceutical Co., Ltd.

A method of controlling floating virus infection. The method includes the step of: supplying chlorine dioxide gas into a space where floating virus can be present by a gas concentration which allows the animal to live or stay, but deactivates the virus.

Latest Taiko Pharmaceutical Co., Ltd. Patents:
- Unit for chlorine dioxide generation and chlorine dioxide generation device
- Chlorine dioxide generator
- Chlorine dioxide production device and chlorine dioxide production method
- ELECTROLYTIC CHLORINE DIOXIDE GAS MANUFACTURING DEVICE
- Portable intake air sterilizing apparatus

Skip to: Description · Claims · References Cited · Patent History · Patent History

Description

CROSS REFERENCE TO RELATED APPLICATIONS

This is a national stage application of PCT/JP2006/323581, filed on Nov. 27, 2006, which claims priority of Japanese application No. 2005-342503, filed on Nov. 28, 2005. The disclosures of these prior applications are incorporated by reference in their entirety.

TECHNICAL FIELD

The present invention relates to a method of controlling floating virus infection.

BACKGROUND ART

In case e.g. a worker infected with a certain type of respiratory virus is present in an office or the like, there is the risk of infection with the same respiratory virus for the other workers working within the same office. In such case, such infected workers may develop poor physical condition and experience eventual onset of the respiratory organ viral disease, thus leading to significant deterioration in the working efficiency in that office.

Here, the term respiratory virus, is a generic name for various viruses which cause respiratory diseases such as pneumonia in animals. Among them are included influenza virus, parainfluenza virus, rhinovirus, bird flu virus, SARS virus, corona virus, etc.

Infection with such respiratory virus and subsequent onset of respiratory virus disease can sometimes result in death of the subject.

Such respiratory viruses exist also in droplets exhaled from a respiratory organ of the infected subject. As the droplets can float in the air, inhalation of droplets containing the respiratory virus leads to spread of the infection and the spread of the respiratory virus.

Incidentally, though not commonly called "respiratory viruses", measles virus and rubella virus belong in the same category as above because inhalation by an un-infected subject of air contaminated with droplets from a respiratory organ of an infected subject causes secondary infection through the respiratory organ of the former.
For preventing spreading of respiratory virus, one effective measure is eliminating and/or deactivating the respiratory virus floating in the room (in the air). As one example of a method of deactivating respiratory virus floating in a room, there is a method called fumigation (see Non-Patent Document 1).
Non-Patent Document: "Sterilization/Disinfection Manual", Ishiyaku Publishing Inc. 1991, Sterilization/Disinfection Manual Compiling Committee.

DISCLOSURE OF THE INVENTION

Object to be Achieved by Invention

Fumigation is a method wherein a hermetically closed room is filled with a gas prepared by evaporating an agent so as to kill insects, mites, fungus present inside the room. Some examples of the agent employed for fumigation are formalin, methyl bromide, aluminum phosphide, cyanide fume, etc.
However, such agents employed for fumigation are very poisonous for living bodies. So, during fumigation process, workers need to stop their works and evacuate from inside the room, thus leading to deterioration in the working efficiency.
The present invention has been made in view of the above-described state of the art. The invention provides a method of controlling floating virus infection, capable of preventing e.g. virus infection to an animal while the animal is allowed to live or stay safely inside a space where the animal is present and viruses are floating.

Means to Achieve the Object

According to a first characterizing feature of the inventive method of controlling floating virus infection for achieving the above-noted object, the method comprises the step of supplying chlorine dioxide gas into a space where floating virus can be present by a gas concentration which allows the animal to live or stay, but deactivates the virus.

Chlorine dioxide gas has strong oxidative power and sterilizing power as well as strong virus deactivating power. For this reason, by exposing the floating virus to chlorine dioxide gas, the floating virus can be deactivated.
In this specification, the term “deactivation” refers to a condition of e.g. floating virus being destroyed, thus becoming unable to proliferate in a host, or a condition of the floating virus being still active, but hardly capable of proliferation in a host.
Therefore, if chlorine dioxide gas is supplied to a certain space and the concentration of the gas within the space is maintained at such a concentration as to deactivate the floating virus, even if floating virus is newly introduced into the space, this floating virus can be deactivated immediately. Accordingly, it is possible to prevent virus infection to the animal present within that space.

Moreover, as the concentration of chlorine dioxide within the space is such that the animal is allowed to live or stay, but the floating virus is deactivated, the animal can lead a normal living in the space. Therefore, it is possible to e.g. maintain air inside an office under the condition for deactivating floating virus, while allowing workers to continue work in this office. Consequently, secondary infection with the virus can be effectively prevented to allow the workers to maintain their health. And, also, there occurs no deterioration in the working efficiency since the work need not be suspended during an air cleaning operation by e.g. fumigation.

Incidentally, the term “animal” refers to any animal or living creature which lives or stays within the space and can be infected with the floating virus, including mammals such as humans, domestic livestock, birds, reptiles, etc.

According to a second characterizing feature of the present invention, the method comprises the step of supplying chlorine dioxide gas into a space where floating virus can be present by a gas concentration which allows the animal to live or stay, but can prevent infection of the animal with the virus.

With this characterizing construction, the floating virus loses its infectability, thus being incapable of inter-host infection. Here, the language “lose infectability” refers to such a condition where the floating virus experiences denaturation in its surface proteins required for host infection, so that the virus can no longer infect the host.

Therefore, inter-host infection can be prevented and the possibility of the animal’s being infected with the floating virus and onset of viral disease associated therewith can be significantly reduced.

