

of bean pathogens. Overall, essential oils extracted from these spices could play an important role in stored bean protection and reduce the risk associated with the use of synthetic insecticides.

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Sustained effective use of phosphine in stored product protection in India: Role of UPL Limited

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Phosphine has a predominant role in stored products protection in India since more than 4 decades. Its use has gained further prominence ever since methyl bromide has been withdrawn (except QPS applications) on environmental concerns. Accordingly, the use of phosphine is being expanded to QPS treatment of certain commodities. Phosphine has several merits and as a stored product fumigant. However, there is a concern about occasional failure to achieve desired 100% mortality of insect pests during phosphine treatment in the country. Hence the factors contributing for control failures have been identified. Also there are reports about need to improve existing fumigation practices and to create awareness about the required parameters to ensure successful treatments. In this context UPL Limited, a leading manufacturer of metal phosphide formulations in the world took important steps: A. To create awareness about proper sealing of fumigation enclosures, phosphine dosage, exposure period and target terminal concentration parameters B. To impart practical demonstrations to the stakeholders in across the country details of phosphine fumigation workshops, demonstrations and industry & end user & farmers interactions conceptualized, funded and executed by UPL Limited in coordination with other lead agencies, will be discussed. Furthermore, focus on the use of on-site phosphine generators which has the advantage of rapid generation and even distribution of the gas facilitating successful treatments by way of demonstration to different end users has also been presented.

Recent Developments in the Global Application of ECO2FUME® and VAPORPH3OS® Phosphine Fumigants

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Abstract

ECO2FUME® (2% phosphine, 98% CO₂ by weight) and VAPORPH3OS® (99.3% phosphine average by weight) are cylinderized gas formulations of phosphine that have achieved significant growth in commercial applications for the disinfestation of food and non-food commodities in the last two decades. The expansion in the global application of these two cylinderized phosphine fumigants is driven by increasing concern for safety, efficacy, unreacted powdered residue and disposal associated with aluminium phosphide tablets, which are promoted as alternatives to methyl bromide, and the concern of insect resistance to phosphine in both developed and developing countries. This paper describes recent developments in the global application of ECO2FUME® and VAPORPH3OS® in terms of commercial in-transit fumigation of grains and logs in ships, fumigation of export distiller's dried grain with solubles (DDGS) in containers and shiphold, best practices in the management of phosphine resistance of insects in grains, and establishment and application of quarantine and preshipment (QPS) phosphine fumigation protocols for selected fresh fruits, vegetables, dried fruits and cut flowers as an alternative to methyl bromide. The growing issue of powdered residue from unspent aluminium phosphide tablets and the use of cylinderized phosphine as an effective solution are discussed.

Keywords: ECO2FUME®, VAPORPH3OS®, cylinderized phosphine, Horn Diluphos System, fumigation applications, aluminium phosphide tablets issue, alternative to methyl bromide, phosphine resistance management

1. Introduction

Among the existing fumigants commercially available in the market, phosphine is considered the most cost-effective and widely used fumigant for protection against stored product pests worldwide. Although using phosphine in a solid metal phosphide formulation has drawbacks –it is slow acting, self-ignites when exposed to air, and requires deactivation and disposal of unspent residue--these disadvantages have been overcome with the introduction of ECO2FUME® and VAPORPH3OS® cylinderized phosphine fumigants.

ECO2FUME® is a cylinderized formulation of a nonflammable, ready-to-use liquefied gas mixture of 2% phosphine and 98% carbon dioxide (CO₂) by weight. It is packaged in high-pressure aluminum or steel cylinders with a net fumigant weight of 31 kg and 620 grams of phosphine. Though the phosphine/CO₂ mixture is liquefied inside the cylinder, it is converted immediately to gaseous form upon release into the atmosphere. The formulation requires simple dispensing equipment made of either a stainless steel double-braided hose or a high-pressure hydraulic hose designed to deliver the fumigant as quickly or slowly as required by individual applications. VAPORPH3OS® is 99.3% average phosphine purity by weight and is designed for use with approved blending equipment for safe on-site dilution with CO₂ or air in nonflammable proportions. It comes in steel cylinders with a net fumigant weight of 22 kg. Due to the larger amount of phosphine contained in a cylinder, VAPORPH3OS® is most suitable for larger volume applications for which it is not practical to store, handle or transport large numbers of cylinders; for price-sensitive applications such as grains; and for locations that conduct frequent fumigations (Tumaming et al., 2012).

