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Updates on the global application of Eco₂Fume and Vaporph₃OS[®] phosphine fumigants

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Abstract

Eco₂Fume (2 % phosphine and 98 % CO₂ w/w) and Vaporph₃OS[®] (99.3 % phosphine w/w) are cylinderised gas formulation of phosphine which are commercially used for safe, effective and user-friendly fumigation of food and non-food commodities. In, response to the increasing global concern on safety and environment, new applications had been developed to expand the use of these two phosphine fumigants. As an alternative to methyl bromide, new fumigation protocols for Eco₂Fume and Vaporph₃OS[®] to kill all stages of insects were established and approved in the USA which allows a shorter fumigation time of 24 hrs at 500-1,000 ppm phosphine concentration and 27 °C or higher temperatures. In Australia, a new fumigation protocol was approved which can completely kill all stages of insects in 3 - 24 days at 70 – 700 ppm phosphine concentration and 15 - > 30 °C temperature. Trials conducted on the fruit fumigation showed that cylinderised phosphine can effectively kill all stages of insects using 1400 ppm at 0 - 6 °C in 48 – 72 hours and a residue level below the maximum residue limit of 0.01 mg/kg. For treatment of exported cut flower and foliage in New Zealand, a shorter fumigation time of 4 hours is in commercial use with Eco₂Fume under vacuum condition. Promising results are

also shown in the trials conducted on timber and log fumigation. Techniques have been developed for the application of Vaporph₃OS[®] in combination with the Horn Diluphos System for fumigation of cereal grain and oil seeds in sealed silos, horizontal sheds and bunkers with capacities ranging from 1000 – 300,000 tonnes. This paper describes the different applications of Eco₂Fume and Vaporph₃OS[®] in North America, South America and Asia Pacific.

Key words: Eco₂Fume, Vaporph₃OS[®], phosphine, Horn Diluphos System, fumigation applications, alternative to methyl bromide.

Introduction

Phosphine is still the world's most widely used and cheapest fumigant for the protection of stored products against insect pests. This is despite the increasing resistance issue of stored product insects to phosphine. The usual disadvantages of phosphine of being self-igniting at over 18,000 ppm and long fumigation times has now been overcome with the introduction of cylinderised phosphine formulations in the form of Eco₂Fume and Vaporph₃OS[®]. Eco₂Fume is 2 % phosphine and 98 % carbon dioxide (CO₂) by weight making it a non-flammable and ready to use gas mixture.

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It comes in high pressure aluminium 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. 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. Most applications of Vaporph₃OS[®] use the Horn DiluPhos System (HDS), a new technology for the safe blending of pure phosphine with air. The HDS comes in three models; HDS 80 (1.2 kg/hr phosphine flow rate), HDS 200 (3 kg/hr phosphine flow rate) and HDS 800 (12 kg/hr phosphine flow rate).

Developments in north America

New Fumigation Protocol

In response to the need of replacing methyl bromide, a new fumigation protocol for phosphine from Eco₂Fume or Vaporph₃OS[®] was developed which can kill all stages of major insect pests in stored grains and other approved commodities using 500 - 1,000 ppm phosphine concentration for 24 hours at a minimum of 26.7 °C. Muhareb et al. (2004) found that at the above conditions with equivalent concentration-time (CT) product of > 21,000 ppm-hr the average mortality of the major insect species were 98 % for eggs and 100 % for post-embryonic stages (larvae, pupae and adults). Increasing the temperature to 35 °C resulted in average mortality rate of 99.7 % for the eggs and 100 % for the post-embryonic stages. The major insect species tested were Indian meal moth (*Plodia interpunctella*), navel orange worm (*Amyelois*

transtella), red flour beetle (*Tribolium castanum*), confused flour beetle (*Tribolium confusum*), warehouse beetle (*Trogoderma variabile*), saw-toothed grain beetle (*Orzaephilus surinamensis*), cigarette beetle (*Lasioderma serricorne*) and dried fruit beetle (*Carpophilus hemipterus*).

