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A Review of the Global Applications of ECO₂FUME and VAPORPH₃ OS Cylinderized Phosphine Fumigants for Stored Products Disinfestation

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Abstract: For decades phosphine has been the world's most widely used and cost effective fumigant for stored product protection. In response for the need to eliminate the associated risks of fire or explosion, need for deactivation, disposal and direct contact with the fumigant, ECO₂FUME, a non-flammable cylinderized formulation of 2% phosphine and 98% carbon dioxide (CO₂) by weight, was developed and made available in the market in late the 1980's. By the year 2000, VAPORPH₃OS, a cylinderized formulation of 99.3% phosphine, entered into the market for large scale application using a safe and effective CYTEC approved on-site mixing equipment with CO₂ or air.

This paper describes the up to date history and the different global applications of ECO₂FUME and VAPORPH₃OS as fumigant for food commodities such stored grains, oilseeds, nuts and beans, fruits and vegetables, animal feed and feed ingredients and non-food commodities such as tobacco, cut flowers and foliages, tires and structural fumigation. ECO₂FUME was first introduced in Australia during the late 1980's for stored grains, oilseeds and nuts both for un-sealed and sealed vertical silos and horizontal sheds. ECO₂FUME is also used in Australia and New Zealand for export cut flowers and foliages. VAPORPH₃OS was first introduced in China in 2000 at Dalian Grain Export Terminal using the on-site mixing with CO₂ technology. In North America, ECO₂FUME was commercially used starting in 2000 in sealed storages for grains, nuts, dried fruits, tobacco, flour, processed foods and feeds as well as structural fumigation. With the development of the Horn Diluphos System (HDS) for safe on-site mixing of VAPORPH₃OS with air in 2004, VAPORPH₃OS has become an increasingly popular phosphine fumigant as a practical and convenient approach for large scale fumigation of grains, oil seeds, nuts and fruits and vegetables in Australia, USA and South America.

Introduction

Phosphine has been for decades the world's most cost effective and widely used fumigant for stored product protection against insect pests. With the introduction of ECO₂FUME and VAPORPH₃OS cylinderized phosphine fumigants, the usual disadvantages associated with the solid phosphine formulation of being self-igniting when exposed to air and the need for deactivation and disposal of unspent residue have been overcome.

ECO₂FUME is a liquefied gas mixture of 2% phosphine and 98% carbon dioxide (CO₂) by weight making it a non-flammable and ready to use. It comes in high pressure aluminum or steel cylinders with a net fumigant weight of 31 kg. It requires simple dispensing equipment designed to deliver the fumigant as quickly or slower as required by each individual application. VAPORPH₃OS is 99.3% phosphine by weight and is designed for use with approved blending equipment for on-site dilution with CO₂ or air

in non-flammable proportions. It comes in steel cylinders with a net fumigant weight of 18 kg and just recently 22 kg. VAPORPH₃OS is most suitable for larger storage volume applications where it is not practical to store, handle or transport large numbers of cylinders, price sensitive applications such as grains and for locations that conduct frequent fumigations.

ECO₂FUME and VAPORPH₃OS have the advantages of being safer, greener and faster. Safer because it is applied externally to the fumigation structure which eliminate confined space entry, reduce worker exposure and eliminate retrieval of partially spent fumigant. It is greener because there is no waste product or residue that requires waste deactivation or disposal. It is environmentally friendly due to its non-ozone depleting property. It has non-phyto-toxic property to sensitive commodities such as cut flowers, fruits and vegetables. The required fumigation time is relatively faster than the solid phosphine formulation since it is easily applied as gas mixture to quickly distribute and achieve uniformly the target concentration. There is

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more effective control of target insects due to better gas distribution and maintenance of target concentration which leads to decreased amount of phosphine applied.

Applications in Australia

ECO₂ FUME (formerly known as Phosfume) was first commercially applied in Australia in 1988 by BOC Gases Australia who produced and patented the phosphine/CO₂ blend and developed special dispensing equipment for fumigating grains and oilseeds in unsealed and good sealed silos and horizontal sheds. This was in conjunction with the CSIRO patented fumigant application technologies called SIROFLO, SIROCIRC and SIROFUME. To date, there are over 150 million tons of grains and oil seeds that have been fumigated with ECO₂ FUME. In 1999, CYTEC Industries Inc. acquired the ECO₂ FUME global fumigant business from BOC Gases including all patents, trademarks, registrations and pending registrations. The SIROFLO dispensing equipment was further improved during the early 2000 for safety and less maintenance. The improved versions were developed by GasApps Australia, ABB Grain Ltd and CYTEC.