According to a third characterizing construction of the present invention, the method comprises the step of supplying chlorine dioxide gas into a space where floating virus can be present by a gas concentration which allows the animal to live or stay, but can prevent onset of viral disease in the animal infected with the virus.
With this characterizing construction, even if the animal is infected with the floating virus, the possibility of onset of viral disease in the infected animal can be reduced.

According to a fourth characterizing construction of the present invention, the method comprises the step of supplying chlorine dioxide gas into a space where floating virus can be present by a gas concentration which allows the animal to live or stay, but can treat the animal infected with the virus and with onset of the viral disease associated therewith.

With this characterizing construction, even if the animal is infected with the floating virus and the animal experiences subsequent onset of the viral disease, the symptoms of this disease can be alleviated and its contraction period can be shortened.

According to a fifth characterizing construction of the present invention, the concentration of the chlorine dioxide gas within the space is set from 0.0001 ppm to 0.1 ppm.

With this characterizing construction, if the concentration of the chlorine dioxide gas within the space is under 0.0001 ppm, it is difficult to deactivate the floating virus. Further, as the working environment standard value for chlorine dioxide is 0.1 ppm, a value greater than 0.1 ppm can be harmful for the animal. Therefore, by setting the chlorine dioxide gas concentration within the space at the extremely low concentration from 0.0001 ppm to 0.1 ppm, the floating virus can be deactivated and at the same time the animal can live or stay more safely in the space.

According to a sixth characterizing construction of the present invention, the floating virus comprises respiratory virus.

With this characterizing construction, prevention of respiratory virus infection and prevention and treatment of possible respiratory disease (e.g. pneumonia) which may develop after the infection can be effectively carried out.
According to a seventh characterizing construction of the present invention, the respiratory virus comprises influenza virus.
With this characterizing construction, prevention of influenza virus infection and prevention and treatment of various possible syndromes (e.g. fever attack, runny nose, sore throat, etc.) which may develop after the infection can be effectively carried out.

BEST MODE OF EMBODYING THE INVENTION

[Embodiments]

The present invention may be implemented with using an appropriate chlorine dioxide generator, for example.
Some non-limiting examples of chlorine dioxide generator suitable for the present invention include a large stationary apparatus, a small stationary apparatus, a small portable apparatus, and an instrument configured to charge a generating agent into gel or mix a dry agent therewith so as to generate a low concentration of chlorine dioxide gas for an extended period of time in a semi-automatic manner. However, the invention is not limited thereto, but it is also possible to employ an apparatus configured to discharge a low concentration of chlorine dioxide gas into a mouth.

The above chlorine dioxide generator apparatus comprises a reaction vessel, drug solution tanks capable of reserving respective drug solutions therein, liquid pumps, an air pump, a diluter, etc.

There are provided two kinds of drug solution tanks, each receiving therein chlorite water solution or acid therein. Some examples of chlorite usable are alkali metal chlorite (sodium chlorite, potassium chlorite, lithium chlorite), or alkali earth metal chlorite (calcium chlorite, magnesium chlorite, barium chlorite) . . . etc. However, the invention is not limited thereto.

Some examples of acid usable are inorganic acids including hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid. However, the invention is not limited thereto.

The liquid pump is provided as accompanying the drug solution tank. The pump is capable of precision control of liquid feed by means of a timer.

By the liquid pump, predefined amounts of chlorite water solution and acid solution are sent into the reaction vessel periodically, in which the solutions are mixed and reacted with each other to generate chlorine dioxide gas. The chlorine dioxide gas thus generated is mixed in the diluter with a predetermined rate of air sent by the air pump to be diluted to a predetermined concentration (preferably, 0.8 ppm).

The diluted chlorine dioxide gas is then supplied into a desired space where floating viruses can be present and the concentration of the chlorine dioxide gas within this space is maintained at a concentration which allows an animal to live or stay, but deactivates the viruses.

This concentration can be a concentration capable of preventing infection of the animal with the floating virus, or a concentration capable of preventing onset of a viral disease in the animal infected with the floating virus, or a concentration capable of treating the animal which has been infected with the floating virus and in which the disease associated therewith has developed.

Specifically, based on results of influenza infection experiments using mice to be detailed later, this concentration is maintained to range from 0.05 ppm to 0.1 ppm.

Further, the concentration of chlorine dioxide can be set in the following manners for example. In the influenza infection experiment using mice to be described later, the mice were infected by administrating thereto a high concentration of virus greater than 10 LD . In general, when there occurs respiratory viral infectious disease within such a large structure as a theater, an extremely low concentration of virus can be a problem. For instance, even such low concentration thereof as low as 0.02 LD can cause infection.

In the above situation, the virus concentration in the air is about 1/500 of the above-noted concentration (10 LD /0.02 LD). Therefore, the concentration of chlorine dioxide gas required for preventing influenza infection is 0.0001 ppm (0.05/500).
That is to say, according to the present invention, by using the chlorine dioxide generator described above, the concentration of chlorine dioxide inside the space is maintained at the extremely low concentration (0.0001 to 0.1 ppm). With this, it becomes possible to maintain the chlorine dioxide gas concentration at such a concentration which can constantly be safe for the animal and which can, at the same time, deactivate the floating virus or deprive it of its infectability.

The space to which the present invention is applicable includes a space that people enter/exit, such as a theater, an airport lobby, a business office, a classroom, or a space where animals are raised or plants are grown such as a mouse cage, a vinyl house, etc. or even such a “space” as oral cavity of a human, etc. However, the invention is not limited thereto. The invention can be applied to any other desired space which can assume, as desired, a closed state or an opened state.