ECO2FUME® and VAPORPH3OS® offer numerous benefits. The conduct of fumigation can be completed safely because it is applied externally to the fumigation structure, thereby removing confined space entry, reducing worker exposure and eliminating retrieval of 3 – 5% unspent powdered residue associated with metal phosphides (van Graver 2001). Due to its gaseous form, there is no residue that requires waste deactivation or disposal. When phosphine gas is vented into the atmosphere during aeration, it will react with oxygen in the air and, in the presence of sunlight, will readily convert to phosphoric acid. It is environmentally friendly as it is non-ozone depleting and does not contribute significantly as a greenhouse gas. It has a non-phytotoxic property and, therefore, does not damage sensitive commodities such as cut flowers, fruits and vegetables during fumigation. Required fumigation time is considerably faster using a phosphine gas than a metal phosphide formulation because the gas mixture can be easily applied to quickly distribute and uniformly achieve the target concentration. Compared to methyl bromide, the dose level for phosphine gas is at least 20 times less in terms of g/m³ application rate for phosphine

environmental and safety benefit. Additionally, phosphine gas is more penetrating and has extremely active molecules, which will enable the gas to distribute quickly and uniformly inside the fumigation structure without the help of a blower. Better gas distribution results in more effective control of target insects. Target concentration can be maintained quickly and safely anytime during the fumigation by top-up, which also decreases the amount of phosphine that needs to be applied. Through the years and over nearly two decades, ECO2FUME® and VAPORPH3OS® have achieved significant growth in commercial application for the disinfestation of food and non-food commodities. The expansion in the global application of these two cylinderized phosphine fumigants has been driven by increasing concern for safety, efficacy, unreacted powdered residue and disposal associated with aluminium phosphide tablets; alternatives to methyl bromide; and the spread of insect resistance to phosphine in both developed and developing countries.

Application for In-Transit Fumigation of Grains and Logs in Ships

In-transit fumigation of grains and logs in ships has been practiced for several years around the world using aluminum phosphide tablets or blankets. However, the use aluminum phosphide in ships has been associated with risk of ignition, fire and explosion, particularly during aeration or gas venting due to ingress of high-humidity air and exposure of still-active fumigant inside the hold, which leads to quicker generation of phosphine gas, exceeding the low flammability limit. Additionally, the use of aluminum phosphide tablets leaves unspent powder residue that contaminates the fumigated commodity in the ship.

Due to safety issues and residue contamination of fumigated commodities in ships, in recent years ECO2FUME® and VAPORPH3OS® have been utilized in commercial fumigation of grains and logs in ships during in-transit journeys at sea. In Turkey, ECO2FUME® is being used for in-transit fumigation of exported corn and soy beans in the Black Sea region. A typical cargo ship with approximately 45,000 m3 volume capacity containing about 30,000 tons of corn and soy bean can be fumigated while in transit for 14 days using a phosphine dose of 400 ppm. As shown in Fig. 1, the complete setup for dispensing ECO2FUME® involved the following (Goztas et al., 2015):

1. A perforated drainage pipe was placed at the bottom of the ship hold.
2. The drainage pipe and a recirculation pipe were connected via a "T" connection.
3. A blower was attached to the recirculation pipe to ensure movement of the gas.
4. After loading of the commodity, the recirculation pipe was placed on top of the commodity.
5. ECO2FUME® cylinders were secured and connected to the system via a standard manifold (Fig. 2).
6. ECO2FUME® was then dispensed into the hold.

In Australia, VAPORPH3OS® in combination with the Horn Diluphos System (HDS) has been used for in-transit fumigation of export grains destined to the Middle East as a mitigation measure. The option of using VAPORPH3OS® instead of aluminium phosphide tablets was prompted when the importing country rejected fumigated grains contaminated with powdered residue. The fumigation protocol and overall setup of gas dispensing and gas distribution is similar to ECO2FUME® except for using VAPORPH3OS® and an HDS fumigation machine. Fig. 3 and 4 show a setup using VAPORPH3OS® and HDS 200 inside a trailer and dispensing the gas through a flexible distribution hose into a hatch in the shiphold (courtesy of Ball, 2016).

