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ECO_2FUME AND VAPORPH$_3$OS PHOSPHINE FUMIGANTS - GLOBAL APPLICATION UPDATES

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ABSTRACT

ECO_2FUME®(2% phosphine, 98% CO_2 by weight) and VAPORPH$_3$OS®(99.3% phosphine average by weight) are cylindered gas formulation of phosphine which have realized significant growth in commercial application for the disinfestation of food and non-food commodities. These two cylindered phosphine fumigants offer numerous advantages over traditional fumigants like methyl bromide and metal phosphide products such as enhanced worker safety, fast action, high effectiveness, ease of application and dose control, absence of waste, absence of residues and preferred environmental profile.

This paper presents the history and recent developments of the different applications of ECO_2FUME®and VAPORPH$_3$OS®as fumigants for food commodities such as stored grains, oilseeds, nuts, pulses, fruits and vegetables, animal feed and feed ingredients and non-food commodities such as tobacco, cut flowers, foliage and structural fumigation.

ECO_2FUME®was first introduced in Australia in 1988 for stored grains, oilseeds and nuts both for unsealed and sealed vertical silos and horizontal sheds using the SIROFLO®, SIROCIRC® and SIROFUME® fumigation methods. ECO_2FUME®was also used in Australia and New Zealand for export cut flowers and foliage. In North America, ECO_2FUME®started its commercialization in 2000 in sealed storages for grains, nuts, dried fruits, tobacco, flour, processed foods, feeds and structural fumigation.ECO_2FUME®is now expanding in several countries in Asia and in the Middle East for grains, pulses, dried fruits, tobacco, cut flowers, nursery trees, structural fumigation, fresh fruits and vegetables. VAPORPH$_3$OS®was first introduced in China in 2000 at Dalian Grain Export Terminal using the on-site mixing with CO_2technology. With the development of the Horn Diluphos System™ for safe on-site mixing of VAPORPH$_3$OS®with air in 2002, VAPORPH$_3$OS®became an increasingly popular phosphine fumigant as a practical and convenient approach for large scale fumigation of grains, oil seeds, nuts and fresh fruits and vegetables in Australia, New Zealand, USA and South America.VAPORPH$_3$OS®is also being applied as replacement to ECO_2FUME®for SIROFLO® applications in Australia.

Key words: phosphine, ECO_2FUME®, VAPORPH$_3$OS®, history, recent developments.

INTRODUCTION

Phosphine is regarded as the world's most cost effective and widely used fumigant for stored product protection against insect pests. The usual disadvantages associated with the solid phosphine formulation of slow acting, self-igniting when exposed to air and the need for deactivation and disposal of unspent residue have been overcome with the introduction of $ECO_2FUME^{®}$ and $VAPORPH_3OS^{®}$ cylinderized phosphine fumigants.

$ECO_2FUME^{®}$ is a non-flammable and ready to use liquefied gas mixture of 2% phosphine and 98% carbon dioxide (CO_2) by weight. It comes in high pressure aluminum or steel cylinders with a net fumigant weight of 31 kg and containing 620 grams of phosphine. It requires simple dispensing equipment designed to deliver the fumigant as quickly or slower as required by each individual application. $VAPORPH_3OS^{®}$ is 99.3% phosphine by weight and is designed for use with approved blending equipment for on-site dilution with CO_2 or air in non-flammable proportions. It comes in steel cylinders with a net fumigant weight of 22 kg. $VAPORPH_3OS^{®}$is most suitable for larger 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.

$ECO_2FUME^{®}$ and $VAPORPH_3OS^{®}$offer the advantages of being safer, greener and faster. Safer because it is applied externally to the fumigation structure which eliminates confined space entry, reduces worker exposure and eliminates retrieval of partially spent fumigant, ECO2FUME® being also non-flammable. It is greener because there is no waste product or residue that requires waste deactivation or disposal. Phosphine vented into the atmosphere 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 non-phytotoxic 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 a gas mixture to quickly distribute and achieve uniformly the target concentration. There is more effective control of target insects due to better gas distribution and maintenance of target concentration by safe and quick top-up which leads to decreased amount of phosphine applied.