(Floating Virus)

The “floating virus” as used herein refers to any virus which can float inside the abovedescribed space. Some examples thereof include respiratory viruses, such as influenza virus, parainfluenza virus, rhinovirus, bird flu virus, SARS virus, corona virus, RS virus,

etc. However, the invention is not limited thereto. The present invention is applicable to prevention and/or treatment of measles virus and rubella virus as inhalation by an uninfected subject of air contaminated with droplets from a respiratory organ of an infected subject causes secondary infection through the respiratory organ of the former, although these are not commonly called “respiratory viruses”.

(Animal)

The living creature or organism to which the present invention is applied includes any animal or living creature which lives or stays within the space and can be infected with the floating virus, including mammals such as humans, domestic livestock, birds, reptiles, etc.

EXAMPLES

Next, the present invention will be described in details with reference to some examples thereof. It is understood; however, that the present invention is not limited thereto.

(Generation of Chlorine Dioxide Gas)

0.25% sodium chlorite (NaClO) and 0.9% hydrochloric acid are charged and kept within separate drug solution tanks. Then, by using the liquid pump attached to each tank, each solution is sent to the reaction vessel.

Chlorine dioxide generated after the mixing and reaction between the sodium chlorite and hydrochloric acid is added with air introduced thereto and the resultant product is discharged as a gas. In this, the discharged chlorine dioxide gas had a concentration of about 50 ppm. The discharged chlorine dioxide gas was then mixed in the diluter with air of a predetermined flow rate to be diluted to a low concentration.

In this experiment, the diluted and discharged chlorine dioxide gas had a concentration of 0.8 ppm. As will be described later, inside a mouse cage, the gas will be further diluted to 0.08 ppm or lower. The concentrations of the chlorine dioxide gases were determined always by a chlorine dioxide meter (4330-SP, Interscan Corporation, U.S.A.)

(Preparation of Influenza Virus)

The influenza virus employed was prepared and obtained by proliferating Type A influenza strain A/PR8 (H1N1) in a culture medium containing 2% bovine fetal serum, with using, as a host, MDCK cell (ATCC CCL34) which is canine renal cell.

The viruses proliferated as above were suspended in a phosphate buffer solution (PBS) and then rendered into aerosol for subsequent use. In the above, the concentration of the suspended virus was adjusted to be 10, 100 or 1000 times of the concentration (LD) which, if introduced as aerosol into the mouse cage, would kill 50% of mice, respectively.

(Animal Experiment)

Animal experiment was conducted with using 8-week old male CD-1 mice. Fifteen mice, as one group, were put into a mouse cage dimensioned as: 25.5 cm×36.8 cm×8.0 cm. Into this, the aerosol of Type A influenza was introduced at the rate of 12.5 liter per minute.

In the above, at the same time, chlorine dioxide gas at 0.8 ppm concentration was fed at the flow rate of 0.6 to 1.8 liter per minute. The chlorine dioxide gas present within the mouse cage was diluted by the aerosol present therein.

In this experiment, concentration settings of 0 ppm, 0.03 ppm, 0.05 ppm and 0.08 ppm, as actually determined within the mouse cage, were possible for the chlorine dioxide gas. Data at these four kinds of concentration were obtained.

The exposure period for the mice to the virus aerosol was set to 15 minutes.
In principle, the introduction of chlorine dioxide gas was effected simultaneously with the introduction of the virus-containing aerosol. In some of the experiments, however, the introduction of chlorine dioxide gas was effected with delays relative to the introduction of the virus-containing aerosol. This was done in order to check whether the chlorine dioxide gas can prevent onset of viral disease resulting from the virus which has entered the lungs already.

As a control experiment, a phosphate buffer solution not containing any virus was employed and aerosol of this phosphate buffer solution was introduced into the mouse cage.

For those mice after the virus exposure, one mouse after another thereof was put into a separate mouse cage and kept therein in isolation for two weeks. During this period, in order to check presence/absence of virus infection and degree thereof (the number of virus), lung tissues were excised from five of the total fifteen mice.

The excised lungs were ground/crushed and then viruses were separated therefrom and the amount thereof was quantified.

For this quantification of the viruses within the lung, the crushed lung substance was suspended and its dilution series were prepared temporarily. Then, these were infected to the culture cells and TCID values (50% tissue culture infection amount) were obtained.

On the other hand, as to the remaining 10 mice, life or death thereof was observed until day 14. During this period, if a mouse died in this period, its lung tissue was excised therefrom and fixed in formalin at that timing. If a mouse did not die in this period, then, its tissue was excreted and fixed in formalin on day 14. And, histophathologic analysis was conducted thereon by the standard method.

(Simultaneous Administration of 0.08 ppm Chlorine Dioxide Gas)
Mice were exposed to aerosol containing 1000 LD virus for 15 minutes and to these mice,

chlorine dioxide gas at 0.08 ppm concentration (final concentration inside the mouse cage) was administered simultaneously. The life and death of these mice are shown below (Table 1)

TABLE 1 Number of mice which died after exposure to virus (data for 10 mice in each group) days after exposure 3 4 5 8 9 10 14 0 ppm 0 8 10 10 10 10 10 group 0.08 ppm 0 0 0 0 6 10 10 group

As may be apparent from Table 1 above, it may be understood that the deaths occurred with delay in the mice administered with the 0.08 ppm chlorine dioxide gas. On this difference, statistical significant difference test can be done. Its significance level (risk rate) was under 0.0001 ($P<0.0001$). That is, this difference was found to have “statistical significance”.

