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SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted
a patent (Rule 4.17(ii)) for the following designations AE,
AG, AL, AU, BA, BB, BR, BZ, CA, CN, CO, CR, CU, DM,
DZ, EC, GE, HR, HU, ID, IL, IN, IS, JP, KP, KR, LC,
LK, LR, LT, LV, MA, MG, MK, MN, MX, NI, NO, NZ, OM,
PG, PH, PL, RO, SC, SG, SL, TN, TT, UA, UG, UZ, VC, VN,
YU, ZA, ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL,
SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG,
KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH,
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CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)
- of inventorship (Rule 4.17(iv)) for US only

Published:

- with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: ABSORBER COMPOSITION FOR ETHYLENE CONTROL

(57) Abstract: With a special application for the control of ethylene gas in fruit and vegetable ripening processes, consisting of a diatomite and potassium permanganate mixture, which is first mixed dry until producing a uniform product, and subsequently mixed with water, the diatomite participating at ratios comprised between 80 and 90%, and the potassium permanganate at a ratio comprised between 1 and 50%, such that the former constitutes a highly absorbent substrate for the latter, which permits increasing the amount of the latter and, accordingly, also increasing the activity of the composition. Said composition can optionally contain calcium chloride at a ratio comprised between 1 and 15% in order to improve the effect or increase of water retention of the composition.



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ABSORBER COMPOSITION FOR ETHYLENE CONTROLDESCRIPTION5 **OBJECT OF THE INVENTION**

 The present invention refers to a new absorber composition provided for the control of ethylene gas in fruit and vegetable ripening applications and, more generally, in the control of volatile organic compounds of the type from the
10 general class of organic components which can oxidize into inoffensive products.

 The object of the invention is to obtain a composition capable of being kept active for a significantly longer period of time, practically twice as long, than with conventional
15 absorber compositions.

BACKGROUND OF THE INVENTION

 The effects of ethylene gas in the ripening and eventual decomposition of fruits and vegetables are known and abundantly documented.
20

 The use of potassium permanganate as an oxidizing agent has been known for many years, and in this aspect it is worth mentioning US Patent 552,142, granted in 1895, that is, over more than 100 years ago, which foresaw using a mixture between
25 calcium chloride and potassium permanganate as an odor absorber means.

 US Patent 3,049,399 discloses a composition and method for deodorizing the air, in which potassium permanganate is also used, but in this case by impregnating an absorbent
30 inorganic activated water adsorbing substrate.

 A more recent patent with a more general current use is US Patent 5,278,112, which also maintains the use of potassium permanganate, but in this case impregnating, in other words using as a substrate, zeolites.

35 Currently, the overwhelming majority of ethylene control

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agents internationally manufactured and sold, are based on this US Patent, that is to say that they use zeolites as a substrate, which are impregnated with potassium permanganate and other additives, where applicable.

5 The practical results of this solution, that is to say the absorber efficacy of this type of compositions, can be cited at approximately 15 days of exposure, after which time the composition becomes ineffective.

10 **DESCRIPTION OF THE INVENTION**

 By means of the use of a new substrate, the absorber composition proposed by the invention, also starting with the use of potassium permanganate, significantly lengthens the efficacy or useful life in the control of odors, specifically remaining active for at least 30 days.

15 More specifically, the invention consists of using diatomite as a substrate in replacement of the classic zeolites.

 Specifically, it has been foreseen that diatomites participate in the composition at a ratio comprised between 80 and 90%, while the rest is potassium permanganate.

 The optimal results of the invention are due to the high porosity of diatomite.

20 This porosity makes them capable of absorbing up to 100% of water (based on dry weight) and yet not have free water on the surface, which permits applying a larger amount of potassium permanganate in the solution and, accordingly, obtaining better activity.

 According to another one of the features of the invention, it has been foreseen that calcium chloride be added to said two basic raw materials, diatomite and potassium permanganate, at a ratio comprised between 1 and 15%, at the expense of a reduction in the same amount of diatomites.

35 **PRACTICAL EMBODIMENT OF THE INVENTION**

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Diatomite is a sedimentary siliceous rock mainly composed of diatom bone remains of diatoms, which in turn consist of a microscopic, unicellular aquatic plant related to algae. Specifically, each diatom consists of a small membrane and internal structure surrounded by a shell or sample of concentrated opaline silica from nearby waters. Analysis shows a latticework structure which is porous and chemically inert. This unusual structure has a low density, high absorption capacity, large surface area and low thermal conductivity.

Diatomite deposits are the result of the accumulation of diatoms in large shallow basins with a sufficient contribution of soluble silica.

A dry mixture of a diatomite substrate and potassium permanganate is carried out until obtaining a uniform product, the desired amount of water is added while blending the mixture.

Permanganate must be in solution to be effective, it having been experimentally proven that dry permanganate is ineffective in the reduction of ethylene concentrations.

An improvement in the composition is obtained by means of the optional addition of calcium chloride or another deliquescent salt, which has the effect of increasing water retention of the material. This is useful in low humidity applications where the drying of the material could cause an activity reduction.

The following tests have been carried out with these raw materials:

The standard test was placing one ripe avocado in a one gallon sealed plastic container, with a standard amount of ethylene control agent. A sample was taken by using an ethylene sampling tube to aspirate a known volume through the tube. The color change of the tube indicates the ethylene concentration. To simulate realistic conditions, and to prevent the buildup of CO₂ gas, which could inhibit ethylene production, the

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Containers were opened after each sampling and thoroughly vented. Sampling frequency was one sample per container per 24 hours. Several different samples of control agents were compared using equivalent amounts of diatomite and zeolite based materials.