Applications in Australia and New Zealand

$ECO_2FUME^{®}$ (originally known as Phosfume) was first commercially applied in Australia in 1988 by BOC Gases Australia which produced and patented the phosphine/CO_2 blend and developed special dispensing equipment for fumigating grains and oil seeds in unsealed and well-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 250 million tons of grains and oil seeds that have been fumigated with $ECO_2FUME^{®}$. In 1999, Cytec Industries Inc. acquired the $ECO_2FUME^{®}$ 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's for extra safety and less maintenance. The improved versions were developed by GasApps Australia, Viterra and Cytec Industries Inc.

SIROFLO® is a continuous slow addition of ECO_2FUME® in an air stream such that phosphine concentration is diluted from 26,000 ppm to about 90 - 160 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 14- 28 days (Fig. 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 permeatesoutward throughout the storedcommodity, 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 for the killing of all stages 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 protocols was established in 2004 covering minimum phosphine concentration of 70 – 700 ppm for 3 – 21 days at 15 - >30°C. There has been in recent years the emergence of strong resistant flat grain beetle particularly in areas with warmer temperature and high relative humidity which render the current fumigation protocols insufficient to achieve complete control. Experimental studies are currently being conducted by postharvest grain protection team of Queensland Department of Employment, Economic Development and Innovation to establish the new phosphine fumigation protocols for complete treatment of strong resistant flat grain beetle.

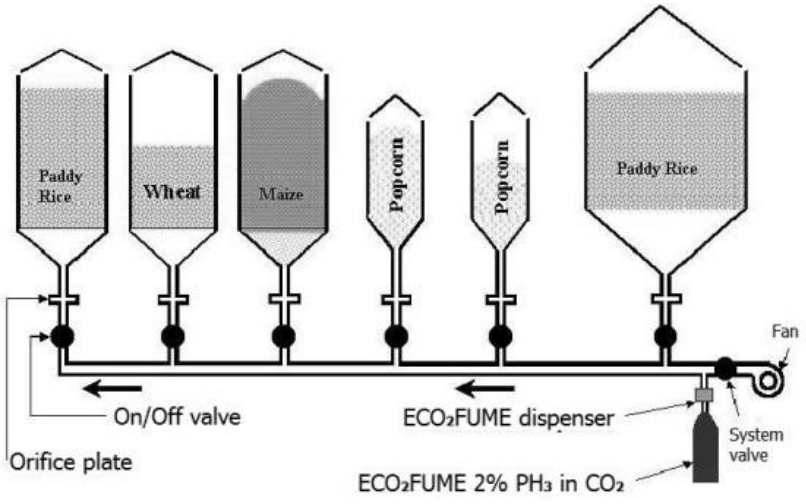

Fig.1- Schematic of SIROFLO fumigation ECO_2FUME®system for unsealed silos.

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 recirculation 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 $VAPORPH_3OS$® with CO_2. GrainCorp's 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 VAPORPH$_3$OS® using on-site phosphine/air mixing equipment.

ECO$_2$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. ECO$_2$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 Industries Inc. approved phosphine/air on-site mixing equipment) in 2004, VAPORPH$_3$OS® became an increasingly popular fumigant for cost effective, flexible and convenient way of fumigating grains and oil seeds 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 four size models (HDS CF/30 – 0.06 – 0.36 kg phosphine/hr, HDS 80 – 1.2 kg phosphine/hr, HDS 200 – 3 kg phosphine/hr and HDS 800 – 12 kg phosphine/hr) which cater to a wide range of storage capacities ranging from 1,000 to 300,000 tons (Fig. 2).