Next, respecting the same experiment, from each 15 mice group 3 days after virus exposure, 5 mice were sampled from each group and their lung tissues were excreted and crushed and the virus contained therein was quantified (Table 2).

TABLE 2 Total virus amount in lung tissues on Day 3 (TClD values) serial mouse number 1 2 3 4 5 0 ppm 10 10 10 10 10 group serial mouse number 6 7 8 9 10 0.08 ppm 10 10 10 10 10 group

As shown in Table 2, when the numbers of virus in all the tissues were represented as TCID values, the average value of the 0 ppm group was 10 , and the average value of the 0.08 ppm administration group was 10 , respectively. That is to say, the values of the group administered with the 0.08 ppm chlorine dioxide gas was only 5% of that of the control group (0 ppm group) (note the values are represented in the logarithm system). Based on the above, it is believed that in the presence of chlorine dioxide gas, proliferation of virus was restricted or the amount of virus having infectability at the time of infection was small.

These conditions can be interpreted to be a condition where the floating viruses lost activity and could hardly proliferate in the bodies of mice or a condition where the infection to the mice was prevented due to insufficient infectability of the floating viruses.

From the above, it has been found that if influenza virus is present at the concentration of 1000 LD , inhibitory effect against onset of influenza can be obtained with administration of 0.08 ppm chlorine dioxide gas.

Subsequently to the above, a similar experiment was conducted with varying the concentration of virus to which mice were exposed.

In this experiment, aerosols of virus with concentrations of 10 LD (10 times greater than LD) and 100 LD (100 times greater than LD) were introduced to the mouse cages for 15 minutes; and at the same time, 0.08 ppm (final concentration inside the mouse cage) chlorine dioxide gas was introduced to the mouse cages.

As a result, in the case of the virus administered group with the 10 LD virus concentration, no onset of influenza was found for 14 days in the group administered with 0.08 ppm chlorine dioxide. (Table 3).

TABLE 3 Number of mice which died after exposure to 10 LD virus (data for 10 mice in each group) days after exposure 3 4 5 8 9 10 14 0 ppm 0 0 0 5 7 10 10 group 0.08 ppm 0 0 0 0 0 0 0 group

Also, the amount of virus in the lungs of the mice on Day 3 after the virus exposure was clearly lower for the chlorine dioxide administered group. (Table 4)

TABLE 4 Total virus amount in lung tissues on Day 3 after 10 LD virus exposure (TClD values) serial mouse number 21 22 23 24 25 0 ppm 10 10 10 10 10 group serial mouse number 26 27 28 29 210 0.08 ppm 10 10 10 10 10 group

Further, in the virus administered group with 100 LD virus concentration too, no onset of influenza after the virus exposure was found (Table 5) and the virus amount in the lung (Table 6) was small for the chlorine dioxide gas administered group.

TABLE 5 Number of mice which died after exposure to 100 LD virus (data for 10 mice in each group) days after exposure 3 4 5 8 9 10 14 0 ppm 0 0 3 6 8 10 10 group 0.08 ppm 0 0 0 0 0 0 0 group

TABLE 6 Total virus amount in lung tissues on Day 3 after 100 LD virus exposure (TClD values) serial mouse number 31 32 33 34 35 0 ppm 10 10 10 10 10 group serial mouse number 36 37 38 39 310 0.08 ppm 10 10 10 10 10 group

From the above, it has been found that in the cases of influenza virus being present at the concentrations of 10 LD and 100 LD , sufficient inhibitory effect against onset of

influenza can be obtained with administration of 0.08 ppm chlorine dioxide gas.
(Simultaneous Administration of 0.05 ppm Chlorine Dioxide)

Next, regarding the case of administration of 10 LD concentration virus, investigation was made on the effect of simultaneous administration of an even lower concentration (0.05 ppm) of chlorine dioxide. The result showed that no onset of influenza was found in the group of chlorine dioxide administered group (Table 7) and the virus amount in the lung (Table 8) was small.

From the above, it has been found that in the cases of influenza virus being present at the concentrations of 10 LD , onset of influenza can be inhibited with simultaneous administration of 0.05 ppm chlorine dioxide gas.

TABLE 7 Number of mice which died after exposure to 10 LD virus with simultaneous administration of 0.05 ppm chlorine dioxide (data for 10 mice in each group) days after exposure 3 4 5 8 9 10 14 0 ppm 0 0 4 5 8 10 10 group 0.05 ppm 0 0 0 0 0 0 0 group

TABLE 8 Total virus amount in lung tissues on Day 3 after 10 LD virus exposure with simultaneous administration of 0.05 ppm chlorine dioxide (TClD values) serial mouse number 41 42 43 44 45 0 ppm 10 10 10 10 10 group serial mouse number 46 47 48 49 410 0.05 ppm 10 10 10 10 10 group

(Simultaneous Administration of 0.03 ppm Chlorine Dioxide)

Next, regarding the case of administration of 10 LD concentration virus, investigation was made on the effect of simultaneous administration with further reducing the concentration of chlorine dioxide to 0.03 ppm. The result showed that between the group of chlorine dioxide administered group (0.03 ppm) and the control group (0 ppm) no significant difference was found in the number of onsets of influenza (Table 9) or the virus amount in the lung (Table 10).

