

## On-site mixing of phosphine – continuous improvements

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### Abstract

Initial investigation of “liquid” phosphine (PH<sub>3</sub>) was control of fruit flies (1976). “Liquid” PH<sub>3</sub> is a high pressure (40 bar) compressed liquefied gas in industrial gas cylinders. Growth in “liquid” PH<sub>3</sub> use over the last two decades has been exponential. “Liquid” PH<sub>3</sub> was initiated by the CIG patented PHOSFUME, a non-flammable mixture of PH<sub>3</sub> in carbon dioxide (CO<sub>2</sub>). The PH<sub>3</sub>/CO<sub>2</sub> support (1986) for the CSIRO patented flow-through fumigation process used in non-gastight grain storages (SIROFLO) initiated a “liquid” PH<sub>3</sub> “boom”. The enthusiasm of bulk grain companies enabled the adoption of SIROFLO (Eastern Australia) and proved the on-site mixing of PH<sub>3</sub>/Air (2000).

Over the last 15 years developments included the market entry of CYTEC who purchased the PH<sub>3</sub> business from BOC (1999); GasApps’ PH<sub>3</sub> dispensing equipment & On-Site mixing of PH<sub>3</sub> (1999); S&A Services, FRISIN PH<sub>3</sub>/N<sub>2</sub> mix (1998); Horn PH<sub>3</sub>/Air dispensing equipment (2001); Specialty Gases P/L., UltraPhos 99% PH<sub>3</sub> (2014) plus global adoption of the “cylinderized” “liquid” PH<sub>3</sub>. “Liquid” PH<sub>3</sub> has resulted in a reduction in use of the traditional “solid” metallic phosphide. The usage trend is “solid” to PH<sub>3</sub>/CO<sub>2</sub> mix to onsite mixing of “liquid” 99% PH<sub>3</sub>.

For over a decade GasApps, an innovator of on-site mixing of PH<sub>3</sub>, has had PH<sub>3</sub> mixers operating successfully at unmanned sites in the demanding agricultural environment. A robust and reliable design is required to counteract rural “road” transport, 24/7 & 21 day exposure times at multiple unmanned sites plus exposure to extreme temperatures. The Version#1 mixer has treated in excess of 10 million tonnes of grain. The UltraPhos Air Mixing System with a more sophisticated design incorporates the proven rugged design of the Version#1 mixer. The UltraPhos Air Mixing System includes multiple fail safe devices and has been subject of independent HAZOP/CHAZOP reviews and external approvals.

Keywords: PH<sub>3</sub> fumigation, on-site mixing PH<sub>3</sub>/CO<sub>2</sub> and PH<sub>3</sub>/Air, cereal grain fumigation, non gastight storage, flow-through fumigation, metallic phosphides, gas dispensing equipment

### 1. Introduction

*“Prior to 1963 insects were accepted components of stored grain”:*

The Australian Government promulgated the Export (Grain) Regulations in 1963 which prohibited the export of grain from Australia unless it was found to be free from insect pests. Initially the insect-free standard was achieved by the use of liquid insecticide “grain protectants” sprays and this was the treatment for most grain stored in Australia. The grain was sprayed using

a number of insecticides including malathion, these residual “grain protectants” achieved insect-free status but created the issue of pesticide residues, in time pesticide residues contamination was raised as a negative marketing issue.

The dual goals of pest-free and residue-free grain was eventually achieved using gas fumigation however to eliminate insect infestations sealed storage was required. The solution adopted to treat the large number of non-gastight storage was SIROFLO<sup>®</sup>, the flow through fumigation system developed by CSIRO’s Stored Grain Research Laboratory (Winks, 1986).