SIROFLO is a continuous slow addition of ECO₂ FUME in an air stream such that phosphine concentration is diluted from 20,000 ppm to about 30 ppm before introducing it into the bottom of the silo or shed and exit at the top of the grain for an exposure period of up to 28 days (see Figure 1). The bottom and the walls of the storage should be reasonably gas-tight to ensure that with the low positive pressure of the gas mixture the fumigant leaks outwards through the storage structure, and there is only minimum ingress of air that could locally dilute the fumigant concentration. The long exposure period to low phosphine concentration will allow the killing of all stage of insects including the less susceptible egg and pupae stages. With the development of increased resistance of some insects species (lesser grain borer and rice weevil) a new set of fumigation protocol was established in 2004 covering minimum phosphine concentration of 70 – 700 ppm for 3 – 21 days at 15 – 30°C.

SIROCIRC is similar to SIROFLO except insofar as it includes a recirculation duct connected between the storage roof and the fan inlet. This allows the recovery of phosphine from the headspace above the grain and its recircula-

tion through the grain mass. At least 90% of phosphine can be recycled in a reasonably well sealed storage. While SIROFLO is a set-and-leave operation, SIROCIRC requires a reduction in the fumigant flow-rate once phosphine begins to recycle back from the top of the storage. This can be done manually, but control is facilitated by the use of an automatic electronic controller that intermittently adjusts the fumigant flow to generate a near-constant phosphine concentration in the delivery duct.

Large storages such as big silos in grain terminals and horizontal sheds have employed the use of on-site mixing of VAPORPH₃OS with CO₂. GrainCorp large storage facilities in Queensland, NSW and Victoria have used on-site mixing equipment developed by CYTEC and GasApps Australia.

SIROFUME differs from the other two in being a “one-shot” technique wherein gaseous phosphine is dumped into the head space of a sealed storage. Nowadays, this fumigation approach is mostly used with VAPORPH₃OS using an on-site phosphine/air mixing equipment.

ECO₂ FUME is also used in Australia and New Zealand for pre-shipment treatment of exported cut flowers and foliage. At normal atmospheric pressure, the protocol used is 700 ppm of phosphine for 15 hours at minimum temperature of 15°C. In New Zealand, a shorter exposure of 3 – 4 hours is adopted at 700 ppm and minimum 15°C with the use of a vacuum chamber at 70 mm Hg absolute pressure. ECO₂ FUME is used to a relatively limited extent for quarantine treatment of imported grains, flours, oil seeds and nuts that come in shipping containers.

With the development and commercialization of the Horn Diluphos System (HDS), (a CYTEC approved phosphine/air on-site mixing equipment) in 2004, VAPORPH₃OS became an increasingly popular fumigant for cost effective, flexible and convenient way of fumigating grains and oilseeds in sealed storages (vertical silos, horizontal sheds and bunkers). The HDS fumigation equipment is manufactured and supplied by Fosfoquim SA in Chile. The HDS comes in three size models (HDS 801. 2 kg phosphine/hr, HDS 2003 kg phosphine/hr and HDS 80012 kg phosphine/hr) which cater to a wide range of storage capacities ranging from 1 000 tons to 300 000 tons. The VAPORPH₃OS phosphine fumigant in combination with the HDS fumigation equipment is now widely used by the three Australian bulk handling companies (GrainCorp,

ABB Grain and CBH Group) which handle over 90% of harvested grains and oilseeds in the country. Figures 24 show examples of current applications of VAPORPH₃OS with the HDS.

Applications in China

China is the first country to commercially apply VAPORPH₃ OS at Dalian Xizui Grain Terminal by on-site mixing with bulk CO₂ in 2000. The on-site mixing of VAPORPH₃OS with bulk CO₂ produces the ECO₂ FUME blend which is introduced for fumigation with the SIROCIRC fumigation system developed by GasApps Australia and constructed by Grain Tech System Pty Ltd. This grain terminal has a 1 million ton grain capacity divided into a block of 144 × 3000 ton sealed silos and another block of 20 × 30000 ton sealed silos both equipped with SIROCIRC fumigation system. The fumigation system is composed of 1) a 5-ton bulk liquid CO₂ tank and VAPORPH₃OS cylinders storage, 2) on-site mixing system (ECO₂ FUME mixer), 3) ECO₂ FUME delivery pipe work and 4) SIROCIRC system. Some components of the fumigation system are shown in Figures 5. During fumigation, a phosphine concentration of 100 ppm is maintained through out the grain mass for a period of 18 days enough to kill all stages of insects.