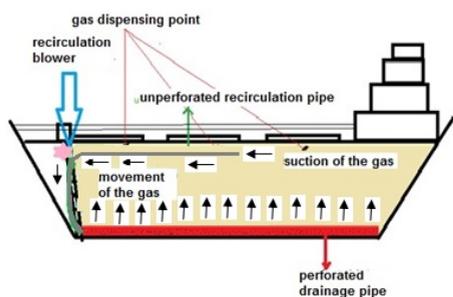


Fig. 1 Schematic of setup of ECO2FUME® during gas dispensing and distribution inside the shiphold.



Fig. 2 Eight ECO2FUME® cylinders secured and connected in manifold during gas dispensing through the hatch.



Fig. 3 VAPORPH3OS® and HDS 200 inside a trailer ready for dispensing gas into a shiphold.

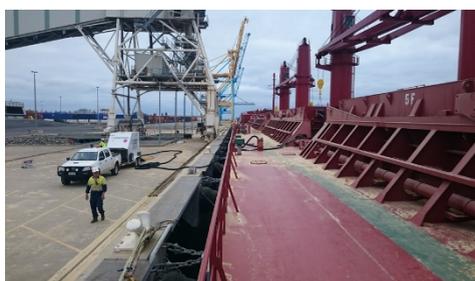


Fig. 4 Setup of flexible gas distribution hose between the trailer and hatch in a shiphold.

For additional safety when using ECO2FUME® and VAPORPH3OS®, guidelines on the use of pesticides applicable to fumigating cargo in ships set by the International Maritime Organization (IMO 2010) are being followed. IMO guidelines have specific instructions for pre-inspection of shipholds for the presence of cracks, and gas monitoring for the presence of gas leaks outside the shiphold and inside the cabin of the crew.

Fumigation of logs with VAPORPH3OS® and HDS destined to China has been practiced in Uruguay in the past two years. Previously, China has accepted the use of phosphine from aluminium phosphide tablets and blankets for in-transit fumigation of logs using a fumigation protocol of 2 g/m³ of phosphine as an initial dose at the wharf and a second dose of 1.5 g/m³ of phosphine as a top-up 5 days later while on the ship to maintain a phosphine concentration of 200 ppm for 10 days (Zhang and van Epenhuijsen, 2005). Chinese authorities have accepted the use of VAPORPH3OS® for in-transit fumigation of logs from Uruguay. In the case of VAPORPH3OS® the fumigation time is cut in half to 5 days using a one-off dose of 3.5 g/m³ of phosphine conducted while the ship is at wharf. With the use of VAPORPH3OS® and HDS, fumigation of logs is accomplished safer and quicker, eliminating the risk of having a fumigator on board to open the hatch and do complete top-up 5 days into the sea journey. The added benefit of using VAPORPH3OS® for in-transit fumigation of logs is the elimination of unspent powdered residue from aluminium phosphide tablets, which is currently not accepted by Chinese authorities.

Fumigation of Export Distillers Dried Grain with Solubles

Distillers dried grain with solubles (DDGS) as a by-product of ethanol production from corn is produced in large quantities in the US and became popular as a feed ingredient for export. However, in the past, as the Vietnamese quarantine authority banned the export of DDGS from the US due to

repeated insect infestation when the grain reached the destination port in Vietnam. The insect infestation issue was resolved with the establishment of fumigation protocols for phosphine gas for complete treatment against insect pests. With new protocols in place, the Vietnam Plant Protection Department lifted the ban on imported DDGS from the US effective September 2017 (Trung, 2017). The new protocols combine phosphine concentration, exposure time and temperature, as indicated below:

- 750 ppm for 3 days at >20°C
- 750 ppm for 4 days at 15 - 20°C
- 750 ppm for 5 days at 10 - 15°C

These protocols are applicable to both DDGS in shipping containers and larger bulk quantities in a shiphold with a gas recirculation system.

Best Practices in the Management of Insect Resistance to Phosphine in Grains

Insect resistance to phosphine has become a major concern in many countries where grains are harvested and stored for a period of 6 months or longer under high temperature and relative humidity favorable for insect growth and reproduction. The phosphine resistance issue emerged due to the use of leaky structures and poor fumigation practices associated with aluminium phosphide tablets. Aside from the common strong resistant strains of the lesser grain borer (*Rhyzopertha dominica*), rice/corn weevil (*Sitophilus sp.*), red flour beetle (*Tribolium castaneum*) and saw toothed grain beetle (*Oryzaephilus surinamensis*) another strongly resistant rusty grain beetle (*Cyptolestes ferrugineus*) is added to the list. This particular insect pest is a concern in Australia, China, India, Thailand, Vietnam, the Philippines and Brazil, among other countries. A series of efficacy studies and field validation trials conducted by the Postharvest Grain Protection Unit of the Queensland Department of Primary Industries have identified the strong resistant rusty grain beetle and established effective fumigation protocols for complete treatment of this insect pest (Kaur and Nayak, 2014; Nayak and Kaur, 2016). The fumigation protocols for the strong resistant rusty grain beetle are shown in Tab. 1 and are now part of the ECO2FUME® and VAPORPH3OS® label in Australia.