*Phosphine (PH<sub>3</sub>) – the fumigant of choice:*

The need to control insects in grain and foodstuffs to prevent food losses and to satisfy marketing requirements resulted in the preference for fumigant gases. The traditional preferred fumigants were methyl bromide (MB) and phosphine (PH<sub>3</sub>) with the latter the fumigant of choice because of cost considerations, superior efficacy and environmental acceptance (MB listing on the Montreal Protocol as an ozone depletor underscored its eventual demise). PH<sub>3</sub> is a naturally occurring gas, albeit short lived because it reacts with atmospheric air forming phosphoric acid - an acid used extensively as a food additive. The PH<sub>3</sub> releasing metallic phosphide (“solid phosphine”) formulations have been commercially available for almost eighty years and have made significant contributions to grain protection. The original “solid” PH<sub>3</sub> fumigation patent was lodged in Germany on Nov 6, 1934 and in the USA on May 10, 1938 (US patent 2,117,158: “Method of exterminating Corn Beetles and other Vermin”). The PH<sub>3</sub> gas is generated from metallic phosphide formulations on their exposure to moisture in atmospheric air. These formulations minimised the flammability hazard by slowly releasing the flammable PH<sub>3</sub> over days to allow dilution with the surrounding air to avoid ignition and fires. While a very low cost PH<sub>3</sub> source there are other issues with the “solid” PH<sub>3</sub> formulations (e.g. unreacted powder residues; disposal costs and long exposure times). Over time the phosphine dose has been dramatically reduced from the 10,000 ppm in early recommendations to the current recommendation as low as 100 ppm. With residue levels of 0.001 ppm PH<sub>3</sub> (Scudamore and Goodship, 1986) was the preferred fumigant to attain insect-free and residue-free foodstuffs; however PH<sub>3</sub> is an extremely flammable gas with a lower explosion limit in air of 1.6%. Discounting its flammability hazard, PH<sub>3</sub> is a very effective fumigant being some fifty times more toxic to insects than MB. After a lapsed Fruit Fly project in 1976 involving Gosford Postharvest Horticultural Laboratory, CIG Ltd (now BOC/The LINDE Group) patented PHOSFUME<sup>®</sup> [now ECO<sub>2</sub>FUME<sup>®</sup>] a non-flammable gaseous mixture of 2 wt% PH<sub>3</sub> in liquid CO<sub>2</sub> (Ryan and Latif, 1989). In August 1999, the “liquid” PH<sub>3</sub> products ECO<sub>2</sub>FUME (2% PH<sub>3</sub>/CO<sub>2</sub>) and VAPORPH<sub>3</sub>OS (99% PH<sub>3</sub>) were sold to CYTEC and the associated dispensing equipment to support this business was carried on by GasApps Australia Pty Ltd (formerly BOC Gases R&D Workshop). Although more expensive, the non-flammable compressed “liquid” PH<sub>3</sub> has many benefits over the traditional metallic phosphide formulations:

- Mixing with CO<sub>2</sub> / Air eliminates PH<sub>3</sub> flammability hazard
- “Liquid” PH<sub>3</sub> allows accurate control to maintain the required PH<sub>3</sub> concentration
- Quick gas release reduces the long exposure times of the “solid” PH<sub>3</sub> formulations.

- “Liquid” PH<sub>3</sub> allows quick distribution in the grain mass without disturbing the grain;
- Regulated PH<sub>3</sub> allows controlled flow for long periods e.g. 24/7; 25days exposure
- Piped gas system contains the PH<sub>3</sub> and minimises OH&S concerns.
- “Liquid” PH<sub>3</sub> eliminate handling and disposal of the "spent" metallic phosphide tablets
- Cylinder gas avoids fires associated with the tablets;
- Dispensing of the gas can be automated - “solid” PH<sub>3</sub> distribution is very labour intensive.

*Fumigation of non gas-tight storages:*

Fumigations to be effective should be carried out in gastight storages which are validated using a decaying pressure test ( $P_{0.5} > 5$  minutes; SCA Technical Report, 1980). Many Australian grain storages fail this test however they can be fumigated using the SIROFLO flow through fumigation technique. The flow-through fumigation technique maintains a small positive pressure throughout the grain mass to ensure a uniform low concentration of PH<sub>3</sub> and can control phosphine-resistant insect's strains in non-gastight storage (Winks and Ryan, 1990). The low PH<sub>3</sub> concentration (~100 ppm) is maintained for a period (up to 25 days) sufficient to kill all stages of insects in non gastight storages that can be effectively "sealed" in critical areas. The small positive pressure is calculated to overcome the forces that would otherwise lead to air ingress with consequent loss of gas and failure of the fumigation. This flow through fumigation technique provides a method for fumigating grain in leaky storage and has made many old silos useful storage facilities again. Advantages of “liquid” PH<sub>3</sub> flow through fumigation include:

- enables the fumigation of “leaky” (non gastight) storages;
- achieves pesticide residue-free and insect-free status for grain in non gastight storage;
- improves efficacy using low concentrations for long exposure periods;
- greater control over fumigant dosage (CxT)- both concentration (C) and time (T);
- improves workers safety, low emissions to the environment and low cost of treatment.