Applications in North America

Commercial applications of ECO₂FUME in the USA started by fourth quarter of 2000 after full registration both for non-food and food use was granted by August 2000. ECO₂FUME is applied into the sealed fumigation structure by direct injection using simple and quick dispensing equipment with variable fumigant flow rates.

Tobacco fumigation is among the first commercial application of ECO₂FUME in the USA. Tobacco bales stored inside large warehouses are fumigated by first sealing the warehouse and injecting ECO₂ FUME from a bank of cylinders in manifold located outside the warehouse. A phosphine concentration of 250 ppm is maintained for a period of 96 hours to achieve successful fumigation. The use ECO₂FUME has the advantages over solid phosphine formulation of 1) quick dispensing and attainment of target concentration throughout the structure, 2) no dependence on humidity and temperature for reaction, 3) eliminate dust or solid waste generated from using solid formulation, 4) no waste

deactivation, 5) eliminate waste disposal and 6) no ammonia residue released that require additional scrubbing.

Among the different commercial applications of ECO₂FUME and VAPORPH₃OS in the USA is either methyl bromide or solid phosphine formulation replacement as below (Figure 6).

1. In-transit fumigation of flour and rice in rail cars using ECO₂FUME

2. Rice, wheat, corn and other grain fumigation in sealed vertical bins using ECO₂FUME or VAPORPH₃OS

3. Fumigation of almonds, walnuts, and pistachio nuts with VAPORPH₃ OS previously were using methyl bromide in fumigation chambers/containers and metal phosphide in metal storage bins

4. Bagged and bulk seed in cold storage warehouses with ECO₂FUME

5. Fumigation of stacked raisins under tarp and other dried fruits using ECO₂FUME or VAPORPH₃OS

6. Structural fumigation (e. g. flour mill, empty warehouse) using ECO₂FUME in combination with heat and CO₂

7. Bunker storage using VAPORPH₃OS

The dosage recommendation for ECO₂ FUME and VAPORPH₃OS in the USA varies in phosphine concentration of 2001000 ppm for 36 hours to 6 days at above 26°C depending on the commodity, target insects and sealing degree of the fumigation structure. There is also a protocol with shorter exposure period of 24 hours at above 26°C using a phosphine concentration of 5001000 ppm. Rodents and other vertebrate pests in storages may be controlled with short-term fumigations within 1 to 4 hours after achieving distribution of phosphine throughout the structure.

Only ECO₂ FUME is currently used in Canada for similar range of applications as in the USA but using the same dosage rate of 2001000 ppm phosphine concentration for an exposure period 214 days and temperature range of 0 – 16 or above.

Applications in Latin and South America

Chile is the first country in the world which has commercially applied VAPORPH₃OS (TK Gas brand name in Chile) for fumigation of export fruits and vegetables. Fosfoquim SA developed the Horn Diluphos System (HDS)

fumigation machine to safely mix VAPORPH₃ OS and air and deliver the phosphine air mixture at small to high flow rates into different sized sealed fumigation structures. Fosfoquim SA has also formed a fumigation company which provides fumigation services to fruit exporters. A fleet of fumigation vans and trained fumigators provide mobile fumigation service to all customers in Chile. Fumigation services provided by Fosfoquim include fruit and vegetable fumigation which accounts for a major portion of the fumigation services. Figure 7 is a sample setup of fruit fumigation using the HDS 800 in a fumigation van.

There are many advantages of using VAPORPH₃ OS in combination with the HDS for fruits and vegetables fumigation as follows:

- Phosphine eliminates the target pests in fruits, like mealy bugs, *Pseudococcus* spp; apple moth, *Cydia pomonella*; eulia, *Proeulia* spp; fruit tree weevil, *Naupactus xanthographus*; mediterranean fruit fly, *Ceratitis capitata*; fruitfly, *Bactrocera* spp, *Anastrepha* spp; and Thrips spp.