Tab. 1 Fumigation protocols for the strong resistant rusty grain beetle as part of the ECO2FUME® and VAPORPH3OS® Australian label

Commodity	Minimum Application Rate (g/m ³) & Minimum Phosphine Concentration (ppm)		
Temperature	0.5 g/m ³ (360 ppm)	1.0 g/m ³ (700 ppm)	1.4 g/m ³ (1000 ppm)
20 – 24°C	30 days	23 days	na
25 – 29 °C	27 days	18 days	12 days
30 - 34°C	na	na	10 days
35°C or higher	na	15 days	6 days

In the US, the USDA Agricultural Research Station conducted phosphine resistance management studies entitled “Technical Framework for Using Cylinderized Phosphine for Managing Phosphine Resistance” and presented the following findings (Walse et al., 2017).

Resistant pests can be effectively controlled with the right dose of phosphine.

- More is not always better - there is a “Sweet Spot” Phosphine concentration, such as 500 – 1000 ppm for lesser grain borer and red flour beetle.
- Narcosis threshold for eggs of major grain insects treated with phosphine is generally ≥ 1000 and ≤ 2000 ppm depending on the insect species.
- Phosphine concentration higher than the threshold concentration will result in narcosis, and much longer time is required to kill the egg stage.
- As shown in Fig. 5, the sweet spot phosphine concentration for the egg stage of susceptible and resistant strains of red flour beetle (RGB) is similar; however, eggs of resistant strains take

relatively longer time to kill compared to eggs of susceptible strains at a given phosphine concentration.

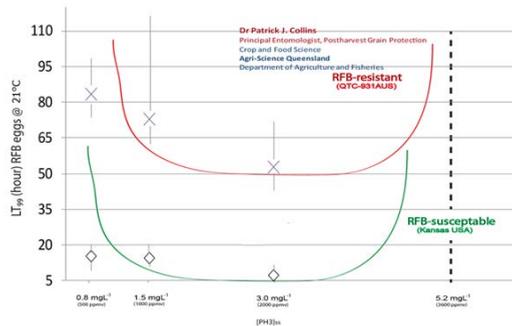


Fig. 5 Time in hours to reach LT99 of susceptible and resistant strains of red flour beetle (RFB) at different phosphine concentrations and 21°C temperature.

Phosphine fumigation protocols for quarantine and pre-shipment

Over the years, phosphine fumigation protocols have been developed in different countries as alternatives to methyl bromide for quarantine and pre-shipment application for selected fruits and vegetables, cut flowers, dried fruits, pine timber and associated nematodes, coffee and cocoa beans. These protocols were established under lab and field scale efficacy studies as conducted by accredited research institutions in different countries. Tab. 2 shows the different phosphine gas fumigation protocols for QPS treatment of selected commodities and corresponding research institutions.

Tab. 2 Phosphine gas fumigation protocols for QPS application of selected exported and imported commodities in different countries.