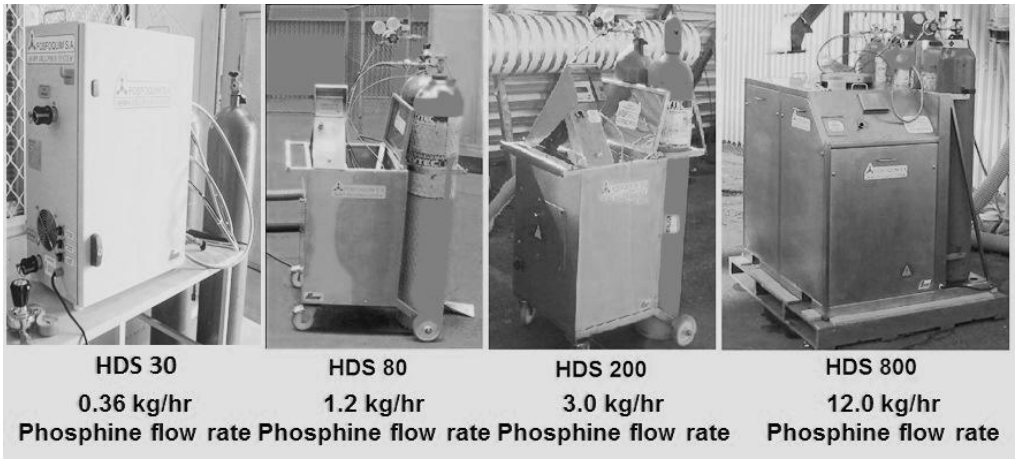

Fig. 2- The four models of the HDS fumigation equipment and corresponding capacities

The VAPORPH$_3$OS® phosphine fumigant in combination with the HDS fumigation equipment is now widely used by the three Australian bulk handling companies (GrainCorp, Viterra and CBH Group) which handle over 90% of harvested grains and oilseeds in the country. The HDS CF/30 model is progressively being adopted by GrainCorp and Viterra in replacing ECO$_2$FUME® with VAPORPH$_3$OS® for SIROFLO® application mainly due to the

ability to simplify the cylinder handling issue. Figs. 3 – 4 show examples of current major applications of VAPORPH$_3$OS® with the HDS.

Fig. 3- The 300,000 ton capacity sealed horizontal shed at CBH Kwinana Grain Terminal Western Australia with insert HDS 800/VAPORPH$_3$OS fumigation setup.

Fig. 4- A 20,000-ton bunker with the HDS 800/VAPORPH$_3$OS fumigation setup at GrainCorp Nhill grain storage center in Victoria Australia.

In New Zealand, VAPORPH$_3$OS® is currently used with the HDS for fumigation of cereal grains in sealed silos, chicken sheds and fruits such as kiwi. The phosphine fumigation protocol for kiwi is 3,000 ppm for 36 hours at 1- 6°C against armored scales.

VAPORPH$_3$OS® application for apples is currently in the fine tuning stage required prior to commercial application.

Application in Asia

China was the first country to commercially apply VAPORPH$_3$OS® at Dalian Xizui Grain Terminal by on-site mixing with bulk CO_2 in 2000. The on-site mixing of VAPORPH$_3$OS® with bulk CO_2 produced the ECO$_2$FUME® blend which was introduced for fumigation with the SIROCIRC® fumigation system developed by GasApps Australia and constructed by Grain Tech System Pty Ltd. This grain terminal had a 1 million ton grain capacity divided into a block of 144 x 3000 ton sealed silos and another block of 20 x 30000 ton sealed silos both equipped with a SIROCIRC® fumigation system. The fumigation system was composed of 1) a 5-ton bulk liquid CO_2 tank and VAPORPH$_3$OS® cylinders storage, 2) on-site mixing system (ECO$_2$FUME® mixer), 3) ECO$_2$FUME® delivery pipe work, and 4) SIROCIRC® system. Some components of the fumigation system are shown in Fig. 5. During fumigation, a phosphine concentration of 100 ppm was maintained throughout the grain mass for a period of 18 days - enough to kill all stages of insects.

Fig. 5- The on-site mixing of VAPORPH$_3$OS® with bulk CO_2at Dalian Phase-2 silo block of 20 bins by 30,000 ton capacity each.

ECO2FUME® is used in the Philippines for structural fumigation of flour mills, feed mills and food processing plants such as dairy powder and cheese factories. The dose can vary from 100 – 500 ppm for 1 – 3 day at 30°C or higher. All the corrosion sensitive components such as PLCs and other electronic controls are well covered with totally impermeable film for easier setup and better protection against corrosion. Other applications are in tarpaulin and container fumigation of cereal grains (rice, corn, seeds)and other commodities (flour, sugar) requiring disinfestation. Efficacy trials are currently being conducted for applications to fruits such as export mango, banana, pineapple and avocados.