TABLE 9 Number of mice which died after exposure to 10 LD virus with simultaneous administration of 0.03 ppm chlorine dioxide (data for 10 mice in each group) days after exposure 3 4 5 8 9 10 14 0 ppm 0 0 3 7 7 10 10 group 0.03 ppm 0 0 3 8 9 10 10 group

TABLE 10 Total virus amount in lung tissues on Day 3 after 10 LD virus exposure with

simultaneous administration of 0.03 ppm chlorine dioxide (TClD values) serial mouse number 51 52 53 54 55 0 ppm 10 10 10 10 10 group serial mouse number 56 57 58 59 510 0.03 ppm 10 10 10 10 10 group

From the above, it has been found that in the cases of influenza virus being present at the concentration of 10 LD , simultaneous administration of 0.03 ppm chlorine dioxide gas is not effective respecting inhibition of influenza in mice.

Hence, it was confirmed that as the influenza onset inhibitory effect in the case of simultaneous administration of chlorine dioxide gas, the chlorine dioxide gas concentration of at least 0.05 ppm or more is effective in case the virus concentration is 10 LD amount.

Based on the above-described experiments, the chlorine dioxide gas concentration to be maintained at a space can be set in a manner as follows for instance.

In general, when there occurs respiratory viral infectious disease within such a large structure as a theater, an extremely low concentration of virus can be a problem. For instance, even such low concentration as low as 0.02 LD can cause infection.
In the above situation, the virus concentration in the air is about 1/500 of the above-noted concentration (10 LD /0.02 LD). It follows that the chlorine dioxide concentration required for preventing influenza virus infection is 0.0001 ppm (0.05/500). Therefore, the effect of deactivating virus and preventing infection can be expected with setting of the chlorine dioxide concentration to such low concentration values as above.
(Delayed Administration of 0.08 ppm Chlorine Dioxide Gas)

Next, regarding the 10 LD concentration virus administered group, the effect of chlorine dioxide gas was investigated for cases of administrating 0.08 ppm chlorine dioxide gas with delays of 5 minutes, 10 minutes and 15 minutes respectively from the start of virus exposure. In the respective cases, the exposure period to the chlorine dioxide gas was 15 minutes.

The object of this experiment is to confirm whether chlorine dioxide gas when administered with a delay is effective for preventing onset of influenza against viruses which have already reached the lungs and proliferated there, that is, whether it has a “treating effect” for influenza or not.

The results are shown in Table 11 and Table 12 below.

TABLE 11 Number of mice which died after exposure to 10 LD virus with delayed administration of 0.08 ppm chlorine dioxide (data for 10 mice in each group) Days after exposure 3 4 5 8 9 10 14 5 minutes 0 0 3 7 7 10 10 delayed administration group 10 minutes 0 0 4 9 10 10 10 delayed administration group 15 minutes 0 2 6 10 10 10 10 delayed administration group

TABLE 12 Total virus amount in lung tissues on Day 3 after 10 LD virus exposure with delayed administration of 0.08 ppm chlorine dioxide (TClD values) Serial Mouse Number 61 62 63 64 65 5 minutes 10 10 10 10 10 delayed administration group Serial Mouse Number 71 72 73 74 75 10 minutes 10 10 10 10 10 delayed administration group Serial Mouse Number 81 82 83 84 85 15 minutes 10 10 10 10 10 delayed administration group

The results of determination of the total virus amounts showed that the amounts were smaller than expected in spite of the fact that chlorine dioxide gas was administered after lapse of 15 minutes from the virus exposure. Based on this, it is reasoned that delayed administration of chlorine dioxide gas can alleviate the symptoms of influenza.

This result shows that even when influenza virus has already been fixed to the tissue of respiratory organ and proliferated, symptoms of influenza can be restricted with delayed administration of chlorine dioxide gas. This suggests the potential of chlorine dioxide gas achieving treating effect to animals with onset of influenza.
(Experiment of Protein Denaturation with Low Concentration Chlorine Dioxide)
In this embodiment, it has been described based on influenza virus infection experiments using mice that chlorine dioxide gas, even at an extremely low concentration of e.g. 0.05 to 0.1 ppm, is capable of deactivating virus or depriving its infectability.

Such anti-virus effect of chlorine dioxide can be explained based on the following experiment.

In this experiment, glucose-6-phosphate dehydrogenase (referred to shortly as “G6PD” hereinafter) which is an enzyme of yeast was reacted with a low concentration of chlorine dioxide and investigation was made to see how the enzyme activity of G6PD would change. Chlorine dioxide was dissolved in PBS buffer (20 mM sodium phosphate buffer, pH7, 130 mM NaCl) to final concentrations of 0.1, 1, 10, 100, 1000 μM (0.007, 0.07, 0.7, 7, 70 ppm, respectively if converted into ppm concentration values) (these will be referred to as chlorine dioxide solutions hereinafter). G6PD was dissolved in each chlorine dioxide solution to a final concentration of 80 μg/mL and reaction was allowed to continue at 25° C. for 2 minutes.

The enzyme activity of G6PD was determined by observing absorption of NADPH by a spectral photometer, with using NADP and glucose-phosphoric acid as the substrate. Specific reaction conditions were set according to the manufacturer's (Sigma Corp.) instructions.

The determination results of the enzyme activity are shown in FIG. 1. The concentration values on the horizontal axis are shown as being converted into the unit of ppm. The "specific activity" on the vertical axis represents enzyme activity (unit/mg) per 1 mg of protein

The results show that when the chlorine dioxide concentration was 0.07 ppm, there was about 60% reduction (45/71) in the enzyme activity, as compared with the case of chlorine dioxide concentration being 0 ppm.
Therefore, it was found that even a very low concentration of chlorine dioxide as low as about 0.07 ppm can inhibit enzyme activity. This suggests that chlorine dioxide, even at an

extremely low concentration range as proposed by the present invention, provides the antivirus effect of inhibiting enzyme activity.
(Experiment for Confirming Effectiveness of Chlorine Dioxide Against Influenza Virus)
Next, there will be described an experiment conducted to investigate the effect of denaturation of surface proteins present in influenza virus in order to confirm the effectiveness of chlorine dioxide against influenza virus.

