

AUSTRALIA

PATENTS ACT 1990

COMPLETE SPECIFICATION

FOR A STANDARD PATENT

ORIGINAL



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Invention Title:

"METHOD AND APPARATUS FOR APPLYING VOLATILE  
SUBSTANCES TO MATERIALS"

Details of Associated Provisional Application No. PO 8738 dated 22nd August, 1997

The following statement is a full description of this invention, including the best method of performing it known to us:-

## METHOD AND APPARATUS FOR APPLYING VOLATILE SUBSTANCES TO MATERIALS

### FIELD OF THE INVENTION

This invention relates to a method and apparatus for the treatment of a material  
5 with a volatile substance entrained in a carrier gas. In a particular application of the invention, the method and apparatus is used to treat a food or pharmaceutical product or ingredient with a natural food acid such as carbonic acid for the purpose of achieving at least partial microbial decontamination and/or shelf-life extension.

### BACKGROUND OF THE INVENTION:

10 Hitherto, conventional gaseous processes aimed at extending the shelf-life of materials prone to microbial spoilage have relied on modified atmosphere (MAP) procedures. In such procedures, the oxygen gas atmosphere surrounding the material is replaced with a food grade carbon dioxide and/or nitrogen atmosphere, and high barrier colaminate packaging is used to maintain the exclusion of oxygen from the package.  
15 The slight acidity produced by the carbonic acid which results from the exposure of the material to carbon dioxide produces a fungicidal effect. However, MAP processes have disadvantages. That is, whilst it has been found that an extension of the shelf-life is achieved in respect of materials treated by the procedures, this extension is limited and considerable costs are involved including the cost associated with the specialised  
20 colaminate film packaging used.

In copending Australian patent application No. 75449/96 (the entire disclosure of which is to be regarded as incorporated herein by reference), a method and apparatus is described for extending the shelf-life of materials prone to microbial spoilage by treating the materials with a volatile substance such as a natural food acid. The method  
25 described in this copending application involves prior evacuation of the vessel containing the material to be treated and, while this may lead to the more effective treatment of some materials, the inventors have now found that prior evacuation of the vessel containing the material is not necessary for the satisfactory extension of shelf-life.

*the other patent  
vacuum process*

## SUMMARY OF THE INVENTION:

Thus, in a first aspect, the present invention provides a method for reducing the viable microbial content of a solid material for human consumption, which is susceptible to microbial spoilage, said method comprising the steps of:

(a) entraining a volatile substance in a liquid form, selected from the group consisting of natural food acids, chemical biocides and mixtures thereof, in a stream of a carrier gas to form a gas mixture substantially free of particles of the volatile substance comprising a major portion of the carrier gas and a minor portion of the volatile substance, and

(b) contacting exposed surfaces of the material with the gas mixture for a **contacting period of 2 minutes or less** during which time the volatile substance partitions into solution upon said exposed surfaces, wherein, at the time of contacting the exposed surfaces of the material with said gas mixture, the exposed surfaces of the material have a water activity ( $A_w$ ) of greater than or equal to 0.85;

wherein said method **does not involve**, prior to step (a) and/or (b), a step of subjecting the material to **a vacuum**.

Preferably, the material is a food or pharmaceutical product or ingredient and the method achieves at least partial microbial decontamination and/or shelf-life extension of the food or pharmaceutical product or ingredient.

The volatile substance is preferably entrained in the carrier gas in saturating amounts. The material may be contacted with the volatile substance/carrier gas mixture provided at pressures greater than ambient:

The method may be performed using a suitable vessel to contain the material during contact with the volatile substance/carrier gas mixture.

In a second aspect, the present invention provides an apparatus for treating a material comprising:

a vessel for containing the material;

means for entraining a volatile substance in a carrier gas; and

means for contacting the material contained within the vessel with the volatile substance entrained in the carrier gas.

Preferably, the **vessel** is adapted to allow the volatile substance/carrier gas mixture to be present at **pressures greater than ambient**. **Open vessels** may, however, also be used.



Unless the context clearly requires otherwise, throughout the description and the claims, the words "comprise", "comprising", and the like are to be construed in an inclusive as opposed to an exclusive or exhaustive sense; that is to say, in the sense of "including, but not limited to".

5 Any discussion of documents, acts, materials, devices, articles or the like which has been included in the present specification is solely for the purpose of providing a context for the present invention. It is not to be taken as an admission that any or all of these matters form part of the prior art base or were common general knowledge in the field relevant to the present  
10 invention as it existed in Australia before the priority date of each claim of this application.

#### DETAILED DISCLOSURE OF THE INVENTION:

15 Materials that can be treated by the method of the invention include any substance for which it is desired to have its chemical and/or physical characteristics altered by means of volatile substances. The method of the invention is suitable for microbial decontamination and/or control of a wide range of food products and ingredients including, but not limited to, baked  
20 goods such as bread, whole grain cereals, whole or diced berries, fruits or vegetables, prepared salads, nuts in their shell, nut meats in storage awaiting drying or while undergoing further processing, cheese, smallgoods, cured meats, chicken flesh, carcass on abattoir chains, sea and fresh water  
25 foodstuffs, and herbs and spices. The method of the invention is also suitable for microbial decontamination and/or control of pharmaceutical compositions and individual pharmaceutical ingredients, for head space sanitation and control of processing plant equipment. Still further, while the method of the invention may be used in isolation, it is also suitable for use with other  
30 treatment processes including for optimising dosing with anti-oxidants where high surface concentrations are desired, for the delivery of soluble food grade or other preservatives, for the depositing of substances onto surfaces with the possible assistance of electrostatic charges or in conjunction with MAP to increase the shelf-life of certain products.

35 The method of the present invention may be performed batch-wise or continuously, and preferably in a suitable vessel. Preferably, the vessel is adapted to allow the volatile substance/carrier gas mixture to be present at pressures greater than ambient. For batch treatments, the material may be



placed in the vessel using an infeed hopper attached to the vessel through, for example, a suitable valve. Alternatively, wrapped unsealed material may be placed in the vessel manually. For continuous treatments, the material may be placed in and out of the vessel by placing the material on a conveyor and passing the conveyor through the vessel and/or via rotary locks or other similar devices.

The duration of contact between the material and the volatile substance/carrier gas mixture may vary, as necessary, to achieve the desired aim, however the duration of the contact should always be for a period of 2 minutes or less. For example, for microbial decontamination of a material, the duration of exposure is that required to sufficiently reduce the total viable microbial content to a desired value and is dependant on a number of variables including surface area of the material to be treated; flow rates of the carrier gas; surface water activity ( $A_w$ ); type and concentration of volatile substance and the bacterial and fungal bioburden of the material. The efficiency of the treatment method is also dependant on the interaction between the matrix geography and/or chemistry and the added volatile substance.

Typically, the duration of the contact between the material and the volatile substance/carrier gas mixture will be in the order of 0.05 to 2 mins; more preferably, 0.15 to 0.5 mins. [REDACTED]

Contact between the material and volatile substance/carrier gas mixture may be achieved by means of one or more spargers. To assist contact between the material and volatile substance/carrier gas mixture, the vessel may be provided with means for tumbling and/or passing the material (eg. through falling under gravity) through the volatile substance/carrier gas mixture. [REDACTED]

The method of the present invention may comprise multiple (eg. up to 3 times) exposures (i.e. contacting) of the material to a volatile substance/carrier gas mixture. The volatile substance(s) used in each exposure may be the same or different. Where multiple exposures are performed using a single vessel, the vessel may be evacuated between exposures and/or flushed with a suitable gas (eg. carrier gas).

The volatile substance can be any substance selected from the group consisting of natural food acids, chemical biocides and mixtures thereof. The volatile substance may be entrained in an inorganic or organic gas, and may



chemically and/or physically alter the treated material. For example, for microbial decontamination and/or extending the shelf-life of food and pharmaceutical products and ingredients, the volatile substance is preferably a natural food acid, more preferably carbonic acid and/or acetic acid, although any other natural food acid having microbicidal or preserving qualities can be used or other volatile preservative substances. Alternatively, a potentially residue-free chemical biocide such as hydrogen peroxide can be used. Mixtures of such volatile substances may also be used. The ratios of the component volatile substances in such mixtures will typically vary depending on the physical and chemical nature of the material being



treated. However, for mixtures such as carbonic acid/acetic acid, carbonic acid/hydrogen peroxide and acetic acid/hydrogen peroxide, the ratio of the component volatile substances may be within the range of 1:10 to 10:1. Moreover, for the mixtures carbonic acid/hydrogen peroxide and acetic acid/hydrogen peroxide, the ratio of the component volatile substances is preferably within the range 1:5 to 5:1, more preferably, about 1:3.

The volatile substance is preferably entrained in the carrier gas by passing the carrier gas through a vessel or vessels containing the volatile substance or by other means by which a sufficient concentration of the volatile substance can be entrained in the carrier gas without the formation of an aerosol. A multiple volatile substance/carrier gas mixture may be provided by mixing a group of parallel preferred volatile substance/carrier gas mixture streams after passing through their respective volatile substance sources or, alternatively, a single carrier gas stream may be passed through a series of volatile substance sources.

Alternatively, the volatile substance can be prepackaged with the carrier gas. The volatile substance is preferably entrained in the carrier gas in saturating amounts.

The carrier gas is preferably carbon dioxide and/or nitrogen gas which can be sourced from a cylinder containing the relevant compressed gas(es). The carrier gas, which is fully or partly stripped of the volatile substance after contact with the material to be treated, may be recycled.

The volatile substance and/or carrier gas may be heated to increase volatility and hence concentration of the volatile substance in the carrier gas. Reduction in carrier gas usage and other efficiencies may result.

In the case of food products and ingredients, the limit to which the material to be treated can be contacted with the volatile substance/carrier gas mixture is generally determined by the flavour resultant from the acidulation of the product. That is, certain volatile substances (eg. acetic acid), have an unfavourable effect on flavour due to acidulation. However, other volatile substances (eg. carbonic acid), have been found to cause relatively little organoleptically detectable acidulation and can in some cases actually impart an appealing smoked flavour and/or aroma. In any case, the inventors

have noted that the acidic flavour effects resulting from the method of the invention may recede during storage. Further, some materials end use involves heating or cooking (eg. crumpets), which will also decrease any lingering acidic flavour effects of the method. Mild surface drying to promote volatilisation of surface acids and post-treatment surface addition of alkalis such as approximately 0.2% w/w of sodium bicarbonate may also be used to reduce or avoid acidic flavour effects. It is also preferred that when the material to be treated has critical flavour specifications, the concentration of the volatile substance in the carrier gas be closely monitored and controlled.

Subsequent packing in packaging materials with poor gas barrier properties or small perforations may also assist in the diffusion of volatile substances from the surface of the material(s) treated by the method of the invention thus reducing any acidic flavour effects. Conversely, packaging with excellent gas barrier properties will aid to maintain an atmosphere of volatile substances thus enhancing the preservative effect of the method. Accordingly, the barrier properties of the packaging may be chosen to suit the treated material.

The material to be treated should have a minimum surface water activity ( $A_w$ ) of approximately 0.85 to allow the volatile substance to quickly transfer across from the carrier gas. An  $A_w$  of approximately 0.95 will allow near optimum transference rates and therefore minimum exposure times. To optimise transfer rates it may be appropriate to dose all the gaseous mixture required to an over-pressure of 0.01-0.25 bar (7.5-190mm Hg) and up to 3 bar (2250mm Hg) above atmospheric pressure and allow the appropriate contact time. Lower  $A_w$  foodstuffs without the addition of a small quantity of water (generally 1-2%w/w), onto the surface of the material to be treated may require longer exposure times. This additional water can be applied as a fine mist in the case of relatively impervious products such as peppercorns or, preferably, by steaming in more difficult applications.

While particularly suited to use with water soluble volatiles, the method of the invention may also be used with other applications such as those requiring the transfer of volatile substances that are soluble in, for example, lipids or other organic or inorganic solvents other than water (eg. some anti-oxidants).

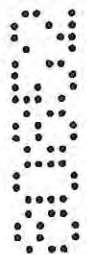
Some post-contamination protection is also offered by the method of the invention and thus mechanical and/or human double handling is feasible.



It is, however, preferable that where surface acidulation has been decreased to minimise acidic flavour effects, sometimes a requirement with bland materials, the material be handled and packaged in a manner so as to minimise microbial contamination.

5        The method of the invention may also be performed in combination with one or more treatments of the material in accordance with the method described in copending Australian patent application No. 75449/96.

10        In addition, the inventors have found that it can be advantageous to dip or spray the material in/with a solution of the volatile substance, preferably prior to contacting the material with the volatile substance/carrier gas mixture. Dipping may be readily achieved by, for example, passing a conveyor with the material through a tank of an aqueous solution of the volatile substance. Following dipping, the material may then



be conveyed to a suitable vessel for treatment with a volatile substance/carrier gas mixture in accordance with the method of the invention.

The invention will hereinafter be further described by way of reference to the following, non-limiting examples and accompanying figures.

5 BRIEF DESCRIPTION OF THE ACCOMPANYING FIGURES:

**Figure 1** provides a schematic representation of a continuous treatment apparatus according to the invention, wherein the material is fed to a commercially available packaging machine for treatment and contacted with a volatile substance/carrier gas mixture provided through a gas sparging head.

10 **Figure 2** provides a schematic representation of an alternative continuous treatment apparatus according to the invention, wherein a treatment vessel is isolated by rotary vacuum locks providing supplementary treatment stages.

**Figure 3** provides a schematic representation of a further alternative continuous apparatus according to the invention, wherein the material falls in counter-current flow to a volatile substance/carrier gas mixture.

MODE(S) FOR CARRYING OUT THE INVENTION

As shown in Figure 1, continuous treatment of materials in accordance with the method of the invention may be achieved through a dedicated treatment system or commercially available packaging machine (1), equipped with a conveyor (2), a gas sparging head (3) and a gas control system (4). Connected to the gas sparging head (3) by means of lines (5), (6), (7) and (8) and valves (9), (10) and (11) is a compressed gas source (12), one or more volatile substance sources (13), preferably sparging vessels, and an aerosol trap (14). The aerosol trap (14) is intended to minimise large droplets of the volatile(s) which can cause undesirable spotting and non-uniform distribution of the volatile(s) on the material surface. Multiple volatile substance sources (13) may be used to assist complete saturation of the carrier gas.