In Korea, ECO$_2$FUME® fumigation protocols were established for quarantine fumigation of export paprika, cherry tomato, strawberry and nursery trees. The effective doses vary from 700 – 1,400 ppm phosphine for 24 hours depending on the temperature of 2 – 15°C. For cut flowers, the effective dose is 1,400 ppm for 24 hours at 8°C.

In Indonesia, fumigation protocols were established for strong resistant strain of cigarette beetle that infest tobacco. The suggested fumigation protocols for achieving 100% efficacy for all stages of strong resistant cigarette beetle in Indonesia are 1,000 ppm for 5 days, 700 ppm for 8 days and 350 ppm for 12 days at average temperature of 28°C or higher.

In Thailand, the largest rice exporter in the world, the established fumigation protocols for complete treatment against major rice insect pests are 1,000 ppm for 36 hours, 700 ppm for 48 hours (2 days) and 350 ppm for 96 hours (4 days) at temperature range of 26 – 35°C. Fig. 6 shows a setup of tarpaulin fumigation of rice in jumbo bags with $ECO_2FUME^{®}$ in Thailand.

Fig. 6- Setup of tarpaulin fumigation of rice in jumbo bags in one of the rice mills in Thailand.

Applications in North America

Commercial applications of $ECO_2FUME^{®}$ in the USA began in the fourth quarter of 2000 after full registration both for food and non-food uses was granted in August 2000. $ECO_2FUME^{®}$ is applied into the sealed fumigation structure by direct injection using simple and quick dispensing equipment with variable fumigant flow rates.

Tobacco fumigation was among the first commercial applications of $ECO_2FUME^{®}$ in the USA. Tobacco bales stored inside large warehouses were fumigated by first sealing the warehouse and injecting $ECO_2FUME^{®}$ from a bank of cylinders in manifold located outside the warehouse. A phosphine concentration of 250 ppm was maintained for a period of 96 hours to achieve successful fumigation. Among the different commercial applications of $ECO_2FUME^{®}$ and $VAPORPH_3OS^{®}$ in the USA is either methyl bromide or solid phosphine formulation replacement as below. Fig. 7 shows some of the applications.

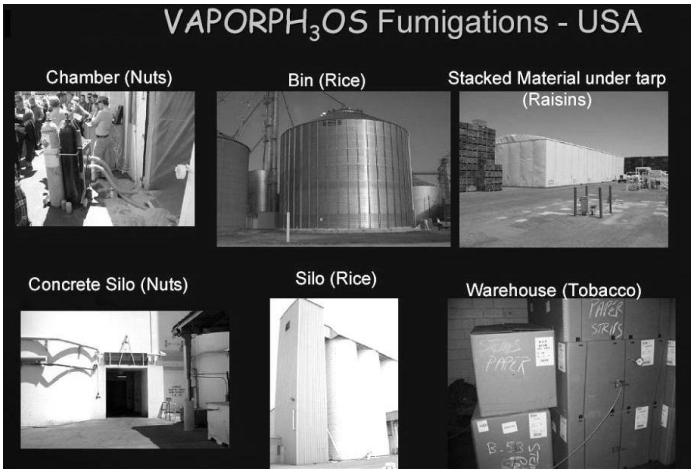

Fig. 7- Methyl bromide replacement applications with VAPORPH$_3$OS for fumigation in the USA.

1. In-transit fumigation of flour and rice in rail cars using ECO$_2$FUME®
2. Rice, wheat, corn and other grain fumigation in sealed vertical bins using ECO$_2$FUME® or VAPORPH$_3$OS®
3. Fumigation of almonds, walnuts, and pistachio nuts with VAPORPH$_3$OS® that were previously fumigated with methyl bromide in fumigation chambers/containers and with metal phosphide in metal storage bins
4. Bagged and bulk seed in cold storage warehouses with ECO$_2$FUME®
5. Fumigation of stacked raisins boxes under tarp and other dried fruits using ECO$_2$FUME® or VAPORPH$_3$OS®
6. Structural fumigation (e.g., flour mills and empty warehouses) using ECO$_2$FUME® in combination with heat and CO_2.
7. Bunker storage using VAPORPH$_3$OS®

