

## Pre-Mix and on-site mixing of fumigants

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### Abstract

Pre-Mix or On-Site mixing, a common practice with liquid insecticides, has benefits of increased synergy with fumigants. Both Pre-Mix and On-Site mixing have some issues with compatibility (e.g., active ingredient chemical stability; material compatibility; reaction with other ingredients). In addition to its fumigant properties, carbon dioxide (CO<sub>2</sub>), has a synergistic effect on other fumigants and reduces flammability. The general consensus on the amount of CO<sub>2</sub> to improve efficacy is in the range 5%-20%. The early recognition of the benefits of CO<sub>2</sub> to overcome the flammability of potential fumigants by Jones (1933), initiated safe and more effective fumigant mixtures: examples are ethylene oxide (12.2 vol%), ethyl formate (14.4 vol%) and propylene oxide (8.3 vol%).

The main advantage of gaseous phosphine (PH<sub>3</sub>) use is reduced generation time and uniform PH<sub>3</sub> distribution in hours not days. Other advantages of gaseous PH<sub>3</sub> include accurate metering of PH<sub>3</sub> fumigation levels and reduction of Occupational Health and Safety exposure to PH<sub>3</sub>. Gaseous PH<sub>3</sub> in a Pre-Mix with liquid CO<sub>2</sub> or mixed On-Site with gaseous CO<sub>2</sub> or N<sub>2</sub>+Air to reduce the PH<sub>3</sub> level below Lower Explosive Level of 16,000 ppm. A critical impurity of CO<sub>2</sub> when mixing with PH<sub>3</sub> is oxygen which must be less than 0.01% to avoid the formation of the polymer, (P<sub>2</sub>H<sub>4</sub>CO<sub>2</sub>)<sub>n</sub>. Large quantities of PH<sub>3</sub> are used to treat grain storage up to 280,000 tonne [CBH, WA] and multiple 30,000 tonne silos at Dalian, China (1.4 Mt facility). Reports indicate synergy with a mixture of propylene oxide (C<sub>3</sub>H<sub>6</sub>O), sulfuryl fluoride (SO<sub>2</sub>F<sub>2</sub>) and CO<sub>2</sub>. This mixture is an attractive candidate for a Pre-Mix or On-Site mixing of a non-flammable synergized mixture with reported 100% efficacy for all insect life stages.

Keywords: Fumigant mixtures, Synergised, Non-flammable, On-site mixing.

### 1. Introduction

Generally fumigants are simple gases/gas mixtures without the complications of reactive adjuncts (e.g., surfactants) used to formulate emulsified concentrate liquid insecticides formulations.

Pre-Mix fumigants have benefits of ease of use but may have shelf-life stability issues. On-Site mixing of individual gases has benefits of flexibility and avoids any long-term storage compatibility issues.

Gaseous PH<sub>3</sub> was made commercially available with the patented non-flammable PH<sub>3</sub>+CO<sub>2</sub> mixture (Ryan and Latif, 1989). This progressed to the PH<sub>3</sub>+Air On-Site Mixing patent (Ryan and Shore, 2005). A critical issue with fumigant gas metering and dispensing is flammability. Flammability is solved by mixing volatile fumigants with inert gases or rapid dilution in turbulent air flow.

The fumigant gas, phosphine (PH<sub>3</sub>), is used as a solid (e.g., aluminium phosphide: AIP), pure PH<sub>3</sub> and non-flammable mixtures of PH<sub>3</sub> in CO<sub>2</sub> or N<sub>2</sub>. The AIP tablets are formulated to react slowly with atmospheric moisture which allows time for the very flammable PH<sub>3</sub> to diffuse away from the tablet, the gas mixture in air is diluted to levels below the flammability limit. There is no issue with the non-flammable 2.6 vol% PH<sub>3</sub> in CO<sub>2</sub> or 2.0 vol% PH<sub>3</sub> in N<sub>2</sub>. The 100% PH<sub>3</sub> can be mixed onsite with an inert gas (e.g., CO<sub>2</sub> or N<sub>2</sub>) or rapidly mixed into a turbulent air stream (best done externally to the fumigation space as a safety measure). The PH<sub>3</sub>/air mix is non-flammable when PH<sub>3</sub> is less than 16000 ppm (about 22.2 g PH<sub>3</sub>/m<sup>3</sup> in air). The early recognition of the benefits of CO<sub>2</sub> to overcome the flammability of potential fumigants by Jones (1933), initiated safe and more effective fumigant mixtures – e.g., ethylene oxide (12.2 vol%), ethyl formate (14.4 vol%) and propylene oxide (8.3 vol%).

The inert gas of choice CO<sub>2</sub>, has benefits of requiring three times (3x) less gas cylinders compared to N<sub>2</sub> and is a synergist which improves the efficacy of fumigants. The general consensus on the amount of CO<sub>2</sub> to improve efficacy is in the range 5% - 20%.