- No changes in taste, smell, texture, color or shelf life of the fruit, if fumigation has been conducted at low temperature. This is mainly because it is possible to fumigate at low temperature with the cooling system running (Figure 1).

- It is not necessary to heat fruits up before fumigation. Therefore, the shelf life of the fruits is extended.

- There are no residues after fumigation on the fruits and no product residues that have to be deactivated and disposed after fumigation.

- Cylindere phosphine does not produce ammonia and it is, therefore, not phytotoxic.

- The fumigation can be done in the same cooling chambers where the fruit is stored prior to shipment.

- There is no need to fumigate at the port of arrival, since the fumigation can be done at the processing plant before shipping.

- The fruit can be delivered immediately upon arrival at the port since the fruit is already fumigated and inspected, increasing capacity of the ports to receive fruits, or giving other ports, that do not have fumigation facilities, an option to deliver fruits to other parts of the receiving countries.

- This fumigation technique has no environmental problems, since only hydrogen phosphide is applied, which is readily deactivated

by sunlight upon release into the atmosphere. Therefore there is no damage to the ozone layer, as it occurs with other fumigants used for fruit fumigation.

- The fumigation is operator friendlier than methyl bromide. The gas concentration can be monitored exactly with different electronic devices in order to ensure minimum exposure of fumigators and plant workers to the gas.

- Gas injection even in the largest fruit fumigation cool houses takes less than one hour and aeration systems are installed in order to allow aerating chambers in less than 90 minutes.

- As the method permits applying the gas from outside the facility, the gas concentration can be changed at any time during the fumigation.

- The gas can be applied to a totally sealed structure without increasing the pressure, if the gas from the cylinders is mixed with air taken from the inside of the structure to be fumigated.

- The HORN DILUPHOS SYSTEM allows stopping gas dispensing at any time during gas injection (Figures 2, 3, 4, 5 and 6). Unlike from what had always been thought, there are no corrosion problems on the cooling.

Tables 1 and 2 show the extent of fresh fruits and vegetables fumigation conducted by Fosfoquim in terms of type and destination country from 2005-2008. The top six export fruit type fumigated are apples, prunes, grapes, peaches, oranges, and pears. The top six destination countries are Mexico, Iran, Korea, Japan, Bolivia and China.

In Trinidad and Tobago, ECO₂ FUME is used for cargo container fumigation, shiphold fumigation, warehouse fumigation, storage bin treatment and fumigation of grains on pallets and in silos. ECO₂ FUME is dispensed using simple and quick dispensing equipment into a sealed structure.

Summary

ECO₂FUME and VAPORPH₃ OS are cylinderized phosphine fumigants that offer safer, greener and faster advantages for disinfestation of food commodities such stored grains, oilseeds, nuts and beans, fruits and vegetables, animal feed and feed ingredients and non-food commodities such as tobacco, cut flowers and foliage, tires and structural fumigation.

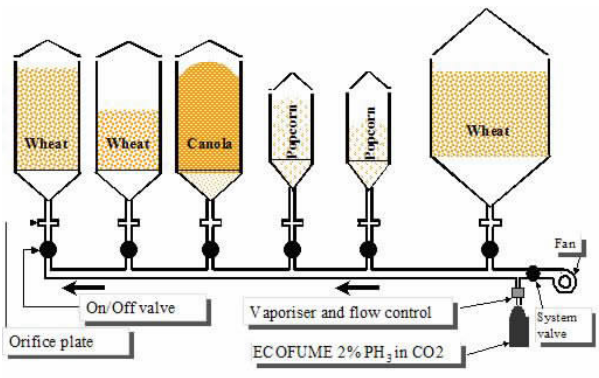


Fig. 1 Schematic of SIROFLO fumigation system for unsealed silos.



Fig. 2 The 300,000 ton capacity sealed horizontal shed at CBH Kwinana Grain Terminal Western Australia with insert HDS 800/VAPORPH₃OS fumigation setup.



Fig. 3 An 8000-ton sealed silo with the HDS 800/VAPORPH₃OS fumigation setup at ABB Wallaroo Grain Terminal in South Australia.

Table 1. Volume of fruit fumigation covered by Fosfoquim SA based on fruit type from 2005 to June 2008.

Fresh Fruit	Volume of Froit Fumigation(m ³)				Sub Total
	2005	2006	2007	2008	
Garlic	810	86	0	0	896



Fig. 4 A 20000-ton bunker with the HDS 800/VAPORPH₃OS fumigation setup at GrainCorp Nhill grain storage center in Victoria Australia.