In the case of treatment with carbonic acid, the volatile substance source (13) may be at least initially filled with purified water such that bubbling of the CO<sub>2</sub> gas therethrough produces carbonic acid thus causing the CO<sub>2</sub> carrier gas to be at least partially saturated with the produced carbonic acid. Some materials will benefit more

after the carrier gas, preferably food grade carbon dioxide, has been passed through multiple volatile sources solvents to achieve a mixture of volatiles in the carrier gas. Various type, combinations and concentrations of saturated carrier gases may be used to treat the material to optimise shelf-life and flavour parameters, particularly various  
5 mixtures of acetic and carbonic acids and hydrogen peroxide. A multiple volatile substance/carrier gas mixture may be provided by mixing a group of parallel preferred volatile substance/carrier gas mixture streams after passing through their respective volatile substance sources or, alternatively, a single carrier gas stream may be passed through a series of volatile substance sources.

10 In use, a batch of material (15) to be treated is introduced to a commercially available packaging machine (1). The carrier gas is forwarded from the compressed gas source (12) to the volatile substance source (13), the volatile substance thereby becoming entrained in the carrier gas, which is then introduced into the packaging machine (1) through gas sparging head (3) to thereby contact the material (15). Valves  
15 (16) and (17) may be operated to bypass the additional volatile substance source (13) if only one volatile substance source is required. The carrier gas, which is at least partially stripped of the volatile substances, is allowed to escape through a pressure regulator valve achieving a desired process overpressure for the desired contact time.

The duration of contact between the material and the volatile substance/carrier  
20 gas mixture may be optimised to provide the maximum reduction in microbial bioburden while achieving the desired flavour and other properties of the material being treated. Once the desired duration of contact is attained, the flow of carrier gas is ceased and the pressure regulating valve released. The treated material is then removed from the vessel and packaged.

25 As shown in Figure 2, an alternative continuous treatment of materials in accordance with the method of the invention is achieved through a dedicated treatment system (22), wherein material (23) is fed to a first rotary vacuum lock (24) (or other effective cavity mechanism) then, in turn, to conveyor (25) within treatment vessel (26) where the material is contacted with a volatile substance/carrier gas mixture, provided  
30 through gas sparging heads (27), without prior evacuation of the treatment vessel (26)

in accordance with the method of the invention. From the conveyor, the treatment material is transferred to a collecting hopper (28) via a second rotary vacuum lock (29) (or other effective cavity mechanism). The first and second rotary vacuum locks (24) and (29) isolate the vessel (26), and permit operation of a two or three stage process  
5 wherein the material is also treated within the first and/or second rotary vacuum locks (24) and (29) with supplemental treatment(s) involving contacting the material with a volatile substance/carrier gas mixture preferably (T) following evacuation (E). The stage performed in the treatment vessel (26) may be of considerably longer duration than either or both of the supplementary treatment(s) and may benefit from cost  
10 efficiencies associated with carrier gas recycling. Each of the stages could use the same or different volatile substances.

As shown in Figure 3, continuous treatment of materials in accordance with the method of the invention may also be achieved through a dedicated treatment system, equipped with a means (31) such as an infeed hopper to deliver material (32) through a  
15 suitable valve (33) (or conveyor) to the top of a vertical vessel (34) provided with one or more gas sparging heads (35) and material outlet valve (36) (or conveyor) located within the base. A collecting hopper (37) is provided adjacent material outlet valve (36). The gas sparging head(s) may be connected to a gas control system and sources of compressed carrier gas and one or more volatile substances in a manner as described  
20 above in connection to Figure 1. The material (32) passes through the vessel to the material outlet valve (36), preferably in counter-current flow to the volatile substance entrained in the carrier gas. The carrier gas may be removed from the top of the vessel (34) through pressure regulator valve (38) and flue (39) and recycled if desired. Residence time of the material within the vessel may be varied by adjusting flow rate of  
25 the material (32) and/or volatile substance/carrier gas mixture and/or by adjusting vessel (34) height so as to achieve a desired duration of contact between the material and volatile substance/carrier gas mixture or, alternatively, by interposing a screw conveyor system within the vessel with variable rotating speed to control the passage of the material (32) as it passes through the vessel (34). In this configuration, the vessel

(34) need not be erected vertically but can be arranged in any position compatible with the angle of repose dictated by the material (32) being treated.

Continuous treatment as shown in Figure 3 may be particularly suitable for grated/shredded cheese, other particulates and leafy materials such as herbs.

5 **Example 1: TREATMENT OF SHREDDED CHEESE**

In this example, shredded cheese was placed in an evacuable test vessel and exposed to a acetic acid/CO<sub>2</sub> gas mixture for the designated period(s) (ie. 2 x 10 seconds - with prior evacuation; 1 x 15 seconds - without prior evacuation) with or without prior evacuation of the vessel. The shredded cheese was contained in plastic  
10 bags and a degree of pressure was allowed to develop in the plastic bags during treatment. The majority of the gas mixture entering the vessel escaped with approximately 50% of the residual gas mixture being expelled manually prior to sealing of the plastic bags. The samples were then stored for approximately twenty four hours prior to microbiological analysis. The results are provided in Table 1.

15 As can be seen from Table 1, a substantial reduction in the microbial bioburden of the shredded cheese was achieved both with and without the assistance of evacuation prior to contact with the acetic acid/CO<sub>2</sub> gas mixture.

**Example 2: TREATMENT OF FRUIT WITH CARBONIC ACID DIPPING**

In this example, a twenty gram piece of skinned mango was dipped into an  
20 equilibrated aqueous solution of carbonic acid for ninety seconds while a continual supply of food grade carbon dioxide was bubbled through the solution in an attempt to maintain an excess concentration of carbonic acid. The mango piece was treated with volatile carbonic acid in CO<sub>2</sub> carrier gas and held in this gaseous atmosphere at approximately 5°C for ten minutes whilst the aqueous carbonic acid dipping solution  
25 equilibrated (pH 4.0 by paper). Following re-dipping of the mango piece for one hundred and eighty seconds, excess water was removed by shaking.

Control and treated samples were stored under identical conditions at approximately 5°C. After three hours the control developed a dark orange colour and syneresis at three days. After three weeks there was very little change in the treated  
30 sample. Furthermore, only a slight amount of syneresis was observed after an additional

24 hour storage time (ie. total 3 weeks and 1 day) at ambient temperatures . No change in colour nor observable mould growth was seen.

In similar trials with avocado, shelf-life was extended from three hours to sixty six hours; the assessment parameters again being colour and observable mould growth.

- 5 It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.

TABLE 1

					Total.	%	Yeast &	%
FOODSTUFF	GAS MIX	No. of	FLOW	EXP.	Plate	Reduction	Mould	Reduction
		FLUSH	RATE	SEC.	Count		Count	
SHREDDED CHEESE	CONTROL	CONTROL	CONTROL	CONTROL	3.61E+05	CONTROL	5.87E+05	CONTROL
CONTROL					4.56E+05	CONTROL	7.80E+05	CONTROL
					2.19E+05	CONTROL	8.16E+05	CONTROL
				Mean	3.45E+05	CONTROL	7.28E+05	CONTROL
SHREDDED CHEESE	ACETIC							
VACUUM/FLUSH								
Sample Wt: 10gms								
Aw	0.86	2	22L/M	10	<10	>99.999	8.00E+00	99.9989
SHREDDED CHEESE	ACETIC							
NO VACUUM								
Sample Wt: 10gms								
Aw	0.86	1	22L/M	15	<10	>99.999	<10	>99.999

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A method for reducing the viable microbial content of a solid material for human consumption, which is susceptible to microbial spoilage, said  
 5 method comprising the steps of:
  - (a) entraining a volatile substance in a liquid form, selected from the group consisting of natural food acids, chemical biocides and mixtures thereof, in a stream of a carrier gas to form a gas mixture substantially free of particles of the volatile substance comprising a major portion of the carrier  
 10 gas and a minor portion of the volatile substance, and
  - (b) contacting exposed surfaces of the material with the gas mixture for a contacting period of 2 minutes or less during which time the volatile substance partitions into solution upon said exposed surfaces, wherein, at the time of contacting the exposed surfaces of the material with said gas mixture,  
 15 the exposed surfaces of the material have a water activity ( $A_w$ ) of greater than or equal to 0.85;

wherein said method does not involve, prior to step (a) and/or (b), a step of subjecting the material to a vacuum.
- 20 2. A method according to claim 1, wherein the volatile substance includes a natural food acid.
3. A method according to claim 2, wherein the volatile substance includes carbonic acid.
- 25 4. A method according to claim 2, wherein the volatile substance includes acetic acid.
5. A method according to any one of the preceding claims, wherein the  
 30 volatile substance includes hydrogen peroxide.
6. A method according to claim 2, wherein the volatile substance is selected from the group consisting of carbonic acid, acetic acid, hydrogen peroxide and mixtures of carbonic acid and acetic acid, and carbonic acid  
 35 and/or acetic acid with hydrogen peroxide.



7. A method according to any one of the preceding claims, wherein the volatile substance is entrained in the carrier gas in saturating amounts.

5 8. A method according to any one of the preceding claims, wherein the carrier gas is carbon dioxide and/or nitrogen gas.

9. A method according to any one of the preceding claims, wherein the method is conducted continuously.

10

10. A method according to an one of the preceding claims, wherein the duration of the step of contacting the exposed surfaces of the material with the mixture is in the range of 0.05 to 2 minutes.

15

11. A method according to any one of the preceding claims, wherein the contacting period is in the range of 0.15 to 0.5 minutes.

20

12. A method according to any one of the preceding claims wherein at the time of contacting the exposed surfaces of the material with said gas mixture, the exposed surfaces of the material have a water activity ( $A_w$ ) of greater than or equal to 0.95.

25

13. A method according to any one of the preceding claims, wherein prior to the step of contacting the exposed surfaces of the material with said gas mixture, the exposed surfaces of the material are wetted with up to about 2.0% w/w of water.

30

14. A method according to any one of the preceding claims, wherein prior to the step of contacting the exposed surfaces of the material with the gas mixture, an aqueous solution of a volatile substance, which may be the same or different to the volatile substance contained in the gas mixture, is applied to the surface of the material.



15. A method according to claim 14, wherein the aqueous solution is applied to the surface of the material by dipping or spraying.

5 16. A method according to any one of the preceding claims, wherein the step of contacting the exposed surfaces of the material with said gas mixture is conducted in a vessel with an over-pressure of up to 3 bar (2250mm Hg) above atmospheric pressure.

10 17. A method according to any one of the preceding claims, wherein the step of contacting the exposed surfaces of the material with said gas mixture is repeated up to 3 times.

15 18. A method according to claim 19, wherein each step of contacting the exposed surfaces of the material with said gas mixture is conducted in separate vessels.

20 19. A method according to claim 18, wherein each step of contacting the exposed surfaces of the material with said gas mixture is conducted in a single vessel.

25 20. A method according to claim 19, wherein between each step of contacting the exposed surfaces of the material with said gas mixture, the vessel is evacuated and/or flushed with a suitable gas.

21. A method according to any one of the preceding claims, wherein the material to be treated is a food, pharmaceutical product or ingredient thereof.

Dated this 4th day of April 2001

**Vaporex Pty Limited**

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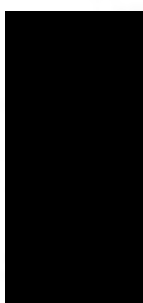


FIGURE 2

22

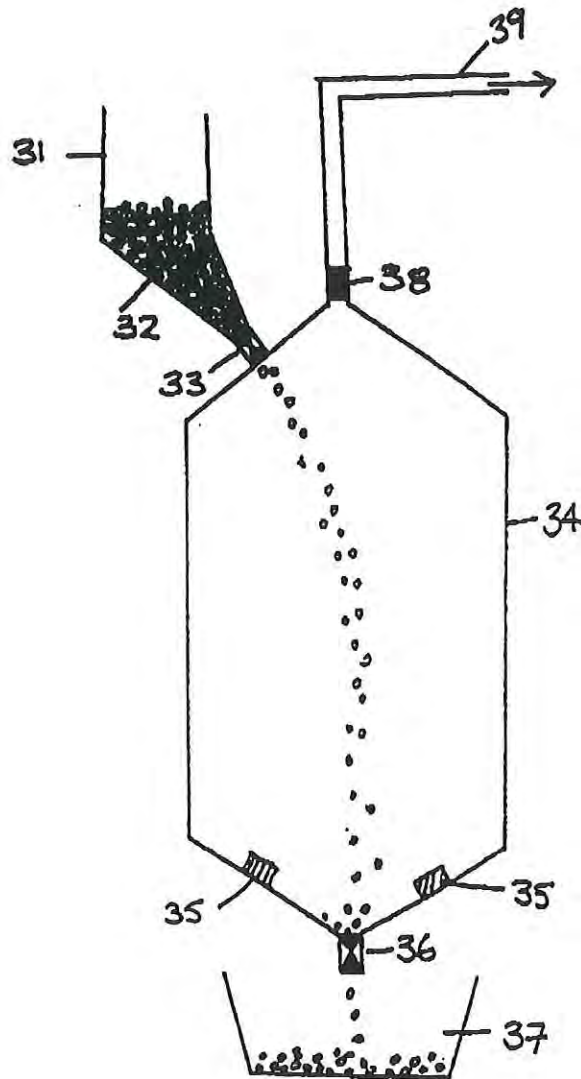


FIGURE 3

**(12) PATENT**  
**(19) AUSTRALIAN PATENT OFFICE**

**(11) Application No. AU 199675449 B2**  
**(10) Patent No. 730402**

(54) Title  
**Method and apparatus for the application of volatile substances conveyed in carrier gas**

(51)<sup>7</sup> International Patent Classification(s)  
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**A23L 003/3409                A23L 003/3445**

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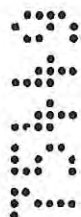
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## ABSTRACT

The invention relates to a method and apparatus for treating a material particularly foodstuffs, pharmaceutical compositions etc. The method comprises placing a material to be treated in a vessel capable of evacuation, evacuating the vessel and

5 contacting the material with a volatile substance entrained in a carrier gas. Preferably the volatile substance is a natural food acid such as acetic or carbonic and the carrier gas is nitrogen or carbon dioxide.



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Invention Title:

"METHOD AND APPARATUS FOR THE APPLICATION OF  
VOLATILE SUBSTANCES CONVEYED IN CARRIER GAS"

Details of Associated Provisional Application No. PN7240 dated 20th December, 1995

The following statement is a full description of this invention, including the best method of performing it known to us:-

### TECHNICAL FIELD

This invention relates to a method and apparatus for the treatment of solid materials intended for human consumption so as to reduce the viable microbial content.