On the surface of influenza virus particle, there are two kinds of protein, referred to as hemagglutinin (referred to as HA hereinafter) and neuraminidase (referred to as NA hereinafter).

HA is a protein required at the initial stage of virus infection, that is, required for the virus to bind to the host cell surface and this protein has a function of promoting virus infection. On the other hand, NA is a protein which provides the function of cutting bond between offspring virus proliferated in the host cell and the surface of the host cell, thus separating the virus from the host cell surface. This facilitates diffusion of offspring viruses and spreading of virus infection.

Therefore, with deletion of the HA function, the virus becomes unable to infect or deletion of the NA function can minimize the number of host cells which will be killed by infection. Therefore, it is believed that the infectability of virus will be reduced when at last one of these two proteins loses its function.

Then, investigation was made to see how the functions of the two proteins would change when influenza virus was reacted with chlorine dioxide.
In this experiment, in order to clearly study the denaturing effect of the two proteins relative to chlorine dioxide, the concentration of chlorine dioxide was set so as to range from 2.7 to 21.4 ppm.

Chlorine dioxide was dissolved in PBS buffer (20 mM sodium phosphate buffer to final concentrations of 40, 80, 160, 240 and 320 μM (2.7, 5.4, 10.7, 16.1 and 21.4 ppm, respectively if converted into ppm concentration values) (these will be referred to as chlorine dioxide solutions hereinafter). Influenza virus was dissolved in each chlorine dioxide solution to a final concentration of 77 μg/mL and reaction was conducted on ice for 2 minutes.

After the reaction, titer values of HA were determined by a known blood coagulation reaction test. The results of determination are as shown in Table 13.
TABLE 13 Concentration of reacted chlorine dioxide (ppm) 0 2.7 5.4 10.7 16.1 21.4 HA titer 512 256 32 32 16 4 value

Further, regarding the case of chlorine dioxide concentration being 5.4 ppm, investigation was made on variation in titer value according to the reaction period. The results of determinations are shown in Table 14.

TABLE 14 Reaction period (seconds) 0 5 10 20 30 40 60 120 HA titer 256 16 16 16 16 16 16 16 value

This suggested that when influenza virus is reacted with chlorine dioxide, HA is denatured immediately to lose its function.

Table 15 shows the determination results of NA titer values.

TABLE 15 Concentration of reacted chlorine dioxide (ppm) 0 2.7 5.4 10.7 16.1 21.4 NA titer value 38.8548 37.3824 32.7322 18.7712 10.4366 7.2408 standard 0.698112 1.59382 1.095355 0.677734 0.265636 0.118774 deviation

This suggested that when influenza virus is reacted with chlorine dioxide, NA is denatured immediately to lose its function.

Based on the above, it was confirmed that chlorine dioxide reduces the infectability of influenza virus.

[Other Embodiments]

In the above embodiment, as an example of the "space", a place where virus is present, such a location as a theater where humans enter/exit was described. However, the present invention is not limited thereto. A location where humans enter/exit can be in a liquid such as a swimming pool, bath, etc.

Further, in the foregoing, animals were described as living creatures as the subjects. However, the present invention is not limited thereto. The invention can be applied to plants which have the possibility of being infected with floating virus.

INDUSTRIAL APPLICABILITY

The present invention can be used in a method of controlling floating virus infection.

BRIEF DESCRIPTION OF DRAWING

[FIG. 1] a view showing determination of enzyme activity of G6PD reacted with chlorine dioxide.

Claims

1. A method of controlling respiratory virus infection comprising the step of: supplying chlorine dioxide gas into air of a space that can assume a closed state or an opened state, where respiratory virus that has hemagglutinin and/or neuraminidase on a surface of viral particle thereof can be present, at a concentration which allows an animal that can be infected with the respiratory virus to live or stay, but deactivates the virus, wherein the concentration of the chlorine dioxide gas in the air of the space is from 0.0001 ppm to 0.1 ppm.

2. The method according to claim 1, wherein the respiratory virus comprises influenza virus.

3. A method of controlling respiratory virus infection comprising the step of: supplying chlorine dioxide gas into air of a space that can assume a closed state or an opened state, where respiratory virus that has hemagglutinin and/or neuraminidase on a surface of viral particle thereof can be present, at a concentration which allows an animal that can be infected with the respiratory virus to live or stay, but can treat

infection of the animal with the virus, wherein the concentration of the chlorine dioxide gas in the air of the space is from 0.0001 ppm to 0.1 ppm.

4. The method according to claim 3, wherein the respiratory virus comprises influenza virus.

5. A method of controlling respiratory virus infection comprising the step of: supplying chlorine dioxide gas into air of a space that can assume a closed state or an opened state, where respiratory virus that has hemagglutinin and/or neuraminidase on a surface of viral particle thereof can be present, at a concentration which allows an animal that can be infected with the respiratory virus to live or stay, but can alleviate a symptom of a viral disease of the respiratory virus in the animal infected with the virus, wherein the concentration of the chlorine dioxide gas in the air of the space is from 0.0001 ppm to 0.1 ppm.