EXAMPLE 1.-

COMPOSITION CONTAINING 12% POTASSIUM PERMANGANATE (KMnO_4) DRY BASE.

12 grams of potassium permanganate, 88 grams of 6-8 meshwork diatomites and 70 grams of water were used.

This material was tested and compared to the material based on classic zeolites, resulting in a useful life in the range of 30 days or more, in other words, more than twice as long as that obtained with said zeolites.

EXAMPLE 2.-

PRODUCT CONTAINING 20% POTASSIUM PERMANGANATE (DRY BASE).

In this case, 20 grams of potassium permanganate, 80 grams of 6-8 meshwork diatomites and 70 grams of water were used.

This material is dry, it shows no free moist surface.

The practical results were equivalent to those of the previous case.

EXAMPLE 3.-

PRODUCT CONTAINING 5% CALCIUM CHLORIDE AND 20% POTASSIUM PERMANGANATE (DRY BASE).

20 grams of potassium permanganate, 5% calcium chloride, 75% diatomite and 70 grams of water were used.

The results were similar to those in Example 1, noting an increase in the water retention capacity of the composition.

Lastly, it is necessary to indicate that it has been shown that placing the absorber composition inside of a Tyvek® bag does not reduce efficacy.

CLAIMS

5 1.- An absorber composition for odor control which, especially designed for the control of ethylene gas in fruit and vegetable ripening. Comprised of a diatomite and potassium permanganate mixture.

10 2.- An absorber composition for ethylene control according to claim 1, comprising diatomites at a ratio comprised between 80 and 90%, whereas the potassium permanganate is comprised between 1 and 50%.

15 3. An absorber composition for ethylene control according to claim 1, comprising diatomites, potassium permanganate and a deliquescent material which calcium chloride is one.

20 4.- An absorber composition for ethylene control according to claim 3, comprising diatomites at a ratio comprised between 75 and 90%, potassium permanganate at a ratio comprised between 1 and 50%, and deliquescent material like calcium chloride at a ratio comprised between 1 and 15%.

25 5.- Any absorber composition for ethylene control using a deliquescent mineral like calcium chloride to attract water back to the absorbent to increase its efficiency or extend its useful life.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB 03/03463

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A61L9/013 A61L9/014 A23B7/152 A23B7/157

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A23B A61L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, FSTA, BIOSIS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 071 533 A (CENTRE EX FRUITS LEGUMES ;TOULOUSE INST NAT POLYTECH (FR)) 9 February 1983 (1983-02-09) page 2, lines 21-38; claim 8 -----	1-4
X	FR 2 535 610 A (ASS RECH DEVEL AMELIO) 11 May 1984 (1984-05-11) page 3, paragraph 1 page 1, lines 1-31; claims 2,4 -----	1-4
X	US 4 535 072 A (KITAYAMA MASAYASU ET AL) 13 August 1985 (1985-08-13) claims 4,6,9,10; example 4 -----	1,2
A	US 552 142 A (PURVES A M) 31 December 1895 (1895-12-31) cited in the application the whole document -----	3,4

Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>
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Date of the actual completion of the international search <p style="text-align: center;">9 March 2004</p>	Date of mailing of the international search report <p style="text-align: center;">05. 07. 2004</p>
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Name and mailing address of the ISA European Patent Office, P.O. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer <p style="text-align: center;">Heirbaut, M</p>
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB 03/03463

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-4

Remark on Protest

- The additional search fees were accompanied by the applicant's protest.
- No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-4

Absorber composition for ethylene control, comprising diatomite and potassium permanganate

2. claim: 5

Absorber composition for ethylene control, comprising a deliquescent material like calcium chloride

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB 03/03463

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0071533	A	09-02-1983	FR 2509964 A1 28-01-1983 AT 23095 T 15-11-1986 DE 3273940 D1 04-12-1986 EP 0071533 A2 09-02-1983
FR 2535610	A	11-05-1984	FR 2535610 A1 11-05-1984
US 4535072	A	13-08-1985	JP 1386345 C 26-06-1987 JP 59049822 A 22-03-1984 JP 61051935 B 11-11-1986 US 4784837 A 15-11-1988
US 552142	A	NONE	

Box No. VIII (ii) DECLARATION: ENTITLEMENT TO APPLY FOR AND BE GRANTED A PATENT

The declaration must conform to the standardized wording provided for in Section 212; see Notes to Boxes Nos. VIII, VIII (i) to (v) (in general) and the specific Notes to Box No. VIII (ii). If this Box is not used, this sheet should not be included in the request.

Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent (Rules 4.17(ii) and 51bis.1(a)(ii)), in a case where the declaration under Rule 4.17(iv) is not appropriate:

WORLD WIDE SALES, INC. is entitled to apply for and be granted a patent by virtue of the following:

an assignment from Shy, Larry, Smith, Barry and Eyde, Dan to **WORLD WIDE SALES, INC.**, dated 22 November, 2002 (22-11-2002)

This declaration is made for the purposes of all designations, except the designation of the United States of America

This declaration is continued on the following sheet, "Continuation of Box No. VIII (ii)".