Rail car fumigation trials

In April 2003, a total of seven pressure differential (PD) rail cars containing flour from Kansas destined to Texas were treated with different dosages of Eco₂Fume over a course of 3 days. Eco₂Fume was injected at the bottom of each car via the “air supply inlet” as the most suitable location and more convenient for the workers (Figures 1-2). The dosage of Eco₂Fume for each car was in the range of 7.5 - 12.4 lbs (3.4 - 5.6 kg) equivalent to 375 -500 ppm of phosphine concentration. Time of gas introduction was in the range of 5 - 10 minutes for each car depending on dosage. The purpose of the this trial was to provide the industry with an alternative to aluminium phosphides for the fumigation of railcars that is safe, environmentally friendly, cost effective, efficacious and easy to use. Results of the trial in Table 1 showed that the phosphine concentration in the head space at the end of in-transit fumigation period of 8 - 12 days was in the range of 100 - 250 ppm which is within the dosage level to kill all stages of insects. This trial came up with the following conclusions:

- Introduction of Eco₂Fume into the bottom of the railcars proved to be very efficient and effective.
- Potential over pressurization of the “PD” railcar with Eco₂Fume was not an issue.
- The use of Eco₂Fume prevents the need for fumigators to work on top of the railcars.
- The required dosage was added quickly and easily, thus allowing the fumigation of a large number of railcars in a short period of time.
- Results of this trial suggest that the dispensing rate of Eco₂Fume not exceed 2lbs./min.

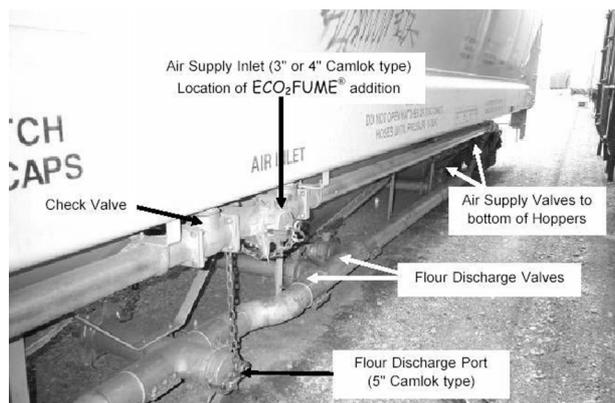


Figure 1. Illustration of “PD” car manifold system.

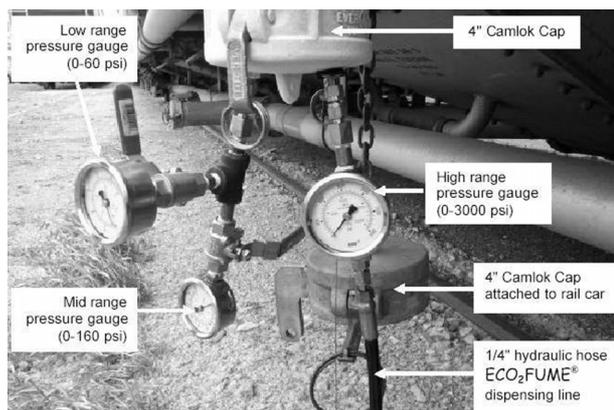


Figure 2. Initial Trial setup of Eco₂Fume fumigant dispensing into the bottom of the “PD” car to measure pressure rise.

Table 1. Summary of rail car fumigation results.

Railcar #	Date of receipt for testing and aeration	# Days under fumigation	Phosphine concentration in Headspace of Railcar (ppm)	Eco ₂ Fume dosage (lbs.)	Dosage equivalent in g/1000 ft ³ (approx.)
SHPX 43291	April, 27, 2003	12	250	12.1	21
NRLX 56338	April, 23, 2003	8	200	12.4	20
NRLX 56591	April, 25, 2003	9	225	10.1	16
NRLX 56215	April, 23 2003	7	225	9.1	15
NCUX 50368	April, 23, 2003	7	150	10	16
NRLX 56252	April, 27, 2003	10	100	7.9	13
NCUX 50337	April, 25, 2003	8	125	7.5	12

- Results suggest that the Eco₂Fume fumigant had made its way up through the flour mass to the headspace after 24 hours.

- Results indicate that lethal concentrations of phosphine are maintained within the railcar over the course of several days in -transit.

- The results of this trial suggest that a dosage of no less than 15-18 g/1,000 ft³ (0.53 – 0.64 g/m³) or 9-11 lbs. (4.1 – 5 kg) of Eco₂Fume is required. This translates into a dosage range of 375-400 ppm phosphine.

- Eco₂Fume eliminates the hazards associated with the handling of aluminum phosphides during their introduction and removal

from a railcar.

- Eco₂Fume fumigant gas also eliminates the deactivation of the partially spent aluminum phosphide material and disposal of this waste at the receiving end.

- The risk of dropping and/or losing aluminum phosphide material into the flour is eliminated with the use of Eco₂Fume.

- Eco₂Fume addressed the growing concerns of both State and Federal Agencies regarding the exposure of workers whose job it is to receive, handle and aerate railcars under fumigation.

- The procedures and associated training required for receiving fumigated railcars would

be simplified and made safer with the use of Eco₂Fume fumigant gas.