### 5 BACKGROUND ART

Hitherto, conventional gaseous processes aimed at extending the shelf life of substances have relied on modified atmosphere packaging (MAP) procedures. In such procedures, the oxygen gas atmosphere surrounding the substance is replaced with a food grade carbon dioxide and/or nitrogen  
10 atmosphere, and high barrier colaminate packaging is used to maintain the exclusion of oxygen from the package. The slight acidity produced by the carbonic acid which results from the exposure of the substance to carbon dioxide produces a fungicidal effect.

MAP processes have disadvantages. Whilst it has been found that an extension of the shelf life is achieved in respect of substances treated by the procedures, this extension is limited and considerable costs are involved including the cost of the specialised colaminate film packaging used.

It is an object of the present invention to provide a method and apparatus to treat a solid material with a gas mixture comprising a volatile substance(s) and a carrier gas(es) to substantially improve material safety with respect to fungal or bacterial spoilage or other hazards and thereby extend the shelf-life of the material.

### DISCLOSURE OF THE INVENTION

According to a first aspect the present invention provides a method for reducing the viable microbial content of a solid material for human consumption which is susceptible to microbial spoilage, said method comprising the steps of:

- (a) placing the material in a vessel capable of evacuation;
- (b) evacuating the vessel;
- 30 (c) entraining a volatile substance in a liquid form, selected from the group consisting of natural food acids, chemical biocides and mixtures thereof, in a stream of a carrier gas to form a gas mixture substantially free of particles of the volatile substance comprising a major portion of the carrier gas and a minor portion of the volatile substance, and
- 35 (d) contacting exposed surfaces of the material with the gas mixture for a contacting period of 60 seconds or less, wherein at the time of contacting



the exposed surfaces of the material with said gas mixture, the exposed surfaces of the material have a water activity ( $A_w$ ) of greater than or equal to 0.85.

Optionally method steps (b) and (d) are repeated in sequence, as necessary, to achieve the desired aim.

The invention is based upon the finding by the inventors that advantageous treatment results may be obtained by the bringing together of the four features highlighted in the preceding paragraph. The volatile biocidal substance used in the method should be a liquid or in solution at the time that it is entrained into a stream of a carrier gas. This ensures that when the gas mixture so formed is brought into contact with an appropriate solid material, i.e. a solid material with an  $A_w$  equal to or greater than 0.85, the volatile substance will rapidly partition into the moisture present at the surface of the solid material. This rapid partitioning of the volatile biocidal substance into the surface water of the solid material will cause that moisture, which is also in contact with any microbes on the surface of the solid material, to transiently have a very high concentration of the biocide. Though transient, the very high concentration of the biocide in the surface water will have a high lethality for the microbes, particularly as at high concentrations the biocide is more likely to be in an undissociated state and therefore more able to penetrate the cell walls of the microbes. The transient nature of the high biocide concentration on the surface of the solid material is due to the short treatment time, i.e. less than 60 sec., and due to the equilibration of the biocide through the solid material after the treatment has finished. The result of the equilibration following the treatment is that the solid material as a whole will end up containing a small concentration of the biocide despite having had a very high surface concentration transiently during the treatment process.

Materials that can be treated by this invention include any substance which is desired to have its chemical and/or physical characteristics altered by means of volatile substances. The process of the present invention is suitable for reducing the viable microbial content (i.e. decontamination) of a wide range of foods and other products including baked goods such as bread, whole grain cereals, whole or diced berries, fruits or vegetables, prepared salads, nuts in their shell, nut meats in storage awaiting drying or while



undergoing further processing, vacuum packed smallgoods, cured meats, chicken flesh, carcass on abattoir chains and herbs and spices.

- 5 It has been found that significant extensions in shelf life of baked goods and smallgoods (up to and exceeding 30 days) have been achieved by the inventive method.

The inventive method is also suitable for reducing the viable microbial content of pharmaceutical compositions including individual pharmaceutical ingredients, for head space sanitation and control of processing plant equipment.



Still further, while the inventive method may be used in isolation, it is also suitable for use with other treatment processes including for optimising dosing with anti-oxidants where high surface concentrations are desired, for the delivery of soluble food grade or other preservatives, for the depositing of substances onto surfaces with the possible assistance of electrostatic charges or in conjunction with conventional MAP to increase the shelf life of certain products.

The means for evacuating the vessel is preferably provided by an external vacuum source. The material to be treated is preferably first evacuated rapidly to sub-ambient pressure.

The material contained in the evacuated vessel is preferably contacted with the gas mixture by means of one or more spargers.

Preferably the carrier gas is carbon dioxide and/or nitrogen gas which can be sourced from a cylinder containing the relevant compressed gas(es).

The volatile substance can be selected from any natural food acid, chemical biocide (such as hydrogen peroxide) or mixtures thereof. For substantially extending the shelf life of foods particularly baked goods, the volatile substance is preferably a natural food acid, most preferably acetic acid and/or carbonic acid, although any other natural food acid having fungicidal or preserving qualities can be used.

The volatile substance is preferably entrained in the carrier gas by passing the carrier gas through a vessel containing the volatile substance. The carrier gas which is stripped of the volatile substance after contact with the material to be treated may be recycled through the method.

Alternatively, the volatile substance can be prepackaged with the carrier gas.

The carrier gas is preferably saturated with the volatile substance. Alternatively, at lower concentrations the method is less biocidal and more inhibitory.

The method of the invention can be performed either as a batch method or in a continuous flow mode. When a batch method is used, wrapped unsealed material is preferably loaded and unloaded into the vessel manually. When a continuous flow mode is desired, commercially available flow wrapping equipment utilising a conveyor and/or exposure in a suitable treatment tunnel can be used.

For reducing microbial content of a material, the duration of exposure is that required to sufficiently reduce the total viable microbial content to a



- desired value and is dependant on a number of variables including surface area of the material to be treated; degree of vacuum; over-pressure; surface water activity( $A_w$ ); flow rates of the carrier gas; type and concentration of the volatile substance; and bacterial and fungal bioburden of the material. The efficiency of the treatment method is also dependant on the interaction between the matrix geography and/or chemistry and the added volatile substance.

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Some materials will need to be treated individually if their matrix or final package configuration is such that, if treated simultaneously, they present a physical barrier to the volatile substance contacting the surface interface of the materials to be treated.

Several cycles of vacuum and exposure may be required depending on the goods  
5 being treated and the concentration of volatile substance entrained in the carrier gas.

In the case of foods, the limit to which the material to be treated can be exposed to the carrier gas/volatile substance is generally determined by the flavour resultant from the acidulation of the product. As will be explained in more detail later, certain volatile substances eg acetic acid, have an unfavourable effect on flavour due to acidulation.

10 Other volatile substances eg carbonic acid, cause little organoleptically detectable acidulation and can in some cases actually impart a smoked flavour and/or aroma to some smallgoods.

Further, some low acid foods particularly smallgoods will achieve additional colour stability after treatment. Manufacturers of bland smallgoods e.g. lower priced  
15 sandwich-type hams, etc. can overcome mild acidulation by making slight changes to their flavour formulations. In some cases, however, the additional acidulation actually aids in completion and enhancement of the flavour profile whilst achieving near to, or complete microbial stability.

The applicants have noted that the acidic flavour effects resulting from the present  
20 inventive method may recede during storage. In all materials tested to date, flavour effects have in fact receded dramatically during the initial 24 hours following exposure, then more gradually on further storage. Some materials end application involves heating

or cooking which will further decrease any lingering unfavourable flavour effects of the process, particularly in bland baked goods such as crumpets.

Packaging materials with poor gas barrier properties or small perforations may also assist in the diffusion of volatile substances from the surface of the material/s treated by the inventive process thus reducing any acidic flavours. Conversely packaging with excellent gas barrier properties will maintain an atmosphere of volatile substances thus enhancing the preservative effect. Accordingly the barrier properties of the packaging may be chosen to suit the treated material.

While particularly suited to use with water soluble volatiles, the inventive process may also be used with other applications such as those requiring the transfer of volatile substances that are not soluble in water e.g. some anti-oxidants.

The material to be treated e.g. foodstuffs, should ideally have a minimum surface water activity ( $A_w$ ) of approximately 0.85 to allow the volatile substance to quickly transfer across from the carrier gas. An  $A_w$  of approximately 0.95 will allow near optimum transference rates and therefore minimum exposure times. To optimise transfer rates it may be appropriate to dose all the gaseous mixture required to an over-pressure of 0.01-0.2 bar (7.5-150mm Hg) and up to 3 bar (2250mm Hg) over atmospheric pressure and allow the appropriate contact time. Lower  $A_w$  foodstuffs without the addition of a small quantity of water (generally 1-2%), onto the surface of the material to be treated may require longer exposure times. This additional water can be applied as a fine mist in the case of relatively impervious products such as peppercorns or by steaming in more difficult applications.

If surface wetting is a technical requirement then mild surface drying will promote the volatilisation of surface acids thereby reducing acidulation. Alternatively post-treatment surface addition of approximately 0.2% w/w of sodium bicarbonate will, in most cases, neutralise all surface acidulation.

5        Once the desired exposure is attained, the vacuum in the vessel may be released and the treated products proceed to final packaging stages.

Some post contamination protection is also offered by this invention thus mechanical and/or human double handling is feasible when using this invention.

It is preferable, however, that once the surface acidulation has been decreased to  
10    minimise unfavourable acidic flavours, sometimes a requirement with bland materials, the material is handled and packed in such a manner as to minimise it from any further microbial contamination especially if a favourable environment exists to initiate and support further microbial growth.

#### BRIEF DESCRIPTION OF THE DRAWINGS

15    The invention will now be described by way of example only with reference to the following, nonlimiting examples and accompanying drawings in which:

Figure 1 shows a schematic elevational representation of a batch treatment apparatus according to a first embodiment of the present invention;

Figure 2 shows a schematic elevational representation of a continuous treatment  
20    apparatus according to a second embodiment of the present invention; and

Figure 3 shows a flowchart of the treatment method and apparatus according to a third embodiment of the present invention.

### MODE(S) FOR CARRYING OUT THE INVENTIONS

As shown in Figure 1, material 2 to be treated is provided in a sanitary pressure vessel 1. The vessel 1 comprises a hinged swing away lid 3 which contains a flange and seal 4. The vessel 1 is also provided with a safety vent 8, a pressure/vacuum gauge 9, a pressure regulator valve 10 and gas sparging ports 11. An external vacuum source 5 is connected by means of a line 6 and valve 7 to the vessel 1. Connected to the gas sparging ports by means of lines 12, 13, 14, 15 and valves 16, 17 and 18 is a compressed gas source 19, one or more volatile substance sources 20, preferably sparging vessels, and an aerosol trap 21.

The aerosol trap 21 is intended to minimise large droplets of the volatile(s) from entering the vessel 1. These droplets are usually in the form of large aerosol droplets but may also be unsuspended in the vapour line as a result of condensed and/or coalesced aerosols or from overflow from the volatile substance source. Droplets can cause undesirable spotting of the material to be treated and non-uniform distribution of the volatile(s) onto the material surface which can result in flavour changes or other undesirable physiological effects. Multiple volatile substance sources 20 can maximise saturation of the carrier gas.

In the case of treatment with carbonic acid, the volatile source 20 may be at least initially filled with purified water such that bubbling of the CO<sub>2</sub> gas therethrough produces carbonic acid thus causing the CO<sub>2</sub> carrier gas to be at least partially saturated with the produced carbonic acid. Some materials will benefit more after the carrier gas, preferably food grade carbon dioxide, has been passed through multiple volatile sources solvents to achieve a mixture of volatiles in the carrier gas. Various types, combinations and concentrations of saturated carrier gases can be used to treat the material to optimise shelf life and flavour parameters, particularly various mixtures of acetic and carbonic acids and hydrogen peroxide. A carrier gas/multiple volatile mixture may be provided by mixing a group of parallel gas/volatile mixture streams after passing through their respective volatile substance sources or, less preferably, a single carrier gas stream may be passed through a series of volatile sources.

In use a batch of material 2 to be treated is introduced through the lid 3 into the vessel 1 and the lid is then sealed. Valve 7 is opened and evacuation is commenced by means of the vacuum pump 5. When the



desired vacuum is achieved valves 16, 17 and 18 are opened and the carrier gas is forwarded from the compressed gas source 19 to the volatile substance source 20, the volatile substance thereby becoming entrained in the carrier gas, which is then introduced into the vessel 1 through sparging ports 11 to thereby contact the material 2. Valves 22 and 23 may be operated to bypass the additional volatile substance source 20 if only one volatile substance source is required.

During the process the carrier gas which is at least partially stripped of the volatile substance is allowed to escape through the pressure regulator valve 10 achieving a desired process overpressure for the predetermined time of exposure. This stripped carrier gas may be recycled back to the process as mentioned above for further entrainment of the volatile substance.

The duration of exposure is optimised to provide the maximum reduction in microbial bioburden while achieving the desired flavour and other properties of the material 2 being treated. Once the desired exposure is attained, the flow of carrier gas is ceased and the pressure regulating valve 10 released. The treated material 2 is then removed from the vessel and sealed.

As mentioned above, the inventive method is suitable for use with natural food acids such as acetic acid and carbonic acid.

Acetic acid is a natural organic food acid with a high degree of biocidal activity and is highly soluble in carbon dioxide. The pH profile of acetic acid is shown in Table 1.

TABLE 1  
pH PROFILE ACETIC ACID

%ACETIC - AQUEOUS SOLUTION	pH
90	0.00
60	1.17
45	1.52
15	1.73
11	1.83

Surprisingly, the applicants have also found that carbonic acid is also suitable for the present inventive method. Carbonic acid is also a natural organic food acid, which to the applicants have found, has a high degree of



biocidal activity. It is also soluble in gaseous carbon dioxide and has a high degree of buffering capacity.

5 Unexpectedly the applicants have determined that carbonic and acetic acids transferred by the inventive gaseous method yield similar titrateable acidities after the gas mixes are "stripped" of their acids by passing them through distilled and neutralised water as shown in Table 2 below.

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As a quality assurance method and to determine the titrateable acidity of acetic acid in a carrier gas as compared to carbonic acid in a carrier gas, the respective gaseous mixtures were passed through a neutralised and distilled water bath and titrated with 0.1 N KOH solution until the bromothymol blue indicator yielded the first faint blue colour which persisted for at least five seconds. It can be seen from Table 2 that the titrateable acidity of acetic acid and carbonic acid is virtually identical. Furthermore, an investigation by CSIRO Australia (Report FSQ96-128) concluded that the titrateable acidities were identical.