One specific issue with gas metering and dispensing of phosphine is polymer formation. Dispensing of gaseous phosphine requires accurate metering using flow meters and gas mixing equipment. The formation of polymers within metering equipment can cause blockages resulting in malfunction. The implication of this is to ensure oxygen is at low levels in PH<sub>3</sub> Pre-Mix and PH<sub>3</sub> On-Site mixtures. It is critical to eliminate air from dispensing equipment by conducting pre- and post-purging of dispensing equipment.

The ultra fine particle polymer which causes blockages and malfunction of dispensing equipment is also very combustible (easily ignited by a trace amount of white phosphorus, P<sub>4</sub>, impurity). There is variation in the structure and the colour of the polymers formed and is related to the PH<sub>3</sub> mixture (canary yellow polymer is associated with 100% PH<sub>3</sub> while an orange-brown polymer is found in PH<sub>3</sub>/CO<sub>2</sub> mixtures). The structure of the polymer in a PH<sub>3</sub>/CO<sub>2</sub> mixture was identified as (P<sub>2</sub>H<sub>4</sub>CO<sub>2</sub>)<sub>n</sub> by Gallagher et al. (1996).

The solvent-propellant property of liquid CO<sub>2</sub> was the basis of a patent by Ryan et al. (1978) where active constituents are dissolved in liquid CO<sub>2</sub> at high pressure (50 bar) and contained in an industrial high pressure gas cylinder fitted with a “dip” tube to enable withdrawal of the liquid mixture. Existing Pre-Mix high pressure liquid CO<sub>2</sub> pesticide formulations in industrial gas cylinders are limited in choice and flexibility.

On-Site mixing using low pressure gaseous CO<sub>2</sub> has potential for a wide range of volatile pesticides. On-Site mixing has more flexibility and lower cost in dispensing mixtures of volatile and fumigant chemicals. GasApps Australia P/L (Kings Park, NSW, Australia) has been using On-Site mixing of PH<sub>3</sub> and CO<sub>2</sub> for over 10 years with SIROFLO, the flow-through fumigation technique for bulk grain which has typical exposure time of 18 days (CSIRO developed SIROFLO which revolutionised fumigation of grain stored in “leaky” storages). Each year Australia uses more than 10 t of gaseous PH<sub>3</sub> in SIROFLO fumigation of “leaky” grain storages. This gaseous PH<sub>3</sub> application is shared between the PreMix (PH<sub>3</sub>/CO<sub>2</sub>) and 100% PH<sub>3</sub> industrial gas cylinder products. The flammability of the 100% PH<sub>3</sub> is overcome by On-Site mixing with CO<sub>2</sub>.

The objective of this review is to report on the On-Site mixing of PH<sub>3</sub> with CO<sub>2</sub> and eventual dilution with air to the fumigation level.

## 2. Materials and methods

The Australian grain industry depends mostly on the fumigant phosphine for insect disinfestations. Historically, the pendulum has swung from the magic days of “malathion and tin sheds” (i.e., residual grain protectants) to non-residual phosphine fumigation. There is movement now from metallic phosphide tablets (AIP) to gaseous phosphine which is marketed as 100% PH<sub>3</sub>; 2.6 vol% PH<sub>3</sub>/CO<sub>2</sub> and 2.0% PH<sub>3</sub>/N<sub>2</sub>. Gaseous phosphine formulations require to be diluted in air which at a minimum requires pre- and post-purging of dispensing equipment. The 100% PH<sub>3</sub> is On-Site mixed with an inert gas (e.g. CO<sub>2</sub> or N<sub>2</sub>) or rapidly mixed into a turbulent air stream (again, pre- and post-purging is critical to avoid flammability issues, prevent polymer formation and for OH&S reasons).

SIROFLO flow-through fumigation installation has a circulation fan which delivers controlled low pressure (500 Pa) air flow through a network of PVC pipes usually connecting multiple grain storages. The fan maintains a constant flow through any grain storage under treatment. The flow through any individual storage is controlled by individually designed metering orifices. The PH<sub>3</sub> is metered into the air stream and quickly mixes prior to entry into the selected grain storage. Exposure time is 18 d and fumigation is often carried out at unmanned rural sites. The PreMix (PH<sub>3</sub>/CO<sub>2</sub>) high pressure industrial gas cylinder mixture using a regulator and flow controller is suited to the long-term metering of PH<sub>3</sub> into the continuous flow-through air stream. The flow rate is one volume change per day for the selected “leaky” grain storage to maintain an efficacious PH<sub>3</sub> level. The low concentration (~120 ppm PH<sub>3</sub>) is compensated by an exposure time of 18 d.

An alternative to the PreMix is On-Site mixing of PH<sub>3</sub> which requires a higher level of equipment reliability because of the dual role of continuous mixing plus metering the exact PH<sub>3</sub> level required for a successful fumigation. These fumigations are often carried out at unmanned isolated rural locations.