Commodity	Plant Pest Type	Phosphine Conc. (Minimum)	Exposure Time	Temperature	Reference
Pineapple	Purple scale, Citrus mealy bug	1400 ppm	24 hours	5 oC or higher	NPQS Korea 2015
Citrus	Queensland fruit fly (<i>Bactrocera tyroni</i>)	1400 ppm	48 hours	23 – 25°C	Williams 2000
Citrus	Citrus red scale	1500 ppm	48 hours	5°C	USDA ARS 2014
Mango	Fruit fly	1400 ppm	24 hours	26 – 33°C	NPQS Sri Lanka 2017
Bitter Gourd	Melon fly	1400 ppm	24 hours	26 – 33°C	NPQS Sri Lanka 2017
Cut flowers (chrysanthemum, rose, lily)	Western flower thrips, two spotted spider mites, cotton aphids	1400 ppm	24 hours	8oC or higher	NPQS Korea 2015
Dracaena house plants	Purple scale, aphids, white fly, scales	1400 ppm	24 hours	15 oC or higher	NPQS Korea 2015
Mushrooms	<i>Lycoriella mali</i>	1400 ppm	24 hours	5 oC or higher	NPQS Korea 2015
Timber pine Pine Nut pine	Pine weevil, white ant, <i>Bursaphelenchus xylophilus</i> , <i>Monochamus alternatus</i> , <i>Monochamus saltuarius</i>	2800 ppm	5 days	5 oC or higher	NPQS Korea 2015
Pineapple	<i>Planococcus minor</i>	200 ppm	7 hours	26 – 30 oC	BIOTROP 2012
Mangosteen	<i>Planococcus minor</i>	200 ppm	7 hours	26 – 30 oC	BIOTROP 2012
Orchids	<i>Planococcus minor</i>	200 ppm	7 hours	26 – 30 oC	BIOTROP 2012
Dried Fruits	<i>Ephestia Interpunctella</i> <i>CautellaPlodia</i>	1000 ppm	24 hours	20 – 27°C	Ankara Univ. 2013
Dates	<i>Ephestia Cautella</i> Red flour beetle <i>Saw toothed grain beetle</i>	700 ppm 1000 ppm 1500 ppm	72 hours 48 hours 24 hours	30°C or higher	ARC Egypt 2013

Conclusions

1. ECO2FUME® and VAPORPH3OS® phosphine fumigants offer advantages over methyl bromide in terms of lower dose for phosphine environmental and safety benefits, greater gas penetration and quicker gas distribution into bulk commodities without the need for recirculation blower and without the need for a heater/vaporizer to dispense the fumigant in form.
2. ECO2FUME® and VAPORPH3OS® phosphine fumigants offer greater benefits over metal phosphide than metal phosphide formulation in terms of reduced worker exposure, no need of deactivation and disposal in unreacted residue, non-phytotoxic to sensitive commodities and quicker fumigation time.
3. The application of these two cylinderized phosphine fumigants has expanded to commercial fumigation of grains and logs in ships during in-transit journeys at sea and fumigation of export distiller's dried grain with solubles (DDGS) in containers and shipholds.
4. The emergence of phosphine resistance insects particularly in grains and oilseeds can be better addressed with the use of cylinderized phosphine fumigants due to its ability to be controlled and maintained at higher dose and longer exposure time.
5. There is sweet spot phosphine concentration that should be used for effective control of resistant insects. Above the sweet spot phosphine concentration narcosis effect could set in resulting in much longer time to kill the egg stage.
6. Phosphine gas fumigation protocols have been developed as alternative to methyl bromide for quarantine and pre-ship treatment of selected fruits and vegetables, cut flowers and nursery trees, dried fruits and pine timber and associated nematodes.

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Effects of *Myristica fragrans* and *Alpinia conchigera* oils against *Callosobruchus maculatus*

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Efficacy of *Myristica fragrans* and *Alpinia conchigera* oils were evaluated against *Callosobruchus maculatus* at Post-harvest Technology on Field Crops Research and Development Group, Post-harvest and Processing Research and Development Office during October 2014 to September 2015. Seed of *M. fragrans* and rhizomes of *A. conchigera* were extracted the essential oils. It was identified the chemical composition by GC-MS which 10 and 12 constituents were found on *M. fragrans* and *A. conchigera* oils. The major component of *M. fragrans* and *A. conchigera* oils were sabinene and 1,8-cineole, respectively. Contact toxicity assay on filter paper of both essential oils, the LC50 value of *C. maculatus* adults when treated with *M. fragrans* oil at 72 h were 4.6 µL/cm² while 1.7 µL/cm² for *A. conchigera* oil. Furthermore, the number of laid egg and adult progeny production of *C. maculatus* were inhibited by treated with *M. fragrans* and *A. conchigera* oils at 8 and 10% under laboratory condition. In additions, the efficacies of both essential oils were conducted for 6 months at warehouse of Lopburi Agricultural Research and Development Center. The results showed that insect pests and natural enemies were more found in the mung bean treated with *M. fragrans* oil than *A. conchigera* oil and *C. maculatus* was the major pest. Furthermore, *C. maculatus* was found on mung bean that coating with *M. fragrans* oil than *A. conchigera* oil. Both essential oils were control insect pests for 1 month.