TABLE 2  
ACID IN CO<sub>2</sub> CARRIER

MIXTURE	VOL. DIS. H <sub>2</sub> O	REACTION TIME (SECONDS)	FLOW RATE CO <sub>2</sub>	TITRE 0.1 N KOH
Acetic	200	10	10 l/minute	44 mils
Acetic	200	10	10 l/minute	38 mils
Acetic	200	10	10 l/minute	41 mils
Carbonic	200	10	10 l/minute	43 mils
Carbonic	200	10	10 l/minute	38 mils

As shown in Figure 2, an alternative application to the batch process is to conduct the method of the invention continuously whilst conveying material through a commercially available flow wrapper 22, or similar packaging system, equipped with a conveyor 23, a gas sparging head 24 and a gas control system 25.

Typically, the process can be balanced to attain treatment times of only seconds. Of course longer treatment times may be necessary depending upon a number of

variables including initial microbial content. This short processing time can yield up to and exceeding 30 days extension in the acceptable shelf life of bread and other baked products. Shelf life is evaluated on the basis of flavour and aroma profiles, as well as apparent fungal and/or bacterial spoilage.

5        An alternative embodiment of an apparatus for carrying out the inventive process is shown in Figure 3 in which compressed gas, typically carbon dioxide 51 passes through regulator 52 when valve 53 is opened. The carrier gas is transferred through transfer line TL1, to flow meter 54. Process controller 55 monitors and controls the flow of carrier gas through the flow meter 54 to the specified rate. The carrier gas is then  
10 transferred through line TL2 to the sparger 56, and sparged through the volatile substance contained in vessel 57. As mentioned above the inventive process can include one or more such vessels to provide a mixture of volatile substances in the carrier gas. If carbonic acid treatment is required vessel 57 may be at least initially filled with water.

Preferably the carrier gas is saturated with volatile substance(s). The carrier  
15 gas/volatile substance mixture is then transferred through line TL3 into the liquid trap 58, to ensure that an aerosol is not transferred into line TL4. In operative mode, the gas mixture is then normally transferred through line TL4 and through valve 59, with valves 64 and 68 closed, through heating manifold 70, which is normally not in heating mode, through to product treatment container 60, which may be the final packaging;  
20 vacuum/pressure vessel; treatment tunnel or other such device as indicated in figures 1 and 2.

After the prescribed treatment the carrier gas stripped of volatile(s) may be transferred through line TL5 with valve 61 open and valve 62 closed, to compressor 63,

and recycled back to compressed gas cylinder 51. Alternatively after leaving treatment container 60 the volatile(s) stripped carrier gas can be transferred through line TL5 and vented to atmosphere with valve 61 closed and valve 62 open.

When a material is not being treated but it is desirable to maintain the carrier gas/volatile substance flow, especially in the case of treatment with carbonic acid, valve 59 is closed and valve 64 is opened with valve 65 closed, the carrier gas/volatile substance mixture is transferred through line TL6 to water scrubber 66 where the volatile substance is stripped from the carrier gas and the gas is vented to atmosphere or recycled.

10        Quality measurements of the carrier gas and the volatile substance are performed by closing valve 59 and 64 and opening valve 65, transferring the gas mixture through line TL7 to quality control station 67 for testing. Test data from control station 67 is sent to process controller 55 which monitors and controls the flow of carrier gas through the flow meter 54. If station 67 identifies that the carrier gas is being slowly diluted by  
15        atmospheric gas the process controller 55 may increase the flow rate through flow meter 54, until the predetermined maximum volatile substance transfer rate is achieved, at which point a predetermined percentage of recycled carrier gas is vented to atmosphere and an equivalent volume of new carrier gas is fed into the circuit from compressed carrier gas vessel 51.

20        If a high concentration of a volatile substance or a mixture of volatile substances is required for a given application, the standard carrier gas/volatile substance mixture transferring through line TL4 may be dosed with additional volatiles by injection of a fine aerosol of the desired volatile substance from a storage tank/atomiser 69 through

opened valve 68. The gas mixture/aerosol continues to transfer along line TL4 and is heated to beyond the vaporisation point of the added aerosol in the heated manifold 70, from where it enters the treatment container 60 as normal. Prolonged production runs employing this additional dosage system may cause condensation on the inner walls of treatment vessels/tunnels if they are not heat lagged.

The following examples illustrate and substantiate various aspects of the present invention.

#### EXAMPLE IA - SANDWICH HAM

In this example, a sandwich ham slice was treated in accordance with the present inventive method. The sliced ham was placed in the vessel, the vessel evacuated and then supplied with a CO<sub>2</sub>/acetic acid gas mixture or CO<sub>2</sub>/carbonic acid gas mixture for the designated period. The gas flow was constant such that the vessel maintained an overpressure 0.01-0.5 bar above atmospheric pressure. The sandwich ham was in plastic bags and a degree of pressure was allowed to develop in the plastic bags during treatment. After the designated period the gas flow was stopped, the bag containing the ham closed and shaken slightly for 15 seconds to provide better contact with the carrier gas/volatile substance mixture.

The vessel was then vacuum flushed again and an additional exposure to the gas mixture performed along with the 15 second post-treatment contact.

The majority of the gas mixture entering the vessel escaped with approximately 50% of the residual gas mixture being expelled manually prior to sealing of the plastic bags. The samples were then stored for approximately one hour prior to microbiological analysis. The results provided under Table 3 follow on page 15. 22

As can be seen from Table 3, there has been a substantial reduction in the bioburden following application of the inventive process. For treatment with a carrier gas/acetic acid, the initial total plate count of  $3.4 \times 10^4$ , and total spores of 35 was reduced to total plate count 65-70, total spore count 10-40. Using a carrier gas/carbonic acid mixture an initial total plate count of  $2 \times 10^0$  and total spores of 250 was reduced to total plate count of  $7 \times 10^3$  at gas flow rate of 10 litres/minute. At a higher gas flow rate of 20 litres/minute total plate count was reduced to less than 10 and total spores to 45.



## EXAMPLE 1B - SANDWICH HAM

In this example sandwich ham is treated with a volatile substance comprising 50% carbonic acid and 50% hydrogen peroxide.

5 As with Example 1A, the ham was placed in the vessel and the vessel evacuated and exposed to the carrier gas/volatile substance mixture. The ham was then subjected to the 15 second post-treatment contact time with agitation. The vessel was then vacuum flushed again and additional exposure to the gas mixture performed followed by the same 15 second post-treatment contact.

10 Shelf life observations were made approximately four days after treatment and further observations were made from nine to twenty days after treatment. The results are provided under Table 4.

15 It can be seen from the microbiological results provided under Table 4 that this particular gas mix is very effective in reducing the microbiological counts. Total treatment times of 10, 20 and 60 seconds resulted in proportional reductions down to 2 vegetative and less than 1 spore organism per gram of sample.



It has been observed that hydrogen peroxide increases the pink colouration and extends the shelf life of the pink colouration of some smallgoods. This effect appears to be intermediary in efficiency between carbonic and acetic acids. Again, smoked aromas were observed along with slight background volatility in some instances.

5      EXAMPLE 2A - CRUMPETS

In this example the same process as Example 1A, was applied to crumpet fingers. Namely the finger(s) were placed in the vessel, the vessel evacuated and then exposed to the carrier gas/volatile substance mixture followed by a 15 second post treatment contact with agitation. The vessel was then vacuum flushed again and an additional exposure to  
10 the gas mixture performed followed by the same 15 second post-contact treatment.

The results are provided under Tables 5A and 5B.

As can be seen from Tables 5A and 5B a significant seven day shelf life extension of crumpets was achieved with CO<sub>2</sub>/carbonic acid gas mixture treatment. Not all mold spores were killed or completely inhibited, however, colony growth was random  
15 indicating entire surface area had been uniformly treated. No unfavourable acidic flavours were detected.

The six second exposure time was found to be optimal. Greater exposures appeared to make no improvement. Indeed it is not entirely clear why higher exposure times did not result in additional benefit. This appears to be a peculiarity of treatment  
20 with carbonic acid.

For treatment with CO<sub>2</sub>/acetic acid 90%/carbonic acid 10% mixture an indefinite shelf life extension was achieved however, after assessing the resultant surface acidulation the realistic shelf life extension was reduced to 13 days. The manufacturers

of these types of products must consider other quality parameters such as syneresis and related textural problems which may further reduce the shelf life extension, however the inventive process will still achieve an increase in food safety to the consumer.

#### EXAMPLE 2B - CRUMPETS

5 In the example the same process as Example 1B was applied to crumpet finger(s).  
The results are shown in Table 6.

It can be seen from the microbiological results provided under Table 6 that this particular gas mix is very effective in reducing the microbiological counts. Total treatment times of 10, 20 and 60 seconds resulted in proportional reductions down to six  
10 vegetative and less than 1 spore organism per gram of sample.

#### EXAMPLE 3A - PEPPERCORNS

In this example the same process as Example 1A was applied to the surface of wetted black peppercorns with the exception that a CO<sub>2</sub>/acetic gas mixture only was used.

#### 15 Example 3B - PEPPERCORNS

In this example, the peppercorns were subjected to four separate treatments of 300 seconds each at 0 hours; 12 hours; 13 hours and 16 hours. Prior to all treatments except the 16 hour treatment, the peppercorns were wetted with 2.0% w/w of water to ensure continuity of acid transfer.

20 Due to the peppercorns low water activity of 0.75, wetting with water is required.

This was achieved by pouring a specified quantity of distilled water onto the peppercorns whilst continuously mixing in a plastic bag. A new plastic bag was then

used for the inventive gaseous treatment. For effective wetting, it is essential to completely wet the entire surface whilst minimising the amount of added water.

This example was intended to assess the effect of increasing the time of contact between the gaseous mixture and the peppercorns at high surface acidity concentrations.

5      EXAMPLE 3C - PEPPERCORNS

In this example the peppercorns were subjected to treatments of 900 seconds each at 0 seconds; 900 seconds; 1800 seconds and 2700 seconds. All treatments except the first treatment were preceded by wetting with 1.0% w/w of water to ensure continuity of acid transfer.

10      The intent of this example was to assess the effect of increasing the contact time to three weeks at high surface acidity concentrations.

The results for examples 3A - 3C are shown in Table 7.

Peppercorns have traditionally been a difficult material to sterilise and this is evidenced in the high bioburden of the controls and results even with long exposure times. However a significant reduction in sporer organisms from  $2.7 \times 10^7$  to less than  $10 \times 10^4$  was achieved with example 3B at 20 hours.

Longer exposure times and contact times of example 3C only marginally improved the overall efficiency of the inventive process. However a significant reduction in sporer from  $2.7 \times 10^7$  to  $5.2 \times 10^4$  was achieved.



## EXAMPLE 3E - PEPPER

The intent of this example was to assess the effect of temperature on the efficiency of the invented method. [REDACTED]

- 5 Two grams of pepper were shaken in 9.0 ml of 0.1% peptone water for 30 minutes to produce a mixed bacterial inoculum representative of normal peppercorn bioflora. A 0.1 ml sample of this inoculum was placed in 9.0 ml solutions of acetic acid (0% (control), 2.5%, 5%, 11%, 22.5%, 45%, 60% and 80% concentrations) for 1 hour. Subsequently, 0.1 ml of each inoculated dilution was pipetted into duplicate 1.0 ml volumes of 0.1% peptone water.
- 10 One of each duplicate was then exposed to room temperature for 30 minutes.



The other of each duplicate was exposed to 80°C for 30 minutes. The results are shown in Table 9.

Lethality due to the acetic acid (i.e. at room temperature) was within the range of 94.6 to 98.9% when compared to the control. With exposure to mild heat (i.e. 80°C), lethality was increased to between 97.8 to 99.9%.

It is also expected that the inventive method may utilise surface heat of the material to volatilise any excessive acidic volatiles i.e. reduce acidulation.

The applicants have also found that even with low acetic acid concentrations, if the treatment vessel is maintained at an over-pressure of up to 3 bar over atmospheric pressure, up to five days shelf life extension may be obtained on crumpets.

It can be seen that the present inventive method is not only suitable as a biocidal process but in lower concentrations has an inhibitory function and substantially extends the shelf life of certain products.

It is also envisaged that the inclusion of a low concentration of acetic acid in the carrier gas/volatile substance mixture may increase the post-protection potential of the gas mixture. Typically such a gas mixture may be made from the following volatile substances e.g. carbonic acid 50%, hydrogen peroxide 30-40%, acetic acid 10-20%.

It has been found that some food products, treated by the method of the invention, particularly bland food products can develop a slightly acidic taste. This can be masked by the use of spreads or condiments or flavour disguising agents.

By means of the invention it is possible to treat a material with a volatile substance to alter its physical or chemical characteristics whilst not severely adversely affecting the properties of the treated material. The method of the invention does not require specialised packaging or costly changes to existing equipment.

It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention without departing from the scope of the invention as described.