The dosage recommendation for ECO$_2$FUME® and VAPORPH$_3$OS® in the USA varies in phosphine concentration of 200 – 1,000 ppm for 36 hours to 6 days at 0 to above 26°C depending on the commodity, target insects and sealing degree of the fumigation structure. There is also a protocol with a shorter exposure period of 24 hours at above 26°C using a phosphine concentration of 500 – 1,000 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 ECO$_2$FUME® is currently used in Canada for a similar range of applications but using the same dosage rate of 200 – 1,000 ppm phosphine concentration for an exposure period 2 – 14 days and temperature range of 0 – 16°C or above.

Applications in Latin America

Chile was the first country in the world which has commercially applied VAPORPH$_3$OS® (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

VAPORPH$_3$OS® and air and deliver the phosphine air mixture at lowto high flow rates into different sized sealed fumigation structures. Fosfoquim SA has also formed a fumigation company that provides fumigation services to fruit exporters. A fleet of fumigation vans and trained fumigators provide mobile fumigation service to all customers in Chile (Fig. 8).

Fig. 8- The HDS 800 in a fumigation van with a two-hose connection to a fruit fumigation chamber.

Fumigation services provided by Fosfoquim include fruit and vegetable fumigation accounts for a major portion of the total fumigation services.
There are many advantages of using VAPORPH$_3$OS® in combination with the HDS for fruit and vegetable fumigation as follows:

- Phosphine eliminates the target pests in fruits.
- No changes in taste, smell, texture, color or shelf life of the fruit, if fumigation has been conducted at low temperature.
- It is not necessary to heat fruits up before fumigation with subsequent shelf life extension.
- There are no need for deactivation and disposal of residues after fumigation.
- Cylinderized 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.
- This fumigation technique has no environmental problems, since phosphine is readily deactivated by sunlight upon release into the atmosphere.
- The fumigation is operator friendlier than methyl bromide in terms of minimizing exposure to workers due to better gas concentration monitoring and control.
- There is uniform gas distribution even in largest fruit fumigation cool houses which takes less than one hour and followed by one hour and a half of venting the gas by aeration.

- 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 due to safe recirculation of inlet mixture of air and gas.
- The HORN DILUPHOS SYSTEM allows flexibility and control in gas dispensing with no corrosion issue on cooling system.

In Trinidad and Tobago, $ECO_2FUME^{®}$ is used for cargo container fumigation, shiphold fumigation, warehouse fumigation, storage silo treatment, and fumigation of grains on pallets and in silos. $ECO_2FUME^{®}$ is dispensed using simple and quick dispensing equipment into a sealed structure.

Applications in Europe, the Middle East and Africa

In Turkey, $ECO_2FUME^{®}$ fumigation protocols for complete treatment of major insect pest of stored grains, dried legumes and tobacco were established as part of the registration label. The recommended dosages are 1,000 ppm phosphine for 3 days, 2 days and 1 day at temperatures of 17°C, 23°C and 28°C, respectively.

In Egypt, $ECO_2FUME^{®}$ recommended protocols for tarpaulin fumigation of stored grains are 600 ppm phosphine for 3days at 20°C or higher for non-porous ground surface and 700 ppm phosphine for 3 days at 20°C or higher for porous ground surface. Fig. 9 shows a setup of fumigating bagged wheat in tarp using $ECO_2FUME^{®}$.

Fig. 9- Setup of fumigation of bagged wheat in tarpaulin plastic sheet in Egypt.

In the Sultanate of Oman, dates had been successfully fumigated with ECO2FUME using a dosage of 1,000 ppm phosphine for 36 hours at 28°C or higher (Fig. 10).

Fig.10- Setup of container fumigation of dates with $ECO_2FUME^{®}$ in the Sultanate of Oman.

Summary

$ECO_2FUME^{®}$ and $VAPORPH_3OS^{®}$ are cylinderized phosphine fumigants that offer safer, greener and faster advantages for disinfestation of food commodities such as stored grains, oilseeds, nuts and beans, fruits and vegetables, animal feed and feed ingredients, and non-food commodities such as tobacco, cut flowers and nursery trees, tires and structural fumigation.