### 3. Results

The On-Site mixing technique developed by GasApps Australia P/L uses a dual chamber pressure equaliser where both PH<sub>3</sub> and CO<sub>2</sub> are maintained at equal pressure in chambers separated by a regulator diaphragm. Pressure in the dual chambers is equalised by the regulator diaphragm moving on a pivot, which controls gas flow into both chambers. The chamber pressure equalises to the lowest inlet gas pressure. The outlet flow of each gas is controlled by separate metering orifices fitted into the exit of each chamber. The area of the CO<sub>2</sub> orifice required for a mixture of 2.8% PH<sub>3</sub> in CO<sub>2</sub> is thirty-eight times the area of the PH<sub>3</sub> orifice i.e., a 1-mm-diameter PH<sub>3</sub> orifice needs a matching 6-mm-diameter orifice for CO<sub>2</sub>. In this way any mixture containing 2.8% PH<sub>3</sub> in CO<sub>2</sub> or less is non-flammable when mixed in any quantity with air. The selected PH<sub>3</sub> in CO<sub>2</sub> mixture is further diluted into a low pressure airflow which can be connected to multiple grain storages. The pressure equaliser mixer, which operates continuously for 18-d exposure time unattended, has performed reliably.

Trials have established that the initiation of polymer formation can be avoided if oxygen levels in the dispensing equipment are less than 100 ppm (all CO<sub>2</sub> cylinders used must be certified less than 0.01% O<sub>2</sub>).

The On-Site mixing technique developed by GasApps Australia P/L has been used to treat millions of tonnes of grain. Current annual usage of this technique by GasApps P/L is ~3 t PH<sub>3</sub> which is equivalent to the treatment of 3 million of grain at a concentration of 1 g PH<sub>3</sub>/t (720 ppm PH<sub>3</sub>).

The On-Site mixed PH<sub>3</sub> and CO<sub>2</sub> is diluted to ~120 ppm PH<sub>3</sub> into the flow-through air with a flow of approximately one volume change per day in the grain storage being treated. The treatment volume is calculated from the volume of the storage independent of amount of grain stored. This treatment continues for an exposure time of 18 days.

### 4. Discussion

The innovative, dual chamber pressure equaliser, gas mixer adopted for On-Site mixing of PH<sub>3</sub> and CO<sub>2</sub> is a proven reliable device. The PH<sub>3</sub> and CO<sub>2</sub> are maintained at equal pressure and the mixing ratio can be selected by the choice of the fixed orifice fitted in the outlets of the dual chambers. The dual chamber pressure equaliser has performed exceptionally well with continuous duty cycles. The dual chamber pressure equaliser was initially preferred because of its ability to deliver a wide choice of mixed gases and long-term continuous use reliability. An earlier innovation tested was a dual piston pumps mixer with piston volumes in a ratio of 40:1 (2.5 vol% PH<sub>3</sub>/CO<sub>2</sub>).

The On-Site mixing of PH<sub>3</sub> and CO<sub>2</sub> for the treatment of grain in “non gastight” storages using the flow-through fumigation technique requires continual dosing of PH<sub>3</sub> over a ~3 wk period at isolated and often unmanned grain terminal facilities is an established and growing application technique. The SIROFLO flow-through technique ensures that an effective concentration of PH<sub>3</sub> is maintained in the storage irrespective of losses due to winds or any leakage. The On-Site mixing of PH<sub>3</sub> and CO<sub>2</sub> at the Xizui Grain Terminal, Dalian, China (Newman et al., 2000), was an earlier milestone. This green field site has multiple 30,000 tonne vertical grain storages which are gastight and the initial site storage capacity was 1.4 million tonne. The mixing was carried out using gaseous PH<sub>3</sub> in cylinders and a bulk refrigerated liquid CO<sub>2</sub> tank.

The ongoing application of PH<sub>3</sub> is growing in volume as the required effective concentration continues to be raised to overcome insect tolerance. The trend to 100% gaseous PH<sub>3</sub> has the benefit of reducing the number of cylinders of PH<sub>3</sub> required on site by a factor of thirty-five times (35x). While there are additional benefits of CO<sub>2</sub>, there is a trend to minimise the transport of heavy industrial gas cylinders. The On-Site mixing of PH<sub>3</sub> and Air is attractive and it is a growth application. There is potential for the use of On-Site Inert Gas Generators including the old-style burner type (bonus of elevated CO<sub>2</sub> however, it has associated high moisture levels) and the more sophisticated PSA or membrane N<sub>2</sub> generators.

The recycling of forgotten volatile flammable liquid as potential new fumigants continues and most are candidates for On-Site mixing with inert gases. The recent paper by Muhareb et al. (2009) reported

synergy with a mixture of propylene oxide (C<sub>3</sub>H<sub>6</sub>O), sulfuryl fluoride (SO<sub>2</sub>F<sub>2</sub>) and CO<sub>2</sub>. This combination is a candidate for a Pre-Mix and On-site Mixing to deliver a non-flammable synergized mixture with reported 100% efficacy for all insect life stages.

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