TABLE 3

ACETIC/CARBONIC ACID - SMALLGOODS

FOODSTUFF	VOLATILE	QA (QUALITY ASSURANCE)	FLOW RATE OF GAS MIXTURE	EXPOSURE TIME (SECONDS)	MICRO ANALYSIS (per gram)	SURFACE AREA/ SAMPLE WEIGHT
Sandwich ham control ( $A_w = 0.95$ )					TPC = $3.4 \times 10^4$ TSP = 35	40.5 cm <sup>2</sup> /10 g
Sandwich ham	Acetic Acid		22 l/minute	16	TPC = 70 TSP = 10	10 g
Sandwich ham	Acetic Acid	38 ml	22 l/minute	20	TPC = 65 TSP = 40	20 g
Sandwich ham control ( $A_w = 0.95$ )					TPC = $2 \times 10^6$ TSP = 250	40.5cm <sup>2</sup> /10 g
Sandwich ham	Carbonic Acid	43 ml	10 l/minute	50	TPC = $7 \times 10^3$ TSP = 500	10 g
Sandwich ham	Carbonic Acid		20 l/minute	50	TPC < 10 TSP = 45	10 g

$A_w$  - Surface water activity

TPC - total plate count/gram

TSP - total spores/gram

10 12 15 18 21 24 27 30 33 36 39 42 45 48 51 54 57 60 63 66 69 72 75 78 81 84 87 90 93 96 99 102 105 108 111 114 117 120 123 126 129 132 135 138 141 144 147 150 153 156 159 162 165 168 171 174 177 180 183 186 189 192 195 198 201 204 207 210 213 216 219 222 225 228 231 234 237 240 243 246 249 252 255 258 261 264 267 270 273 276 279 282 285 288 291 294 297 300 303 306 309 312 315 318 321 324 327 330 333 336 339 342 345 348 351 354 357 360 363 366 369 372 375 378 381 384 387 390 393 396 399 402 405 408 411 414 417 420 423 426 429 432 435 438 441 444 447 450 453 456 459 462 465 468 471 474 477 480 483 486 489 492 495 498 501 504 507 510 513 516 519 522 525 528 531 534 537 540 543 546 549 552 555 558 561 564 567 570 573 576 579 582 585 588 591 594 597 600 603 606 609 612 615 618 621 624 627 630 633 636 639 642 645 648 651 654 657 660 663 666 669 672 675 678 681 684 687 690 693 696 699 702 705 708 711 714 717 720 723 726 729 732 735 738 741 744 747 750 753 756 759 762 765 768 771 774 777 780 783 786 789 792 795 798 801 804 807 810 813 816 819 822 825 828 831 834 837 840 843 846 849 852 855 858 861 864 867 870 873 876 879 882 885 888 891 894 897 900 903 906 909 912 915 918 921 924 927 930 933 936 939 942 945 948 951 954 957 960 963 966 969 972 975 978 981 984 987 990 993 996 999 1002 1005 1008 1011 1014 1017 1020 1023 1026 1029 1032 1035 1038 1041 1044 1047 1050 1053 1056 1059 1062 1065 1068 1071 1074 1077 1080 1083 1086 1089 1092 1095 1098 1101 1104 1107 1110 1113 1116 1119 1122 1125 1128 1131 1134 1137 1140 1143 1146 1149 1152 1155 1158 1161 1164 1167 1170 1173 1176 1179 1182 1185 1188 1191 1194 1197 1200 1203 1206 1209 1212 1215 1218 1221 1224 1227 1230 1233 1236 1239 1242 1245 1248 1251 1254 1257 1260 1263 1266 1269 1272 1275 1278 1281 1284 1287 1290 1293 1296 1299 1302 1305 1308 1311 1314 1317 1320 1323 1326 1329 1332 1335 1338 1341 1344 1347 1350 1353 1356 1359 1362 1365 1368 1371 1374 1377 1380 1383 1386 1389 1392 1395 1398 1401 1404 1407 1410 1413 1416 1419 1422 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2025 2028 2031 2034 2037 2040 2043 2046 2049 2052 2055 2058 2061 2064 2067 2070 2073 2076 2079 2082 2085 2088 2091 2094 2097 2100 2103 2106 2109 2112 2115 2118 2121 2124 2127 2130 2133 2136 2139 2142 2145 2148 2151 2154 2157 2160 2163 2166 2169 2172 2175 2178 2181 2184 2187 2190 2193 2196 2199 2202 2205 2208 2211 2214 2217 2220 2223 2226 2229 2232 2235 2238 2241 2244 2247 2250 2253 2256 2259 2262 2265 2268 2271 2274 2277 2280 2283 2286 2289 2292 2295 2298 2301 2304 2307 2310 2313 2316 2319 2322 2325 2328 2331 2334 2337 2340 2343 2346 2349 2352 2355 2358 2361 2364 2367 2370 2373 2376 2379 2382 2385 2388 2391 2394 2397 2400 2403 2406 2409 2412 2415 2418 2421 2424 2427 2430 2433 2436 2439 2442 2445 2448 2451 2454 2457 2460 2463 2466 2469 2472 2475 2478 2481 2484 2487 2490 2493 2496 2499 2502 2505 2508 2511 2514 2517 2520 2523 2526 2529 2532 2535 2538 2541 2544 2547 2550 2553 2556 2559 2562 2565 2568 2571 2574 2577 2580 2583 2586 2589 2592 2595 2598 2601 2604 2607 2610 2613 2616 2619 2622 2625 2628 2631 2634 2637 2640 2643 2646 2649 2652 2655 2658 2661 2664 2667 2670 2673 2676 2679 2682 2685 2688 2691 2694 2697 2700 2703 2706 2709 2712 2715 2718 2721 2724 2727 2730 2733 2736 2739 2742 2745 2748 2751 2754 2757 2760 2763 2766 2769 2772 2775 2778 2781 2784 2787 2790 2793 2796 2799 2802 2805 2808 2811 2814 2817 2820 2823 2826 2829 2832 2835 2838 2841 2844 2847 2850 2853 2856 2859 2862 2865 2868 2871 2874 2877 2880 2883 2886 2889 2892 2895 2898 2901 2904 2907 2910 2913 2916 2919 2922 2925 2928 2931 2934 2937 2940 2943 2946 2949 2952 2955 2958 2961 2964 2967 2970 2973 2976 2979 2982 2985 2988 2991 2994 2997 3000 3003 3006 3009 3012 3015 3018 3021 3024 3027 3030 3033 3036 3039 3042 3045 3048 3051 3054 3057 3060 3063 3066 3069 3072 3075 3078 3081 3084 3087 3090 3093 3096 3099 3102 3105 3108 3111 3114 3117 3120 3123 3126 3129 3132 3135 3138 3141 3144 3147 3150 3153 3156 3159 3162 3165 3168 3171 3174 3177 3180 3183 3186 3189 3192 3195 3198 3201 3204 3207 3210 3213 3216 3219 3222 3225 3228 3231 3234 3237 3240 3243 3246 3249 3252 3255 3258 3261 3264 3267 3270 3273 3276 3279 3282 3285 3288 3291 3294 3297 3300 3303 3306 3309 3312 3315 3318 3321 3324 3327 3330 3333 3336 3339 3342 3345 3348 3351 3354 3357 3360 3363 3366 3369 3372 3375 3378 3381 3384 3387 3390 3393 3396 3399 3402 3405 3408 3411 3414 3417 3420 3423 3426 3429 3432 3435 3438 3441 3444 3447 3450 3453 3456 3459 3462 3465 3468 3471 3474 3477 3480 3483 3486 3489 3492 3495 3498 3501 3504 3507 3510 3513 3516 3519 3522 3525 3528 3531 3534 3537 3540 3543 3546 3549 3552 3555 3558 3561 3564 3567 3570 3573 3576 3579 3582 3585 3588 3591 3594 3597 3600 3603 3606 3609 3612 3615 3618 3621 3624 3627 3630 3633 3636 3639 3642 3645 3648 3651 3654 3657 3660 3663 3666 3669 3672 3675 3678 3681 3684 3687 3690 3693 3696 3699 3702 3705 3708 3711 3714 3717 3720 3723 3726 3729 3732 3735 3738 3741 3744 3747 3750 3753 3756 3759 3762 3765 3768 3771 3774 3777 3780 3783 3786 3789 3792 3795 3798 3801 3804 3807 3810 3813 3816 3819 3822 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4425 4428 4431 4434 4437 4440 4443 4446 4449 4452 4455 4458 4461 4464 4467 4470 4473 4476 4479 4482 4485 4488 4491 4494 4497 4500 4503 4506 4509 4512 4515 4518 4521 4524 4527 4530 4533 4536 4539 4542 4545 4548 4551 4554 4557 4560 4563 4566 4569 4572 4575 4578 4581 4584 4587 4590 4593 4596 4599 4602 4605 4608 4611 4614 4617 4620 4623 4626 4629 4632 4635 4638 4641 4644 4647 4650 4653 4656 4659 4662 4665 4668 4671 4674 4677 4680 4683 4686 4689 4692 4695 4698 4701 4704 4707 4710 4713 4716 4719 4722 4725 4728 4731 4734 4737 4740 4743 4746 4749 4752 4755 4758 4761 4764 4767 4770 4773 4776 4779 4782 4785 4788 4791 4794 4797 4800 4803 4806 4809 4812 4815 4818 4821 4824 4827 4830 4833 4836 4839 4842 4845 4848 4851 4854 4857 4860 4863 4866 4869 4872 4875 4878 4881 4884 4887 4890 4893 4896 4899 4902 4905 4908 4911 4914 4917 4920 4923 4926 4929 4932 4935 4938 4941 4944 4947 4950 4953 4956 4959 4962 4965 4968 4971 4974 4977 4980 4983 4986 4989 4992 4995 4998 5001 5004 5007 5010 5013 5016 5019 5022 5025 5028 5031 5034 5037 5040 5043 5046 5049 5052 5055 5058 5061 5064 5067 5070 5073 5076 5079 5082 5085 5088 5091 5094 5097 5100 5103 5106 5109 5112 5115 5118 5121 5124 5127 5130 5133 5136 5139 5142 5145 5148 5151 5154 5157 5160 5163 5166 5169 5172 5175 5178 5181 5184 5187 5190 5193 5196 5199 5202 5205 5208 5211 5214 5217 5220 5223 5226 5229 5232 5235 5238 5241 5244 5247 5250 5253 5256 5259 5262 5265 5268 5271 5274 5277 5280 5283 5286 5289 5292 5295 5298 5301 5304 5307 5310 5313 5316 5319 5322 5325 5328 5331 5334 5337 5340 5343 5346 5349 5352 5355 5358 5361 5364 5367 5370 5373 5376 5379 5382 5385 5388 5391 5394 5397 5400 5403 5406 5409 5412 5415 5418 5421 5424 5427 5430 5433 5436 5439 5442 5445 5448 5451 5454 5457 5460 5463 5466 5469 5472 5475 5478 5481 5484 5487 5490 5493 5496 5499 5502 5505 5508 5511 5514 5517 5520 5523 5526 5529 5532 5535 5538 5541 5544 5547 5550 5553 5556 5559 5562 5565 5568 5571 5574 5577 5580 5583 5586 5589 5592 5595 5598 5601 5604 5607 5610 5613 5616 5619 5622 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6225 6228 6231 6234 6237 6240 6243 6246 6249 6252 6255 6258 6261 6264 6267 6270 6273 6276 6279 6282 6285 6288 6291 6294 6297 6300 6303 6306 6309 6312 6315 6318 6321 6324 6327 6330 6333 6336 6339 6342 6345 6348 6351 6354 6357 6360 6363 6366 6369 6372 6375 6378 6381 6384 6387 6390 6393 6396 6399 6402 6405 6408 6411 6414 6417 6420 6423 6426 6429 6432 6435 6438 6441 6444 6447 6450 6453 6456 6459 6462 6465 6468 6471 6474 6477 6480 6483 6486 6489 6492 6495 6498 6501 6504 6507 6510 6513 6516 6519 6522 6525 6528 6531 6534 6537 6540 6543 6546 6549 6552 6555 6558 6561 6564 6567 6570 6573 6576 6579 6582 6585 6588 6591 6594 6597 6600 6603 6606 6609 6612 6615 6618 6621 6624 6627 6630 6633 6636 6639 6642 6645 6648 6651 6654 6657 6660 6663 6666 6669 6672 6675 6678 6681 6684 6687 6690 6693 6696 6699 6702 6705 6708 6711 6714 6717 6720 6723 6726 6729 6732 6735 6738 6741 6744 6747 6750 6753 6756 6759 6762 6765 6768 6771 6774 6777 6780 6783 6786 6789 6792 6795 6798 6801 6804 6807 6810 6813 6816 6819 6822 6825 6828 6831 6834 6837 6840 6843 6846 6849 6852 6855 6858 6861 6864 6867 6870 6873 6876 6879 6882 6885 6888 6891 6894 6897 6900 6903 6906 6909 6912 6915 6918 6921 6924 6927 6930 6933 6936 6939 6942 6945 6948 6951 6954 6957 6960 6963 6966 6969 6972 6975 6978 6981 6984 6987 6990 6993 6996 6999 7002 7005 7008 7011 7014 7017 7020 7023 7026 7029 7032 7035 7038 7041 7044 7047 7050 7053 7056 7059 7062 7065 7068 7071 7074 7077 7080 7083 7086 7089 7092 7095 7098 7101 7104 7107 7110 7113 7116 7119 7122 7125 7128 7131 7134 7137 7140 7143 7146 7149 7152 7155 7158 7161 7164 7167 7170 7173 7176 7179 7182 7185 7188 7191 7194 7197 7200 7203 7206 7209 7212 7215 7218 7221 7224 7227 7230 7233 7236 7239 7242 7245 7248 7251 7254 7257 7260 7263 7266 7269 7272 7275 7278 7281 7284 7287 7290 7293 7296 7299 7302 7305 7308 7311 7314 7317 7320 7323 7326 7329 7332 7335 7338 7341 7344 7347 7350 7353 7356 7359 7362 7365 7368 7371 7374 7377 7380 7383 7386 7389 7392 7395 7398 7401 7404 7407 7410 7413 7416 7419 7422 7425 7428 7431 7434 7437 7440 7443 7446 7449 7452 7455 7458 7461 7464 7467 7470 7473 7476 7479 7482 7485 7488 7491 7494 7497 7500 7503 7506 7509 7512 7515 7518 7521 7524 7527 7530 7533 7536 7539 7542 7545 7548 7551 7554 7557 7560 7563 7566 7569 7572 7575 7578 7581 7584 7587 7590 7593 7596 7599 7602 7605 7608 7611 7614 7617 7620 7623 7626 7629 7632 7635 7638

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TABLE 5A

CARBONIC ACID - BAKED GOODS

FOODSTUFF	VOLATILE	QA (QUALITY ASSURANCE)	FLOW RATE OF GAS MIXTURE	EXPOSURE TIME (SECONDS)	SHELF LIFE OBSERVATION	SURFACE AREA/SAMPLE WEIGHT
Crumpets (Control)				0	4 days - 4 colonies	Whole Fingers
Crumpets	Carbonic	38 ml	22 l/min	6	11 days - 3 to 10 colonies on all samples. End shelf life due to mold growth	Whole Fingers
Crumpets	Carbonic			10	End shelf life due to mold growth	Whole Fingers
Crumpets	Carbonic			16	End shelf life due to mold growth	Whole Fingers
Crumpets	Carbonic			20	End shelf life due to mold growth	Whole Fingers
Crumpets	Carbonic			26	End shelf life due to mold growth	Whole Fingers
Crumpets	Carbonic			32	End shelf life due to mold growth	Whole Fingers
Crumpets	Carbonic			40	End shelf life due to mold growth	Whole Fingers
Crumpets	Carbonic			50	End shelf life due to mold growth	Whole Fingers
Crumpets	Carbonic			60	End shelf life due to mold growth	Whole Fingers