Fig. 5 Dalian Phase-2 silo block of 20 bins by 30 000 ton capacity each. The CO₂ storage-tank and ECO₂FUME on-site mixing enclosure are dwarfed by the silos. Around the lower part of each silo is the fumigant delivery ducting.

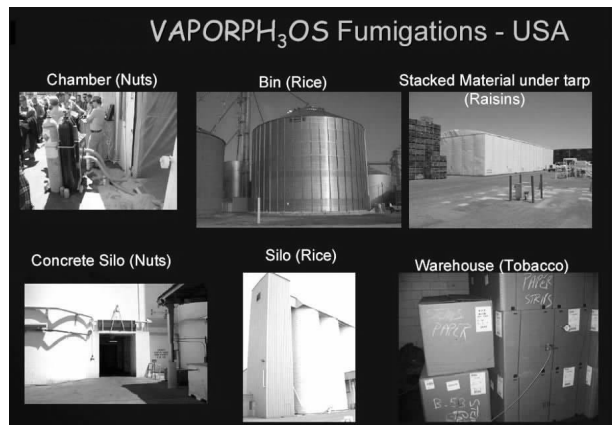


Fig. 6 Methyl bromide replacement with VAPORPH₃OS for fumigations in the USA.

Fresh Fruit	Volume of Froit Fumigation(m ³)				Sub Total
	2005	2006	2007	2008	
Parsimon	83	2.474	2.187	734	5.478
Onions	0	0	856	0	856



Fig. 7 The HDS 800 in a fumigation van with a two-hose connection to a fruit fumigation chamber.

Table 2. Volume of fruit fumigation covered by Fosfoquim SA based on destination countries from 2005 to June 2008.

Fresh Fruit	Volume of Fruit Fumigation (m ³)				Sub Total
	2005	2006	2007	2008	
Chenies	0	5.744	426	0	6.170
Prunes	34 056	82 260	11 363	11 978	139 657
Clementines	4 786	11 214	6 232	0	22 232
Apricots	2 706	249	354	83	3 392
Pomegranate	0	0	0	1 246	1 246
Kiwifruits	462	7 716	9 206	856	18 240
Lemons	2 614	166	4 428	8 565	15 773
Apples	58 843	286 807	279 202	107 873	732 725
Quinces	83	1 065	660	1 704	3 512
Oranges	10 098	34 541	35 648	513	80 800
Nectarines	5 321	3 415	581	2 545	11 862
Avocado	2 656	1 638	1 280	0	5 574
Pers	6 867	18 264	13 875	16 507	55 513
Grapefruit	0	4 783	2 376	249	7 408
Grapes	688	14 178	33 134	52 284	100 284
Total	189 561	523 086	404 423	211 495	1 328 565

1m³ = 22 standard fruit trays 11.5million trays in 2006

Destination Country	Fruit Volume Fumigated (m ³)				Sub Total
	2005	2006	2007	2008	
Argentina	0	2 659	3 372	332	6 363
Bolivia	0	11 926	24 000	19 031	54 957
Brazil	0	0	415	0	415
China	0	0	19 370	3 226	22 596
Colombia	0	0	4 072	1 354	5 426
Korea	0	2 250	32 516	29 919	64 685
Costa Rica	0	83	640	83	806
Ecuador	0	0	2 266	1 852	4 118
Spain	0	0	582	0	582
Europe	0	1 092	4 770	5 032	10 894
Hong Kong	0	0	166	0	166
Netheriands	0	0	320	0	320
India	0	0	6 000	332	6 332
Iran	0	44 149	40 860	49 739	134 748
Japan	0	7 508	37 260	17 050	61 818
Far East	0	0	5 829	0	5 829
Mexico	49 694	368 079	196 214	72 978	686 965
New Zealand	0	0	684	817	1 501
Panama	0	0	6 195	3 004	9 199
Peru	0	166	1 181	700	2 047
Russia	0	0	2 064	166	2 230
Taiwan	0	0	1 092	1 162	2 254
USA	0	415	12 749	4 635	17 799
Venezuela	0	0	83	0	83
Other markets	139 867	84 759	1 723	83	226 432
TOTAL	189 561	523 086	404 423	211 495	1 328 565