- This trial has proven that Eco₂Fume fumigant gas is a practical, safe and effective alternative to aluminum phosphide pre-pacs for the fumigation of railcars.

Another trial was conducted using eight hopper type cars containing rice destined to Memphis Tennessee in July 2003. The hopper car fumigation trial demonstrated that it was feasible and effective to add Eco₂Fume fumigant gas into the top of a sealed hopper-type railcar of finished rice for in-transit fumigation. The gas was added within five to eight minutes to each car, with the flow of Eco₂Fume controlled at about 2 pounds per minute by a 1/16 inch (1.59 mm) nozzle tip. After 5 to 8 days in transit, readings above 100 ppm of phosphine were seen in the headspace and the rice mass in 20 of the 21 compartments measured in the hopper cars that were fumigated with this method. This indicated that lethal concentrations had been maintained for the duration of the fumigation. This was comparable to an identical hopper car that had been fumigated with metallic phosphides.

Methyl Bromide Replacement

- Conversion of a rice mill in Louisiana previously using about 15 metric tons of methyl bromide a year to Eco₂Fume.

- Memphis rice facility commercialized Vaporph₃OS[®] with the two units of Horn Diluphos System (HDS 200 model) in May 2004. Addition of fumigant from centralized location at the bottom of the facility with internal recirculation.

- California producers of almonds and pistachios previously were using methyl bromide in fumigation chambers/containers and metal phosphide in metal storage bins now using Vaporph₃OS[®].

- Bagged cocoa beans fumigation in sealed containers, trailers and tarps.

- Fumigation of stacked raisins under tarp using Vaporph₃OS[®].

- Tobacco fumigation in warehouse using Vaporph₃OS[®].

Developments in Australia and New Zealand

New fumigation protocol

In view of the problem of insect resistance to phosphine in Australia, a new fumigation protocol was developed and implemented nationwide for Eco₂Fume and Vaporph₃OS[®] (Table 2). There is a separate set of phosphine concentration, exposure time and temperature schedule for the strong resistant lesser grain borer (*Rhyzopertha dominica*), other known resistant strains and pea weevil. The new protocol allows complete kill of all stages of insects at phosphine concentration of 70 - 700 ppm, exposure time of 3 - 24 days and temperature of 15 - > 30 °C.

Commercial application of Vaporph₃OS[®] for sealed storage

Commercial fumigation of a 300,000-tonne max capacity sealed horizontal shed at Kwinana Grain Terminal in Western Australia (Figure 3) was done in June 2005 using the HDS 800 (Thornton, et al., 2006). This horizontal shed is probably the largest in the world equipped with recirculation system at every 50 m length. The recirculation fan at the other end of the shed was kept running during gas delivery to enable quicker distribution of the gas on the 300 m length of head space. A total of 126 kg of Vaporph₃OS[®] was delivered for 10.5 hours (0.45 g/tonne application rate) to fumigate 280,000 tonne of wheat loaded in the shed. All the six recirculation fans were kept running after gas delivery and good gas distribution was achieved within 24 hours including gas delivery time. As shown in Table 2, the K value of 4.0404 for complete kill using the CⁿT equation developed by Collins (2004) was achieved at the 8th day of fumigation based on the lowest phosphine concentration readings.

Another large horizontal shed at 240,000-tonne at Merredin Western Australia was successfully fumigated with the HDS 800 In June 2006. This shed was without a recirculation

system. A single hose connection at the pressure relief duct was used to inject Vaporph₃OS[®] through the head space (Figure 4). There was no pressure build up after gas delivery due to the relatively large volume of head space common

on horizontal sheds. An application rate of 0.35 g/tonne was employed and the good gas distribution at about 300 ppm was achieved after 24 hours.

Table 2. Phosphine fumigation schedule for Australia.

Stored product	Commodity temperature	Minimum Application Rate (g/m ³) and Minimum Phosphine Concentration (ppm)						
		0.04 g/m ³ 30 ppm	0.1 g/m ³ 70 ppm	0.2 g/m ³ 140 ppm	0.3 g/m ³ 215 ppm	0.5 g/m ³ 360 ppm	0.7 g/m ³ 500 ppm	1.0 g/m ³ 700 ppm
<i>Rhyzopertha dominica</i> present	15 – 19°C	na	25 days	16 days	14 days	13 days	12 days	10 days
	20 – 24°C	na	24 days	15 days	12 days	10 days	10 days	9 days
	25 – 29 °C	na	Do not fumigate	16 days	10 days	7 days	6 days	5 days
	30°C or higher	na	Do not fumigate	18 days	11 days	7 days	4 days	3 days
All other species and known resistant strains	15 – 19°C	na	18 days	16 days	14 days	13 days	13 days	12 days
	20 – 24°C	na	16 days	14 days	12 days	10 days	10 days	9 days *
	25 – 29 °C	na	12 days	10 days	8 days	7 days	6 days	5 days
	30°C or higher	na	11 days	6 days	5 days	4 days	4 days	3 days
<i>Bruchus pisorum</i> (Pea weevil)	15 – 20°C	na	21 days	na	na	na	na	na
	>20°C	21 days	na	na	na	na	na	na