TABLE 5B

ACETIC ACID - BAKED GOODS

FOODSTUFF	VOLATILE	QA (QUALITY ASSURANCE)	FLOW RATE OF GAS MIXTURE	EXPOSURE TIME (SECONDS)	SHELF LIFE OBSERVATION	SURFACE AREA/SAMPLE WEIGHT
Crumpets (Control)				0	4 days - 5 colonies	Whole Fingers
Crumpets	90% Acetic 10% Carbonic	44.5 ml	22 l/min	6	11 days - 1 small colony weak acid/flour aroma, no taste - raw. No aroma or taste during or after cooking	Whole Fingers
Crumpets	90% Acetic 10% Carbonic			10	15 days - 1 small dense colony. Slight acid aroma, no taste - raw. Very slight acid aroma, no taste - cooked	Whole Fingers
Crumpets	90% Acetic 10% Carbonic			16	15 days - no colonies. Slight acid aroma and flavour - raw. Very slight toasted/acid aroma and flavour - cooked. End shelf life due to deleterious flavour	Whole Fingers
Crumpets	90% Acetic 10% Carbonic			20	End shelf life due to deleterious flavour	Whole Fingers
Crumpets	90% Acetic 10% Carbonic			26	End shelf life due to deleterious flavour	Whole Fingers
Crumpets	90% Acetic 10% Carbonic			32	End shelf life due to deleterious flavour	Whole Fingers
Crumpets	90% Acetic 10% Carbonic			40	End shelf life due to deleterious flavour	Whole Fingers
Crumpets	90% Acetic 10% Carbonic			50	End shelf life due to deleterious flavour	Whole Fingers
Crumpets	90% Acetic 10% Carbonic			60	End shelf life due to deleterious flavour	Whole Fingers

TABLE 6  
50% CARBONIC ACID/50% HYDROGEN PEROXIDE - BAKED GOODS

FOODSTUFF	VOLATILE	FLOW RATE OF GAS MIXTURE	EXPOSURE TIME	SHELF LIFE OBSERVATIONS MICRO ANALYSIS/g	SAMPLE WEIGHT
Crumpets (Control)	50% carbonic acid/50% hydrogen peroxide	22 litres/minute	0 seconds	1 day - 3 mold colonies, end shelf life TPC = $4.5 \times 10^4$ TSP = $2.8 \times 10^4$	10 g
Crumpets	50% carbonic acid/50% hydrogen peroxide	22 litres/minute	10 seconds	9 days - no observable microbial activity 20 days - no observable microbial activity End realistic shelf life due to leathery texture TPC = $3.6 \times 10^2$ TSP = $2.8 \times 10^2$	10 g
Crumpets	50% carbonic acid/50% hydrogen peroxide	22 litres/minute	20 seconds	4 days - one dead/stressed mold colony 9 days - no observable microbial activity 20 days - no observable microbial activity. End realistic shelf life due to leathery texture TPC = 30 TSP = < 1	10 g
Crumpets	50% carbonic acid/50% hydrogen peroxide	22 litres/minute	60 seconds	4 days - very slight oxidant note 9 days - no observable microbial activity 20 days - no observable microbial activity. End realistic shelf life due to leathery texture. Shelf life extension 19 days TPC = 6 TSP = < 1	10 g

TABLE 7

ACETIC ACID - PEPPERCORNS

EXAMPLE	FOODSTUFF	VOLATILE	QA (QUALITY ASSURANCE)	FLOW RATE OF GAS MIXTURE	EXPOSURE TIME (SECONDS)	MICRO ANALYSIS/g	SURFACE AREA/SAMPLE WEIGHT
Control	Peppercorns				0	TPC = $3.7 \times 10^7$ TSP = $2.7 \times 10^7$	39 g
3A	Peppercorns	Acetic Acid	38	12 l/min	300	TPC = $> 10 \times 10^6$ TSP = $5.0 \times 10^6$	39 g 1 g H <sub>2</sub> O (2.5%)
	Peppercorns	Acetic Acid	38	12 l/min	180	TPC = $8 \times 10^6$ TSP = $1.2 \times 10^7$	39 g 1 g H <sub>2</sub> O (2.5%)
3B	Peppercorns	Acetic Acid	38	22 l/min	Exposures of 300 seconds each at 0, 12, 13 and 16 hours (total 1200)	20 hours after first treatment TPC = $9.0 \times 10^6$ TSP = $< 10.0 \times 10^4$	50 g + 1 g H <sub>2</sub> O (2.0%)
3C	Peppercorns	Acetic Acid	38	14 l/min	4 exposures of 900 seconds each at 0, 900, 1800, and 2700	3 weeks after first treatment TPC = $7.9 \times 10^4$ TSP = $5.2 \times 10^4$	98 g + 2 g H <sub>2</sub> O (2.0%)

TABLE 8

50% CARBONIC ACID/50% HYDROGEN PEROXIDE - PEPPERCORNS

FOODSTUFF	VOLATILE	EXPOSURE TIME <i>seconds</i> 7	SHELF LIFE OBSERVATIONS MICRO ANALYSIS/g	SAMPLE WEIGHT
Peppercorns (control)		0	TPC = $8.9 \times 10^7$ TSP = $7.1 \times 10^7$	10 g
Peppercorns	50% carbonic acid 50% hydrogen peroxide	10	TPC = $6.9 \times 10^5$ TSP = $5.6 \times 10^5$	10 g
Peppercorns	50% carbonic acid 50% hydrogen peroxide	20	TPC = $6.9 \times 10^4$ TSP = $4.1 \times 10^3$	10 g
Peppercorns	50% carbonic acid 50% hydrogen peroxide	60	4 days - threshold volatility detected by taste and aroma  TPC = $9.0 \times 10^3$ TSP = $7.5 \times 10^3$	10 g

TABLE 9

% DILUTIONS OF ACETIC ACID	ROOM TEMPERATURE/ 30 MINUTES	80.0°C/30 MINUTES
	VEGETATIVE CIDAL EFFECT	SPORE CIDAL EFFECT
	C.F.U. per GRAM	C.F.U per GRAM
2.5	15	5
5	4	3
11	20	4
22.5	4	6
45	6	0
60	7	0
80	5	0

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## THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A method for reducing the viable microbial content of a solid material for human consumption which is susceptible to microbial spoilage, said method comprising the steps of:
  - (a) placing the material in a vessel capable of evacuation;
  - (b) evacuating the vessel;
  - (c) entraining a volatile substance in a liquid form, selected from the group consisting of natural food acids, chemical biocides and mixtures thereof, in a stream of a carrier gas to form a gas mixture substantially free of particles of the volatile substance comprising a major portion of the carrier gas and a minor portion of the volatile substance, and
  - (d) contacting exposed surfaces of the material with the gas mixture for a contacting period of 60 seconds or less, wherein at the time of contacting the exposed surfaces of the material with said gas mixture, the exposed surfaces of the material have a water activity ( $A_w$ ) of greater than or equal to 0.85.
2. A method according to claim 1, wherein steps (b) and (d) are repeated sequentially.
3. A method according to claim 1 wherein step (d) comprises feeding the gas mixture to the vessel to achieve a desired over-pressure in the vessel during the contacting period.
4. A method according to claim 1 wherein step (d) comprises continually feeding the gas mixture to the vessel to maintain a desired over-pressure in the vessel during the contacting period.
5. A method according to claim 4 or 5 wherein the over-pressure is up to 3 bar (2250mm Hg) above atmospheric pressure.
6. A method according to claim 2 wherein prior to repeating steps (b) and (d), said material is agitated.



7. A method according to any one of the previous claims, wherein step (d) involves contacting exposed surfaces of the material with the gas mixture for a contacting period of 30 seconds or less.
8. A method according to any one of the previous claims, wherein step (d) involves contacting exposed surfaces of the material with the gas mixture for a contacting period of 10 seconds or less.
9. A method according to any one of the previous claims wherein the material to be treated is chosen from the group consisting of foods, pharmaceutical compositions, and ingredients of pharmaceutical compositions.
10. A method according to any one of the previous claims wherein the volatile substance is a natural food acid.
11. A method according to claim 10 wherein the natural food acid is acetic acid.
12. A method according to claim 10 wherein the natural food acid is carbonic acid.
13. A method according to any one of claims 1 to 9 wherein the volatile substance is a chemical biocide.
14. A method according to claim 13 wherein the chemical biocide is hydrogen peroxide.
15. A method according to any one of claims 1 to 9 wherein the volatile substance present in the gas mixture is a mixture of acetic acid and carbonic acid.
16. A method according to claim 15, wherein the volatile substance present in the gas mixture consists of 90% (w/w) acetic acid and 10% (w/w) carbonic acid.



17. A method according to any one of claims 1 to 9 wherein the volatile substance present in the gas mixture is a mixture of carbonic acid and hydrogen peroxide.
18. A method according to claim 17 wherein the volatile substance present in the gas mixture consists of 50% (w/w) carbonic acid and 50% (w/w) hydrogen peroxide.
19. A method according to any one of claims 1 to 9 wherein the volatile substance present in the gas mixture is a mixture of acetic acid, carbonic acid and hydrogen peroxide.
20. A method according to claim 19 wherein the volatile substance present in the gas mixture consists of 10-20% (w/w) acetic acid, 50% (w/w) carbonic acid and 30-40% (w/w) hydrogen peroxide.
21. A method according to any one of the previous claims wherein the carrier gas is saturated with the volatile substance.
22. A method according to any one of the previous claims wherein the volatile substance is entrained in the carrier gas by passing the carrier gas through a vessel(s) containing the volatile substance(s) in liquid form.
23. A method according to any one of claims 1 to 21 wherein the volatile substance is prepackaged with the carrier gas.
24. A method according to any one of claims 1 to 21 wherein the volatile substance is injected directly into a gas line feeding the carrier gas to the vessel thereby forming said gas mixture.
25. A method according to claim 24, wherein after said volatile substance is injected, said gas line is heated to maintain said gas mixture in the gaseous state prior to entry into said vessel.
26. A method according to any one of the previous claims wherein the vessel is initially evacuated rapidly to sub-ambient pressure.



27. A method according to any one of the previous claims wherein the carrier gas is carbon dioxide and/or nitrogen gas.

28. A method according to any one of the previous claims wherein the method is conducted either batchwise or continuously.

29. A method according to any one of the previous claims, wherein at the time of contacting the exposed surfaces of the material with said gas mixture, the exposed surfaces of the material have a water activity ( $A_w$ ) greater than or equal to 0.95.

30. A method according to any one of the previous claims further comprising the step of:

(e) packing the material within gas barrier packaging to form and/or maintain an atmosphere of said volatile substance substantially in equilibrium with the volatile substance that has partitioned into the solid material.

Dated this 20th day of December 2000

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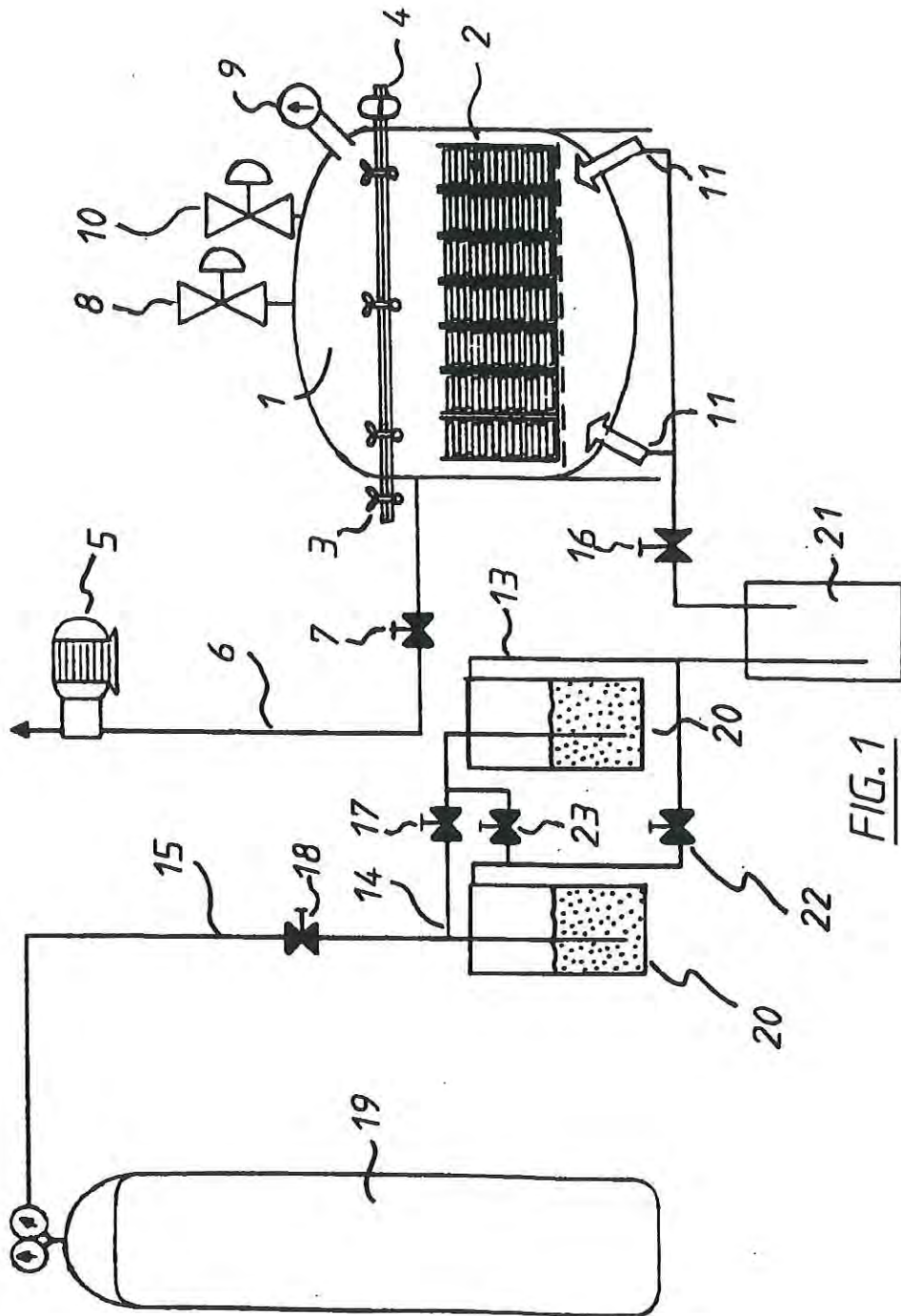