6. The method according to claim 5, wherein the respiratory virus comprises influenza virus.

7. A method of controlling respiratory virus infection comprising the step of: supplying chlorine dioxide gas into air of a space that can assume a closed state or an opened state, where respiratory virus that has hemagglutinin and/or neuraminidase on a surface of viral particle thereof can be present, at a concentration which allows an animal that can be infected with the respiratory virus to live or, but can treat the animal infected with the virus in which a viral disease of the respiratory virus has already occurred, wherein the concentration of the chlorine dioxide gas in the air of the space is from 0.0001 ppm to 0.1 ppm.

8. The method according to claim 7, wherein the respiratory virus comprises influenza virus.

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Patent History
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Inventor: Norio Ogata (Osaka)
Primary Examiner: Ernst Arnold
Application Number: 12/085,553
Classifications
Current U.S. Class: Biocides; Animal Or Insect Repellents Or Attractants (e.g., Disinfectants, Pesticides, Etc.) (424/405); Process Disinfecting, Preserving, Deodorizing, Or Sterilizing (422/1); A Gas Is Substance Acted Upon (422/4); Using Gaseous Preservative, Preservative Added To Gaseous Phase Of Environment, Or Maintaining Gaseous Phase Nondestructive (422/9); Using Disinfecting Or Sterilizing Substance (422/28); Using Halogen Or Halogen-containing Compound (422/37); Elemental Chlorine Or Elemental Chlorine Releasing Inorganic Compound (e.g., Chlorties, Hypochlorites, Etc.) (424/661)
International Classification: A01N 25/00 (20060101); A01N 59/00 (20060101); A61L 9/015 (20060101); A61L 2/20 (20060101); A61K 33/20 (20060101);

Biological Efficacy of Chlorine Dioxide

Spaulding Classification:

Bacterial Endospores
(*Clostridium, Bacillus*)
⬇
Mycobacteria
(*Mycobacterium*)
⬇
Non-enveloped, non-lipid viruses
(Parvoviruses)
⬇
Fungi
(*Aspergillus, Stachybotrys*)
⬇
Gram negative vegetative bacteria
(*Escherichia, Pseudomonas*)
⬇
Gram positive bacteria
(*Enterococcus, Staphylococcus*)
⬇
Enveloped, lipid viruses
(Influenza)

Chlorine dioxide gas is highly effective against fungi, viruses, bacteria, and spores both in the laboratory and in real-world settings. Extensive testing has been done using chlorine dioxide on a multitude of specific organisms, and that information can be found in each of the listed tables below. It is not a complete list of organisms in which chlorine dioxide gas is effective against, only a sample of organisms in which chlorine dioxide has been successfully tested against. To date, no organism tested against chlorine dioxide gas has proved resistant. The Spaulding classification listed on the left lists organisms in order of decreasing resistance to sterilizing agents.

As testing is continually being performed on other organisms, updated data will be added to this list as the results come in. If an organism is not listed here, it does not necessarily mean that chlorine dioxide gas is ineffective against it. Please contact us to see if there is any data or information regarding your specific organism, or to arrange for specific organism testing.

Bacteria	Ref.
Blakeslea trispora	28
Bordetella bronchiseptica	8
Brucella suis	30
Burkholderia mallei	36
Burkholderia pseudomallei	36
Campylobacter jejuni	39
Clostridium botulinum	32
Corynebacterium bovis	8
Coxiella burneti (Q-fever)	35
E. coli ATCC 11229	3
E. coli ATCC 51739	1
E. coli K12	1
E. coli O157:H7 13B88	1
E. coli O157:H7 204P	1
E. coli O157:H7 ATCC 43895	1
E. coli O157:H7 EDL933	13

Bacteria	Ref.
Leuconostoc mesenteroides	5
Listeria innocua ATCC 33090	1
Listeria monocytogenes F4248	1
Listeria monocytogenes F5069	19
Listeria monocytogenes LCDC-81-861	1
Listeria monocytogenes LCDC-81-886	19
Listeria monocytogenes Scott A	1
Methicillin-resistant Staphylococcus aureus (MRSA)	3
Multiple Drug Resistant Salmonella typhimurium (MDRS)	3
Mycobacterium bovis	8
Mycobacterium fortuitum	42
Pediococcus acidilactici PH3	1
Pseudomonas aeruginosa	3
Pseudomonas aeruginosa	8
Salmonella	1
Salmonella spp.	2
Salmonella Agona	1
Salmonella Anatum Group E	1
Salmonella Choleraesins ATCC 13076	1
Salmonella choleraesuis	8
Salmonella Enterica (PT30) BAA-1045	1
Salmonella Enterica S. Enteritidis	13
Salmonella Enterica S. Javiana	13
Salmonella Enterica S. Montevideo	13
Salmonella Enteritidis E190-88	1
Salmonella Javiana	1
Salmonella newport	4
Salmonella Typhimurium C133117	1
Salmonella Anatum Group E	1
Shigella	38
Staphylococcus aureus	23
Staphylococcus aureus ATCC 25923	1
Staphylococcus faecalis ATCC 344	1
Tuberculosis	3
Vancomycin-resistant Enterococcus faecalis (VRE)	3
Vibrio strain Da-2	37
Vibrio strain Sr-3	37
Yersinia enterocolitica	40
Yersinia pestis	30
Yersinia ruckerii ATCC 29473	31