NB: na = not applicable. * = 10 days if resistant Psocoptera present



Figure 3. The HDS 800 2-hose connection setup for fumigation of the 300,000-tonne shed at Kwinana Grain Terminal in Western Australia.



Figure 4. The 240,000-tonne sealed horizontal shed at CBH Merredin WA with single hose connection to pressure relief duct for gas delivery into the head space.

Trials were conducted at GrainCorp Red Bend NSW using a much larger capacity HDS 800 model at 12 kg/hr phosphine flow rate. This is in response to the need for quicker fumigation time. When fumigating the Red Bend bunker (13,327 tonnes) an auxiliary fan (Dawn 6B) was added, delivering additional air of 1600 m³/hr (Figure 5).

Results of the fumigation trial at Red Bend is shown as follows:

- Application rate of 0.45g/tonne (6 kg PH₃)
- Gas delivery time is 30 min
- Phosphine gas concentration varies from approx. 1,300 ppm at inlet end to approx. 1,000 ppm at the other end of the bunker
 - PH₃ concentration after 24 hours were in the range 340 – 520 ppm
 - Phosphine gas readings at 117 – 151 ppm after 17 days.
 - Concentration-time (CⁿT) product for strong resistant *R. dominica* achieved in 7- 9 days (Table 3).

The HDS is already in commercial application for bunker storage with capacities in the range of 10,000 - 50,000 tonnes at ABB Grain Ltd in South Australia and CBH Group in Western Australia. The dose of phosphine from Vaporph₃OS[®] used is 0.35 - 0.5 g/tonne with equivalent initial phosphine concentration of



Figure 5. Setup of HDS 800 and Dawn 6B blower for GrainCorp Red Bend bunker.

300 - 400 ppm. The fumigation period takes 7 - 14 days depending on the temperature and minimum gas concentration. The hose connection of the HDS is customised to retrofit to the existing bunker setup.

The HDS is also in commercial use in sealed steel silos with capacities of 1,000 - 10,000 tonnes of ABB Grain Ltd and CBH Group (Figures 6-7) with recirculation systems. The dose used is flexible at 300 - 500 ppm initial phosphine concentration and fumigation period of 7-12 days.

The main benefits of the HDS/VVaporph₃OS[®] technology that most of the bulk handling companies in Australia can derive are as follows:

- Operational flexibility - ability to do quick fumigation in 5 - 7 days to overcome “over the horizon shipping” (arrival of ship to port with limited notice of less than 14 days) to save on demurrage fee or longer fumigation of 14 days to save on gas.



Figure 6. Setup of HDS 80 connections to 10,000-tonne capacity sealed steel silo at ABB Wallaroo Grain Terminal in South Australia.



Figure 7. Setup of HDS 200 connection to 1,000-tonne silo at CBH Metro Grain Centre in Perth Western Australia.

- Better control of fumigation and easy to top up when needed.
- Reduced man hours to fumigate and remove and dispose of residues.
- Convenient to operate and allows the fumigators to devote application time to other productive activities.
- Reduced occupational health and safety risks.

Eco₂Fume Fumigation under Vacuum

Unlike pure phosphine, Eco₂Fume is safe to use for fumigation even under any vacuum condition due to its non-flammable mixture with carbon dioxide (Pearson, 2002). This feature of Eco₂Fume was applied for shorter time of fumigating cut flowers, and foliage in New

Table 3. Minimum phosphine concentration in the grain inside the Kwinana shed, daily CⁿT and cumulative CⁿT during the 19 days of monitoring (CⁿT = K, 4.04 value will kill all stages of insects of strong resistant lesser grain borer).