FIG. 1

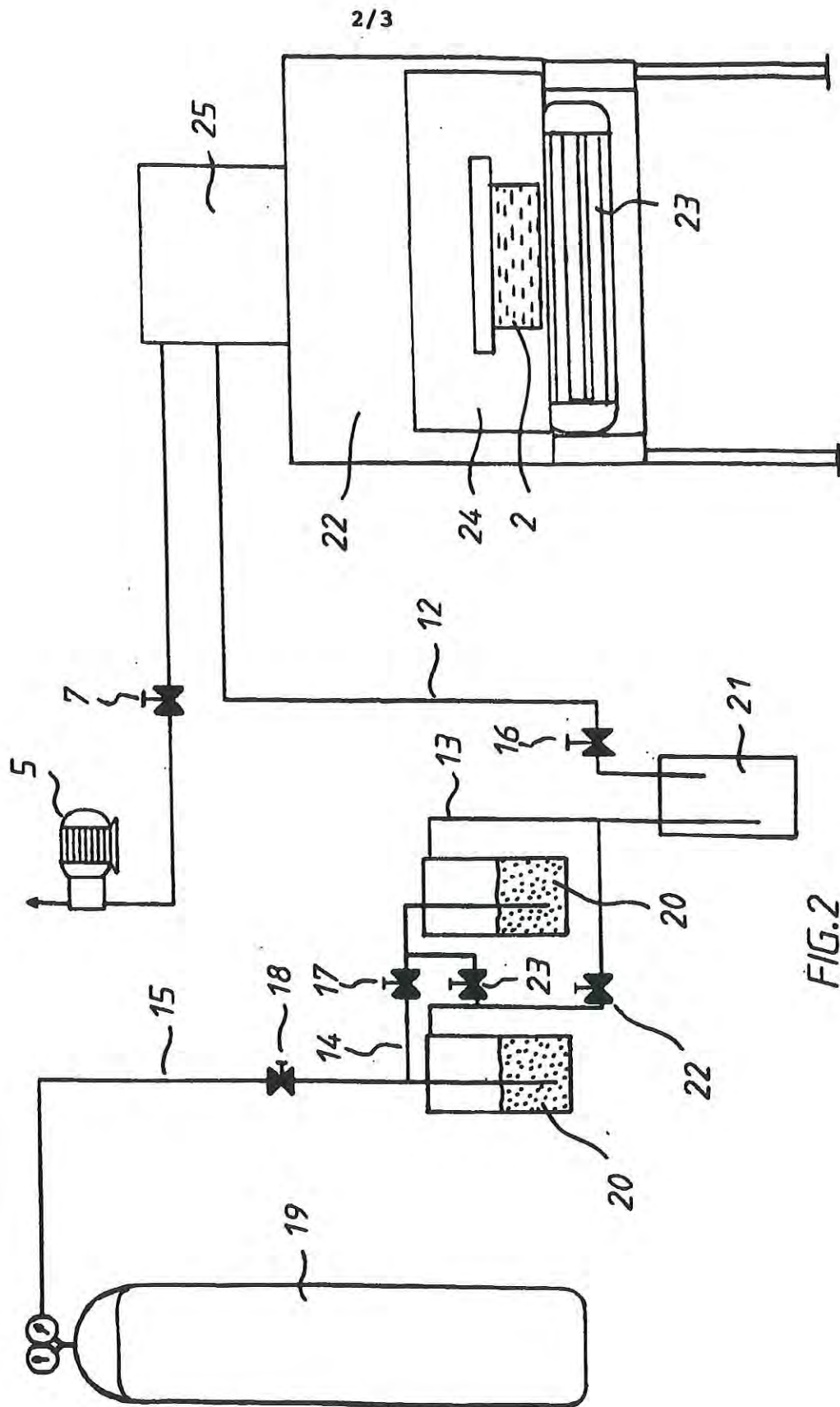


FIG. 2

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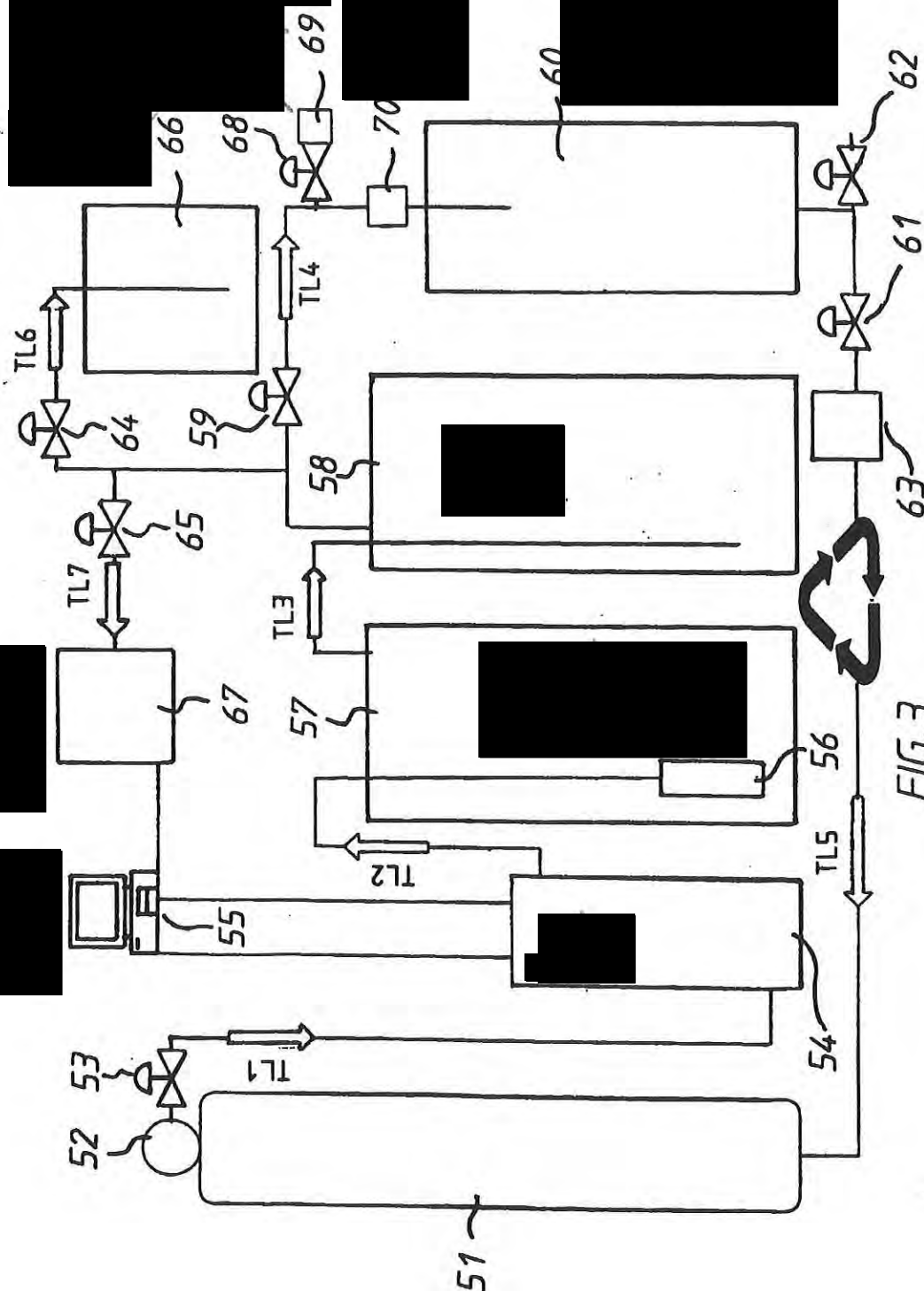


FIG. 3

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**Method and apparatus for applying volatile substances to materials**

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## ABSTRACT

A method and apparatus is disclosed for applying volatile substances, particularly microbicidal substances, to materials such as foods, pharmaceutical products and ingredients thereof for the purpose of achieving at least partial microbial

- 5 decontamination and/or shelf-life extension. The volatile substance (13), which is preferably carbonic acid, acetic acid, hydrogen peroxide and mixtures thereof, are entrained in a carrier gas (12) and preferably applied to the material at an over-pressure of up to 3 bar (2250mm Hg) above atmospheric pressure.

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MBF

# Vapor Phase Hydrogen Peroxide Decontamination of Food Contact Surfaces

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## SUMMARY

Decontamination of food contact surfaces, equipment and general work areas is important for prevention of transmission of foodborne microorganisms. Many liquid-based disinfectants that are widely used for this purpose may not be appropriate for electrical equipment and for relatively large surface areas. Fumigation with vapor phase hydrogen peroxide (VPHP) is an option in these cases and is discussed in this report. VPHP is a dry and rapidly effective antimicrobial vapor. A typical decontamination cycle consists of four phases in a one-step process that is documented and can be validated for a given application. VPHP has been shown to have potent antimicrobial activity against bacteria, viruses, fungi and bacterial spores. Recently, efficacy has been confirmed against known foodborne pathogens, including *Listeria monocytogenes* and *E. coli* O157:H7. Because the VPHP process is dry, it is compatible with many materials, including electronics. In the case study presented, VPHP was shown to be effective in decontaminating a simulative room, including an electrical appliance, in an automated, validated process. VPHP is a possible alternative to liquid-based disinfectants for decontamination of food contact surfaces and equipment.

A peer-reviewed article.

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## INTRODUCTION

Hydrogen peroxide ( $H_2O_2$ ) is a widely used biocide in the food industry because of its rapid antimicrobial efficacy and because it breaks down into environmentally innocuous residues (water and oxygen). First used as an antimicrobial agent in 1880, it is now used for a wide range of applications, including disinfection, odor control, skin antisepsis, bioremediation and paper bleaching (4). In its liquid form, hydrogen peroxide is clear and colorless and has little or no odor. It is widely available in a range of concentrations, from 3 to 90%; 35% food grade is routinely used in the food industry. Liquid hydrogen peroxide solutions have been successfully used for a variety of applications, including sanitization of general food contact surfaces (12), food surfaces (5, 13, 14), and packaging material/equipment (2, 3).

Hydrogen peroxide owes its broad-spectrum antimicrobial efficacy to its activity as a powerful oxidizing agent that is known to damage cellular proteins, lipids and nucleic acids (4). Liquid hydrogen

**TABLE 1. Comparison of liquid and vaporized hydrogen peroxide antimicrobial efficacy, based on Block, 1991 (4)**

Test Organism (Spores)	D-value (time in minutes for a one-log reduction of test organism)	
	Liquid	Vapor
	H <sub>2</sub> O <sub>2</sub> Concentration: 370 mg/l	H <sub>2</sub> O <sub>2</sub> Concentration: 1-2 mg/l
	Temperature: 24-25°C	Temperature: 24-25°C
<i>B. stearothermophilus</i>	1.5	1-2
<i>B. subtilis</i>	2.0-7.3	0.5-1
<i>C. sporogenes</i>	0.8	0.5-1

**TABLE 2. Effect of VPHP concentration and temperature on antimicrobial efficacy**

Temperature (°C)	Concentration (mg/l)	Typical <i>B. stearothermophilus</i> spore D-value
4	0.3-0.5	8-12 mins
25	1-2	1-2 mins
37	3-4	0.5-1 min
55	10-12	1 sec

Note: the condensation point of VPHP increases as temperature increases.

peroxide, either alone or in combination with other antimicrobial agents, has some disadvantages that may limit its use. For example, the higher concentrations required for killing spores (4) may damage a surface with repeated applications. Further, manual application of liquid products for sanitization can be time consuming, hard to control and difficult to validate, especially for larger surface applications. Fogging applications are often used but may also be difficult to control and reproduce. A more recent development is the use of vapor phase hydrogen peroxide (VPHP). VPHP has been widely used for sterilization in pharmaceutical settings, including production filling lines, sterility test-

ing environments, sealable enclosures, production rooms and lyophilizers (7, 10, 15). The vapor is antimicrobial at relatively low concentrations (typically sporicidal at 0.1-2 mg/l at 25°C), in contrast to the liquid hydrogen peroxide (4). Methods of application include both atmospheric and vacuum systems; the latter allows greater active penetration for complex device decontamination/sterilization. Atmospheric systems are widely used for enclosure, isolator, room and equipment decontamination. The most widely used system is the VHP® 1000 Biodecontamination Series. The use of VPHP for the sanitization of food contact surfaces and controlled environments is reviewed in this report.

## VPHP cycle description

The VHP® Biodecontamination Systems generate, deliver, control and remove VPHP for an enclosed environment. For example, a single VHP® 1000 is capable of decontaminating a volume of up to 7,500 ft.<sup>3</sup> with decontamination of larger volumes made possible by using multiple generators in tandem (Fig. 1). The system is directly linked to any enclosure or room to allow for the continuous generation, circulation and removal of VPHP (a typical room arrangement is shown in Fig. 2).

A typical decontamination cycle consists of 4 phases: dehumidification, conditioning, decontamination and aeration (Fig. 3). During dehumidification, drying reduces the relative humidity to less than 40% as is air circulated in a closed loop. During conditioning, VPHP is produced by vaporization of 35% liquid hydrogen peroxide, which is then introduced into the recirculating air stream to achieve the desired VPHP concentration rapidly. The decontamination phase consists of a steady state injection and recirculation flow rate to maintain the VPHP concentration for the desired exposure time. As hydrogen peroxide can be degraded rapidly to water vapor and oxygen, during a typical decontamination phase, the VPHP concentration is maintained steady by introducing and subsequently removing VPHP. By this means, a set concentration is maintained and breakdown products are not allowed to build up during decontamination. VPHP decontamination is a dry process, as the concentration in the enclosure is maintained below the condensation point. Condensation of hydrogen peroxide should be avoided to prevent surface damage and to ensure efficient decontamination. The vapor is rapidly antimicrobial at relatively low concentrations, with typical use conditions at 0.5-2 mg/l in vapor at 25°C. Finally, during aeration, VPHP is no longer introduced and the residual vapor is catalytically decomposed into water vapor and oxygen. A microprocessor control automatically monitors, con-

**TABLE 3. Materials demonstrating compatibility with VPHP.** Compatibility is defined as the material's ability to undergo exposure to VPHP with no significant changes in physical or chemical properties (e.g., no changes in strength, flexibility, chemical composition, corrosiveness, etc.)

<b>Metals</b>	
	Aluminum
	Stainless steel (all grades)
	Titanium
	Brass*
	Copper*
<b>Plastics</b>	
	Polycarbonate
	Nylon
	ABS
	PVC
	Polypropylene
<b>Elastomers</b>	
	Viton
	Polyurethane
	EPDM
<b>General</b>	
	Oil and Latex paint
	Olefin blend and polyester blend carpet
	Ceiling tiles, including compressed wood, cellulose-based, fiber glass and plaster-based
	Electronics (including computers, calculators, scanners, equipment)

\* Will cause degradation of the hydrogen peroxide and may undergo some color change after extended exposure.

trols and records the process parameters during each cycle.

