Pre-Mix and on-site mixing of fumigants

Ryan, R.F.*#[1], Shore, W.P.[2]
[1] VAPORFAZE, , PO Box 4, Sans Souci NSW 2219, Australia. Email: robert.ryan.consultant@gmail.com
[2] GasApps Australia Pty Ltd; 6/20 Valediction Rd, Kings Park NSW 2148, Australia

* Corresponding author
\# Presenting author

DOI: 10.5073/jka.2010.425.113

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_2), has a synergistic effect on other fumigants and reduces flammability. The general consensus on the amount of CO_2 to improve efficacy is in the range 5%-20%. The early recognition of the benefits of CO_2 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_3) use is reduced generation time and uniform PH_3 distribution in hours not days. Other advantages of gaseous PH_3 include accurate metering of PH_3 fumigation levels and reduction of Occupational Health and Safety exposure to PH_3. Gaseous PH_3 in a Pre-Mix with liquid CO_2 or mixed On-Site with gaseous CO_2 or N_2+Air to reduce the PH_3 level below Lower Explosive Level of 16,000 ppm. A critical impurity of CO_2 when mixing with PH_3 is oxygen which must be less than 0.01% to avoid the formation of the polymer, $(P_2H_4CO_2)_n$. Large quantities of PH_3 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_3H_6O), sulfuryl fluoride (SO_2F_2) and CO_2. 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_3 was made commercially available with the patented non-flammable PH_3+CO_2 mixture (Ryan and Latif, 1989). This progressed to the PH_3+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_3), is used as a solid (e.g., aluminium phosphide: AlP), pure PH_3 and non-flammable mixtures of PH_3 in CO_2 or N_2. The AlP tablets are formulated to react slowly with atmospheric moisture which allows time for the very flammable PH_3 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_3 in CO_2 or 2.0 vol% PH_3 in N_2. The 100% PH_3 can be mixed onsite with an inert gas (e.g., CO_2 or N_2) or rapidly mixed into a turbulent air stream (best done externally to the fumigation space as a safety measure). The PH_3/air mix is non-flammable when PH_3 is less than 16000 ppm (about 22.2 g PH_3/m^3 in air). The early recognition of the benefits of CO_2 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_2, has benefits of requiring three times (3x) less gas cylinders compared to N_2 and is a synergist which improves the efficacy of fumigants. The general consensus on the amount of CO_2 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_3 Pre-Mix and PH_3 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_4, impurity). There is variation in the structure and the colour of the polymers formed and is related to the PH_3 mixture (canary yellow polymer is associated with 100% PH_3 while an orange-brown polymer is found in PH_3/CO_2 mixtures). The structure of the polymer in a PH_3/CO_2 mixture was identified as $(P_2H_4CO_2)_n$ by Gallagher et al. (1996).

The solvent-propellant property of liquid CO_2 was the basis of a patent by Ryan et al. (1978) where active constituents are dissolved in liquid CO_2 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_2 pesticide formulations in industrial gas cylinders are limited in choice and flexibility.

On-Site mixing using low pressure gaseous CO_2 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_3 and CO_2 for over 10 years with SIROFLO, the flow-though 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_3 in SIROFLO fumigation of "leaky" grain storages. This gaseous PH_3 application is shared between the PreMix (PH_3/CO_2) and 100% PH_3 industrial gas cylinder products. The flammability of the 100% PH_3 is overcome by On-Site mixing with CO_2.

The objective of this review is to report on the On-Site mixing of PH_3 with CO_2 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 (AlP) to gaseous phosphine which is marketed as 100% PH_3; 2.6 vol% PH_3/CO_2 and 2.0% PH_3/N_2. Gaseous phosphine formulations require to be diluted in air which at a minimum requires pre- and post-purging of dispensing equipment. The 100% PH_3 is On-Site mixed with an inert gas (e.g. CO_2 or N_2) 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_3 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_3/CO_2) high pressure industrial gas cylinder mixture using a regulator and flow controller is suited to the long-term metering of PH_3 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_3 level. The low concentration (~120 ppm PH_3) is compensated by an exposure time of 18 d.