Algae/Fungi/Mold/Yeast	Ref.
Aspergillus egyptiacus	28
Aspergillus elongatus	28
Aspergillus fischeri	28
Aspergillus fumigatus	28
Aspergillus giganteus	28
Aspergillus longivesica	28
Aspergillus niger	12
Aspergillus ochraceus	28
Aspergillus parvathecius	28
Aspergillus sydowii	28
Aspergillus unguis	28
Aspergillus ustus	28
Aspergillus versicolor	28
Botrytis species	3
Candida spp.	5
Candida albicans	28
Candida dubliniensis	28
Candida maltosa	28
Candida parapsilosis	28
Candida sake	28
Candida sojae	28
Candida spp.	5
Candida tropicalis	28
Candida viswanathil	28
Chaetomium globosum	7
Cladosporium cladosporioides	7
Debaryomyces etchellsii	28
Eurotium spp.	5
Fusarium solani	3
Lodderomyces elongisporus	28
Mucor circinelloides	28
Mucor flavus	28
Mucor indicus	28
Mucor mucedo	28
Mucor rademosus	28
Mucor ramosissimus	28
Mucor saturnus	28
Penicillium chrysogenum	7
Penicillium digitatum	3
Penicillium herquei	28
Penicillium spp.	5

Beta Lactams	Ref.
Cephalexin	29
Imipenem	29
Penicillin G	29
Penicillin V	29

Protozoa	Ref.
Chironomid larvae	27
Cryptosporidium	34

Viruses	Ref.
Adenovirus Type 40	6
Calicivirus	42
Canine Parvovirus	8
Coronavirus	3
Feline Calici Virus	3
Foot and Mouth disease	8
Hantavirus	8
Hepatitis A Virus	3
Hepatitis B Virus	8
Hepatitis C Virus	8
Human coronavirus	8
Human Immunodeficiency Virus	3
Human Rotavirus type 2 (HRV)	15
Influenza A	22
Minute Virus of Mouse (Parovirus)(MVM-i)	8
Minute Virus of Mouse (Parovirus)(MVM-p)	8
Mouse Hepatitis Virus (MHV-A59)	8
Mouse Hepatitis Virus (MHV-JHM)	8
Mouse Parvovirus type 1 (MPV-1)	8
Murine Parainfluenza Virus Type 1 (Sendai)	8
Newcastle Disease Virus	8
Norwalk Virus	8
Poliovirus	20
Rotavirus	3
Severe Acute Respiratory Syndrome (SARS) Coronavirus	43
Sialodscryoadenitis Virus (Coronavirus)(SDAV)	8
Simian rotavirus SA-11	15
Theiler's Mouse Encephalomyelitis Virus (TMEV)	8
Vaccinia Virus	10

Algae/Fungi/Mold/Yeast	Ref.
Phormidium boneri	3
Pichia pastoris	3
Poitrasia circinans	28
Rhizopus oryzae	28
Roridin A	33
Saccharomyces cerevisiae	3
Stachybotrys chartarum	7
T-mentag (athlete's foot fungus)	3
Verrucarin A	33

Bacterial Spores	Ref.
Alicyclobacillus acidoterrestris	17
Bacillus coagulans	12
Bacillus anthracis	10
Bacillus anthracis Ames	30
Bacillus atrophaeus	14
Bacillus atrophaeus ATCC 49337	31
Bacillus megaterium	12
Bacillus polymyxa	12
Bacillus pumilus ATCC 27142	12
Bacillus pumilus ATCC 27147	11
Bacillus subtillis (globigii) ATCC 9372	11
Bacillus subtillis ATCC 19659	31
Bacillus subtillis 5230	12
Clostridium. sporogenes ATCC 19404	12
Geobacillus stearothermophilus ATCC 12980	11
Geobacillus stearothermophilus ATCC 7953	31
Geobacillus stearothermophilus VHP	11
Bacillus thuringiensis	18

Chemical Decontamination	Ref.
Mustard Gas	
Ricin Toxin	10
dihydronicotinamide adenine dinucleotide	24
microcystin-LR (MC-LR)	25
cylindrospermopsin (CYN)	25

Beta Lactams	Ref.
Amoxicillin	29
Amplicillin	29
Cefadroxil	29
Cefazolin	29

Protozoa	Ref.
Cryptosporidium parvum Oocysts	9
Cyclospora cayetanensis oocysts	41
Giardia	34

Microsporidia	Ref.
Encephalitozoon intestinalis	27

Bacteria	Ref.
E. coli O157:H7 G5303	1
E. coli O157:H7 C7927	1
Erwinia carotovora (soft rot)	21
Franscicella tularensis	30
Fusarium sambucinum (dry rot)	21
Fusarium solani var. coeruleum (dry rot)	21
Helicobacter pylori	8
Helminthosporium solani (silver scurf)	21
Klebsiella pneumonia	3
Lactobacillus acidophilus NRRL B1910	1
Lactobacillus brevis	1
Lactobacillus buchneri	1
Lactobacillus plantarum	5
Legionella	38
Legionella pneumophila	42
Leuconostoc citreum TPB85	1

Algae/Fungi/Mold/Yeast	Ref.
Alternaria alternata	26
Aspergillus aeneus	28
Aspergillus aurolatus	28
Aspergillus brunneo-uniseriatus	28
Aspergillus caespitosus	28
Aspergillus cervinus	28
Aspergillus clavatonanicus	28
Aspergillus clavatus	28

ClorDiSys' gaseous chlorine dioxide is registered with the EPA as a sterilant

Product: CSI CD CARTRIDGE
EPA Reg#: 80802-1
Registrant: CLORDISYS SOLUTIONS, INC
Approval Date: 02/25//2005
Active Ingredients: Sodium chlorite 72.8%

Contact us for more information on the power of a TRUE GAS and to discuss your project

908.236.4100

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