Because application conditions vary, a cycle development guide is used to develop biodecontamination cycles for different applications. Spores of *B. stearothermophilus*, the most resistant organism (9), are generally used to verify and validate biodecontamination cycles. Typical overall biodecontamination times

will depend on factors such as the VPHP concentration, and the enclosure temperature/volume, but they are generally on the order of 2 to 4 hours.

#### Antimicrobial efficacy

VPHP is a broad spectrum, fast-acting antimicrobial that demonstrates greater efficacy than liquid peroxide at relatively low concen-

trations (4). A comparison of vapor and liquid is shown in Table 1. The efficacy of VPHP against a wide range of microorganisms has been shown (summarized in Fig. 4), and it is highly sporicidal, even at concentrations as low as 0.1mg/l. All efficacy tests were performed essentially as described by Heckert et al. (6). Overall, bacterial spores (particular by *Bacillus stearothermophilus* spores) have been shown to be the most resistant to VPHP. The sporicidal activity will depend on the enclosure VPHP concentration and temperature (for examples see Table 2).

As is true for any decontamination process, the activity of VPHP can be significantly affected by the presence of gross soil contamination. Therefore, for optimal activity and reproducibility, surfaces should be precleaned of visible contamination prior to decontamination. Testing has shown that the VPHP process can decontaminate in the presence of low levels of soil (5% serum) (8, 9). In addition, the process has been shown to pass the AOAC sporicidal test (1), in which two carrier materials (porcelain penicylinders and silk suture loops) are inoculated with *Clostridium sporogenes* or *Bacillus subtilis* ( $>10^5$  spores) in the presence of soil and then desiccated. Following exposure to VPHP; no growth was seen in any of the  $>800$  carriers tested in two studies.

More recent experiments have been performed to confirm the efficacy of VPHP against foodborne pathogens, including *Listeria monocytogenes*, *Escherichia coli* O157:H7, *Salmonella choleraesuis*, *Staphylococcus aureus*, *Klebsiella pneumoniae* and *Bacillus cereus* spores. In addition, a *Legionella pneumoniae* isolate was tested in this series. For all vegetative bacteria, overnight cultures of each organism were centrifuged and resuspended in trypticase soy broth (TSB; Becton Dickinson, Sparks, MD) with 5% serum to obtain concentrations of  $10^8$  to  $10^9$  CFU/ml. More than  $1 \times 10^6$  (in 10 $\mu$ l) of each test organism

Figure 1. VHP® 1000 Biodecontamination System



was inoculated onto 1 cm<sup>2</sup> 304 grade stainless steel coupons and briefly air dried. *Bacillus cereus* spores (Presque Isle Cultures, Erie, PA) were centrifuged, resuspended and inoculated as just described, to obtain samples with 10<sup>6</sup> spores per coupon. The test system used a VHP1000 that was directly attached to an enclosure and modified with an access tube to allow the coupon to be inserted, exposed to VPHP and removed during the cycle. A typical cycle consisted of dehumidification (20 min), conditioning (20 min), decontamination (1 h at ~1.7mg/l, 95% saturation at 25°C) and aeration (1 h). Coupons were individually exposed to VPHP, during the decontamination phase only, for 10 and 20 min, and immediately placed into a 0.05% catalase/growth media (to neutralize any residual peroxide) and incubated. The growth medium and incubation method varied depending on the test organism. Typical microbiologi-

cal positive (growth promotion) and negative (growth media) controls were performed; in addition, the initial organism population on unexposed coupons were determined. Results indicated a reduction of more than 6-log (complete kill) of each organism for both the 10 min and 20 min contact times.

#### Material compatibility

Because VPHP decontamination is a "dry" process that uses much lower concentrations than processes that use alternative oxidizing agent-based liquids (e.g., bleach, hydrogen peroxide/peracetic acid combinations), VPHP is compatible with a wide range of materials, including electronics, plastics, metals, and elastomers. Table 3 lists the materials most commonly subjected to decontamination processes and their respective compatibility. Minor changes have been observed with a small number of materials, e.g., colored anodized alu-

minum, titanium and copper, in which slight cosmetic discoloration or bleaching may occur. In addition, materials that absorb hydrogen peroxide (including silicone and cellulotics) may require extended cycle time for decontamination and aeration.

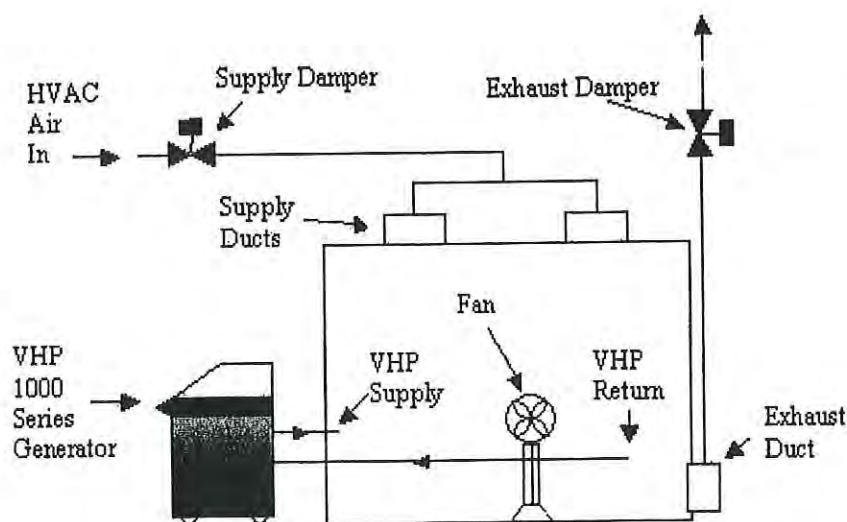
#### Worker health and safety

Of all the gaseous methods currently available for room decontamination, VPHP has probably the best safety and environmental profile. In the United States, OSHA has established a limit of 1 ppm (NIOSH PEL) for an 8-h time weighted average for worker exposure to hydrogen peroxide vapor. The short-term danger level for hydrogen peroxide vapor is 75 ppm for 30 min (IDLH). To reduce the risk of leakage, enclosures are sealed (e.g., by taping around doors and over HVAC vents), and the process is operated at ambient pressure, to prevent flow of gases either into or out of the enclosure. Hand-held and wall-mounted hydrogen peroxide detection systems may be deployed to provide added assurance that the vapor remains contained. In general, personnel can safely work in adjacent monitored areas while a room is being decontaminated with VPHP. The treatment area can be reoccupied only after it has been determined that the concentration of hydrogen peroxide is below the established permissible levels. Removal of VPHP is performed during the aeration phase of the process, after which no further clean-up or conditioning is required. In addition, VPHP is non-flammable and is rapidly degraded in the environment to water vapor and oxygen, both of which are innocuous.

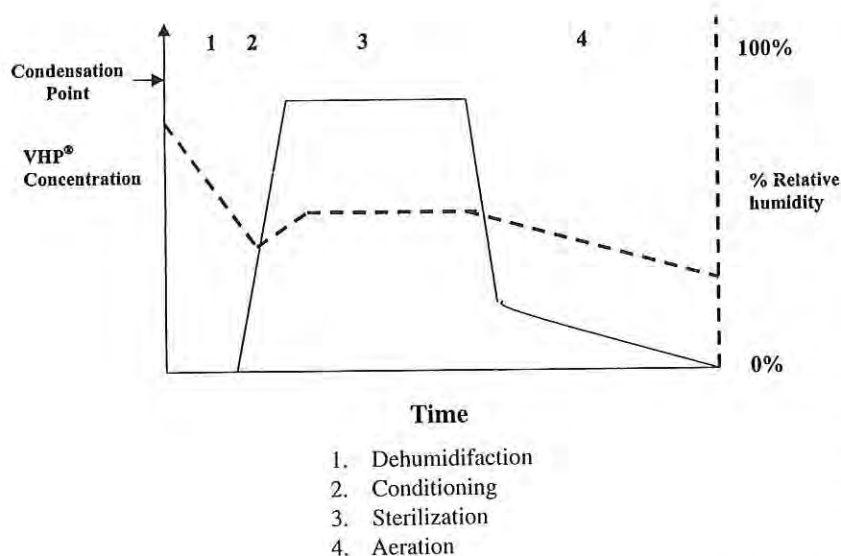
#### CASE STUDY

A case study was performed in which electrical equipment was decontaminated by use of a Spiro-Matic ham slicer (Model A-5500, "The Spiral-Viper," Spiral-Matic Corporation, Brighton, MI). Testing was performed on the fully assembled, precleaned slicer with the

**Figure 2.** Typical room setup with VPHP for decontamination. In other cases the HVAC system may also be fully decontaminated by being used to introduce and circulate VPHP



**Figure 3.** Typical VPHP Biodecontamination cycle



access door to the lower electronics compartment open during the entire decontamination cycle. The decontamination tests were conducted in a 336 ft.<sup>3</sup> flexible wall enclosure constructed of polyvinylchloride (PVC) and attached to a VHP 1000 System. The flexible enclosure was designed to simulate an enclosed decontamination area/room for equipment at a processing plant. The slicer was centrally

placed in the enclosure; a 20" circulating fan was used for circulating the peroxide vapor within the enclosure. To test for process effectiveness, VPHP chemical and biological indicators (with  $10^5$  *B. stearothersophilus* spores) were directly attached to the slicer at various locations and on the walls, ceiling and floor of the enclosure (a total of 20 test sites) prior to decontamination. The test cycle

consisted of dehumidification (30 min), conditioning (25 min), decontamination (85 mins at  $\sim 1.5$  mg/l, 90% saturation at 20°C) and aeration (120 mins). Immediately upon completion of the aeration phase of the VPHP cycle, the chemical and biological indicators were retrieved. The chemical indicators were examined for the color change (from blue-grey to beige) that indicates the presence of VPHP. The biological indicators were inoculated into TSB, incubated at 56°C for 7 days, and recorded as growth/no growth. Biological positive and negative controls were also performed on the culture media lot used. All chemical indicators signaled the presence of hydrogen peroxide at the various locations. No growth was observed for any exposed biological indicators following incubation, or for the negative controls; all unexposed positive controls demonstrated growth. The slicer and the enclosure had undergone no apparent physical, mechanical, cosmetic or material changes after multiple exposure cycles.

Decontamination may also be performed in any sealed room, whether or not it contains equipment, and can be subsequently validated during cycle development. Typical case studies on room decontamination have previously been published (7, 10, 11).

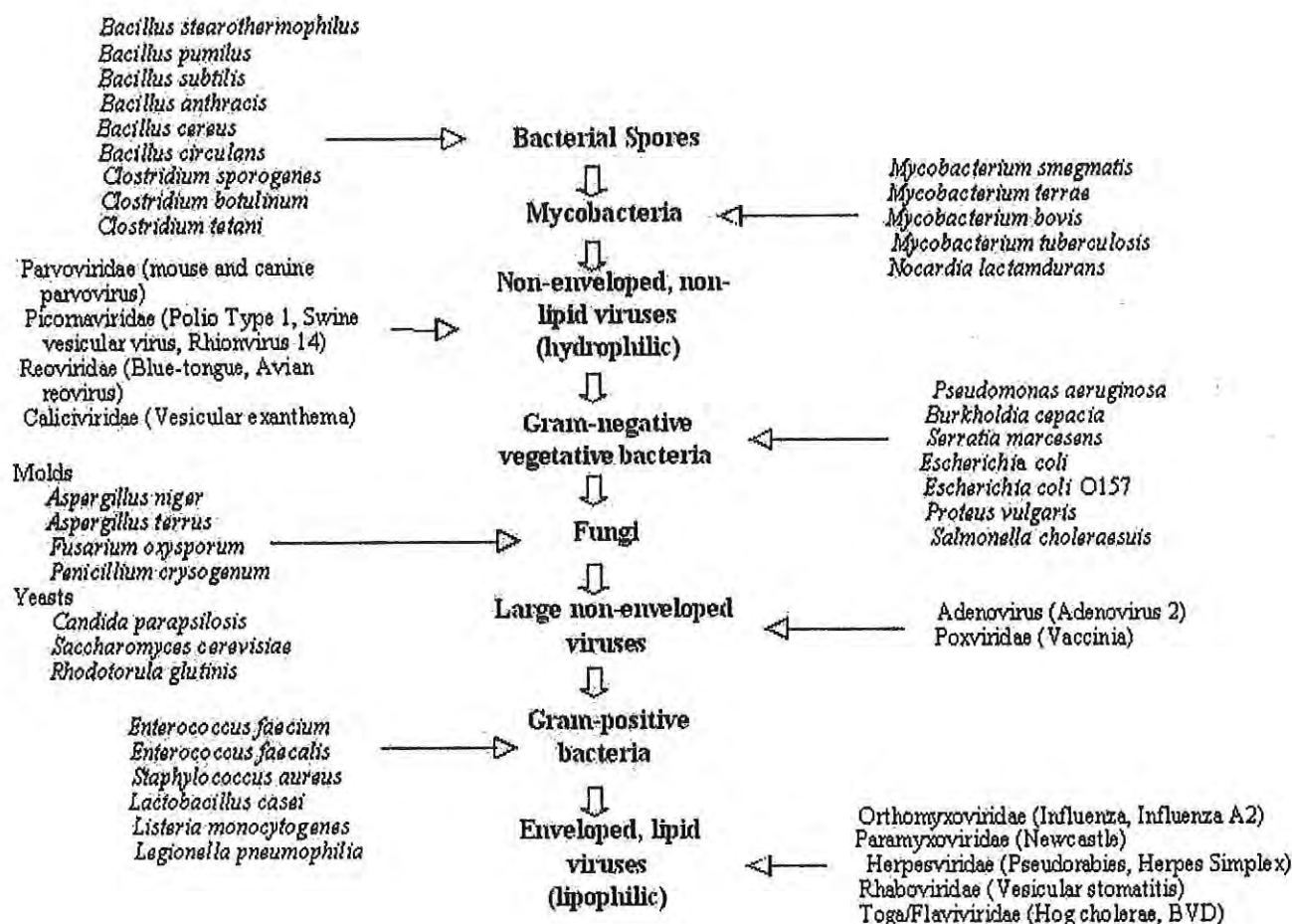
## CONCLUSION

VPHP may be used as an alternative to manual and liquid-based decontamination methods for rooms, enclosed areas and food-contact equipment in the food industry. When correctly applied, the technology offers broad-spectrum antimicrobial efficacy, material compatibility and an automated process that can be validated.

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**Figure 4.** Descending order of microbial resistance to VPHP. Microorganisms are listed from the most resistant (bacterial spores) to the most sensitive (enveloped, lipid viruses) to VPHP



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