An alternative to the PreMix is On-Site mixing of PH_3 which requires a higher level of equipment reliability because of the dual role of continuous mixing plus metering the exact PH_3 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_3 and CO_2 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_2 orifice required for a mixture of 2.8% PH_3 in CO_2 is thirty-eight times the area of the PH_3 orifice i.e., a 1-mm-diameter PH_3 orifice needs a matching 6-mm-diameter orifice for CO_2.In this way any mixture containing 2.8% PH_3 in CO_2 or less is non-flammable when mixed in any quantity with air. The selected PH_3 in CO_2 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_2 cylinders used must be certified less than 0.01% O_2).

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_3 which is equivalent to the treatment of 3 million of grain at a concentration of 1 g PH_3/t (720 ppm PH_3).

The On-Site mixed PH_3 and CO_2 is diluted to ~120 ppm PH_3 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_3 and CO_2 is a proven reliable device. The PH_3 and CO_2 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_3/CO_2).

The On-Site mixing of PH_3 and CO_2 for the treatment of grain in "non gastight" storages using the flow-through fumigation technique requires continual dosing of PH_3 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_3 is maintained in the storage irrespective of losses due to winds or any leakage. The On-Site mixing of PH_3 and CO_2 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_3 in cylinders and a bulk refrigerated liquid CO_2 tank.

The ongoing application of PH_3 is growing in volume as the required effective concentration continues to be raised to overcome insect tolerance. The trend to 100% gaseous PH_3 has the benefit of reducing the number of cylinders of PH_3 required on site by a factor of thirty-five times (35x). While there are additional benefits of CO_2, there is a trend to minimise the transport of heavy industrial gas cylinders. The On-Site mixing of PH_3 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_2, however, it has associated high moisture levels) and the more sophisticated PSA or membrane N_2 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_3H_6O), sulfuryl fluoride (SO_2F_2) and CO_2. 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.

Acknowledgements

Special thanks to Reji Peruvelil of GasApps Australia P/L for on-going support for equipment modifications.

References

Gallagher, M., Diep, B., Reibelt, G., Ryan, R., Hook, J., Kim, J.H., 1996. The Use of Phosphine as an Agricultural Fumigant, Phosphorus, Sulfur and Silicon, and the Related Elements 111, p89.

Jones, R. M., 1933. Reducing inflammability of fumigants with carbon dioxide. Industrial and Engineering Chemistry 25, 394-396.

Muhareb, J., Hartsell, P., Pena, B., Hurley, J.M., 2009. Evaluation of combining sulfuryl fluoride, propylene oxide & CO_2 for stored product insect control 16th Annual International Research Conference on Methyl Bromide Alternatives and Emissions Reduction, 10-13 November 2009, San Diego, CA, USA, pp. 64-1 – 64-2

Newman, C., Russell, G., Shore, W., Gock, D., Ryan, R.F., 2000. Australian SIROCIRC Recirculatory Phosphine Fumigation Systems at Xizui Grain Terminal and Inland Depots in China. In: Donahaye, E.J., Navarro, S., Leesch, J.G., (Eds), Proceeding of the International Conference on Controlled Atmospheres Fumigation in stored Products, 29 October -3 November 2000, Fresno, CA, USA, pp. 297-306.

Ryan, R.F., Catchpoole, D., Shervington, E., 1978. Pesticide Distribution System, Australian Patent 494,198: 26 June 1978.

Ryan, R.F., Latif S.E., 1989. Fumigant System, U.S. Patent No. 4,889,708.

Ryan, R.F., Shore, W.P., 2005. Process and Apparatus for Supplying a Gaseous Mixture, U.S. Patent 6,840,256 B1.