Exposure Day	PH ₃ Conc. Min ppm	PH ₃ Conc. mg/L	Daily C ⁿ T	Cumulative C ⁿ T
1	320	0.4457	0.6106	0.6106
2*	294	0.4095	0.5798	1.1903
3*	267	0.3719	0.5467	1.7370
4*	240	0.3343	0.5122	2.2492
5	214	0.2981	0.4776	2.7268
6*	203	0.2827	0.4624	3.1893
7	192	0.2674	0.4470	3.6362
8	190	0.2646	0.4441	4.0804
9*	180	0.2507	0.4297	4.5101
10*	171	0.2382	0.4165	4.9266
11*	161	0.2242	0.4014	5.3280
12*	152	0.2117	0.3876	5.7156
13	142	0.1978	0.3718	6.0874
14	140	0.1950	0.3686	6.4559
15	133	0.1852	0.3572	6.8132
16	130	0.1811	0.3523	7.1655
17	128	0.1783	0.3490	7.5144
18	123	0.1713	0.3406	7.8550
19	119	0.1657	0.3338	8.1888

* Interpolated values

Zealand. The New Zealand Crop and Food Research Institute (CRI) conducted trials in 2003 and developed a fumigation protocol for Eco₂Fume (700 ppm for 3 - 4 hours at 15 °C) under vacuum condition of 70 mm Hg absolute pressure (Zhang, 2004). The equivalent oxygen concentration at this vacuum condition is about 2 %. This reduced fumigation time is about 4 times less than the protocol of 15 hours using 700 ppm at 15 °C and normal atmospheric pressure. This fumigation protocol is being practiced by cut flower and foliage exporters in New Zealand such as Westbay Waratahs Pty Ltd in Kati Kati. Figure 8 shows the vacuum chamber setup and Eco₂Fume cylinder connection outside the adjacent wall.

Timber Fumigation Trials

Successful small scale fumigation trials with test insects on sawn timber were conducted during the period 13-16 December 2005 at Port Tauranga in Mt. Maunganui, New Zealand. A new fumigation protocol with an initial dose of 1,400 ppm of phosphine either from Eco₂Fume or Vaporph₃OS[®] for 16 hours at minimum temperature of 15°C was established for treating sawn timber exported to Australia (Tumaming et al., 2005). The high initial dose will cover the gas loss due to sorption and leaks. The above



Figure 8. Setup of vacuum chamber and Eco₂Fume cylinder for fumigating export foliage at Westbay Waratah in Kati Kati New Zealand.

protocol will ensure 100 % mortality of adult *Arhopalus tristis* timber pest which are hitch hikers to sawn timber during loading on the ship. This protocol will be suitable for the in-transit fumigation of sawn timber during the 5-day ship journey from New Zealand to Australia.

Preliminary results of the log fumigation experimental trials conducted by New Zealand Crop and Food Research Institute are very promising as an alternative treatment for all stages of logs pests in a single dose. Currently, export logs with very high moisture content of 160 % dry basis are treated with aluminium phosphide tablets or blankets at an initial phosphine dose of 2 g/m³ (1,400 ppm) at the port and top up with a dose of 1.5 g/m³ after 5 days in the sea to maintain a minimum phosphine concentration of 200 ppm for 10 days. At a single dose of 2,100 ppm for 72 hours adult stages of major log pests (*Arhopalus* sp., *Hylastes* sp., *Prionoplus reticularis* and *Kaloterme brouni*) and juveniles of *Kaloterme brouni* were completely killed. However, the mortality of eggs and larvae were less than 100 % at 94 % for *Arhopalus* sp and 80 % for larvae of *Hylastes* sp (Zhang et al., 2006). It is recommended that complete kill of all stages of the above log pests can be achieved by extending the fumigation time from 3 days to 5 days which is half the time for the current practice. This needs to be verified by further experimental trials and commercial trials.

Developments in South America

A new fumigation protocol using Vaporph₃OS[®] was developed by Fosfoquim in Chile for fruits and vegetables while in cold storage (Horn, 2004). At cold storage temperature of 0-6 °C, all stages of major fruit pests can be completely killed in 48 - 72 hours at 1,400 ppm. The protocol for a long list of fruits and vegetables is in the process of approval at EPA in the USA. The main advantages of using cylinderised phosphine for fumigation are as follows:

- It is possible to fumigate at low temperature (0-6 °C) with the cooling system running.

- It is not necessary to heat fruits up before fumigation.
- Phosphine eliminates the target pests in fruits.
- There is no corrosion if ammonia cooling systems are used due to no exposed copper based materials.
- It does not produce ammonia and is therefore, not phytotoxic.
- The fumigation can be done in the same cooling chambers where the fruit is stored.
- No changes in taste, smell, texture, colour or shelf life of the fruit if fumigation has been conducted at low temperature (non-phytotoxic).
- All stages of insects infesting fruits are killed in 48 hours
- Provides greater flexibility in handling and transport scheduling of packaged fruits for export.
- Phosphine residue is reduced to below maximum residue limit (MRL) of 0.01 mg/kg after 48 hours of aeration/ventilation.

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