*Global Technology Transfer:*

*China:*

A fumigation demonstration installation at the Beijing Grain Centre (Nov 1997) led to the largest onsite mixing of PH<sub>3</sub> and CO<sub>2</sub> to date installed by Grain Tech Systems at the Xizui Grain Import and Export Terminal, Dalian, China [150 x 3000 tonne + 20 x 30,000 tonne = 1.05 million tonne storage]. The Xizui onsite mixing of PH<sub>3</sub> and CO<sub>2</sub> is carried out using a unique and very simple mixing system developed by GasApps Pty Ltd, Australia which incorporates no moving parts. Liquid CO<sub>2</sub> was delivered by bulk road-tanker and stored at low temperature in a 5 tonne cryogenic tank. The PH<sub>3</sub> was dispensed from industrial gas cylinders (holding up to 22 kg of the liquefied PH<sub>3</sub> gas). A small PLC (programmable logic controller) controls the opening and closing of solenoid valves for the release of the two gases for passage through the mixer, making the mixing process a safe and automated operation. The main advantage of on-site mixing is that

it saves cost by avoiding the transport, storage and handling of hundreds of cylinders of pre-mixed gas. One 22 kg cylinder of PH<sub>3</sub> contains the same quantity of PH<sub>3</sub> as 35 x 31 kg cylinders of the PH<sub>3</sub>/CO<sub>2</sub> premix.

#### *Cyprus:*

Following the installation of PH<sub>3</sub>/CO<sub>2</sub> demonstration unit at Larnaca, the Cyprus Grain Commission installed flow through fumigation SIROFLO technology in all steel vertical grain silos. In addition demonstration PH<sub>3</sub>/CO<sub>2</sub> trials were carried out New Zealand, Bahrain, Qatar, Vietnam, Thailand and Indonesia.

## **2. Materials and Methods**

### *2.1. Dispensing equipment*

The onsite mixing of PH<sub>3</sub> and CO<sub>2</sub> eliminates flammability issues and is used to fumigate some 2 million tonne/year of grain in Australia. The on-site mixing technology can treat grain storages that are not gastight using PH<sub>3</sub> flow-through technique. The treatment of unsealed grain storage fitted with a flow through fumigation system requires GasApps to supply/connect gas dispensing/mixing equipment to the installed air blower and fumigant gas distribution pipe work. This pipe work directs the dispensed PH<sub>3</sub>/CO<sub>2</sub>/Air mixture at a calibrated low pressure to the individual grain storage. Orifice plates installed in the pipe work meter the diluted PH<sub>3</sub>/CO<sub>2</sub> in air mixture to ensure the individual storage or sections of the same storage receives the target PH<sub>3</sub> concentration. The flow through fumigation system is designed to ensure the treated storage has approximately one air volume change each day to ensure the PH<sub>3</sub> concentration is maintained for the duration of the fumigation exposure period (up to 25 days).

GasApps supply the required quantity of PH<sub>3</sub> and CO<sub>2</sub> in high pressure industrial gas cylinders. These gases are connected to the dispensing/mixing equipment and adjustments made to deliver the gas flows required to achieve the specified PH<sub>3</sub> concentration 24/7 for exposure periods up to 25 days. Once everything is connected the system is activated and the blower provides the Air carrier flow to dilute and dispense the PH<sub>3</sub> and CO<sub>2</sub> mixture through the storage.

The external control of dispensing the gaseous PH<sub>3</sub> outside the grain storage eliminates the need for fumigation space entry. The precise control and instant dispensing of gaseous PH<sub>3</sub> from a high pressure industrial gas cylinder are reasons for the continued acceptance of “liquid” PH<sub>3</sub>. Proprietary dispensing equipment has been developed that is capable of 24/7 dispensing a PH<sub>3</sub>/CO<sub>2</sub> mixture unattended over 4 week’s exposure period.

#### *2.1.1. Pre-Mix PH<sub>3</sub>/CO<sub>2</sub> dispensing equipment:*

Specialised PH<sub>3</sub>/CO<sub>2</sub> dispensing equipment was developed to satisfy the requirements of PH<sub>3</sub> flow through technology. Innovations include: regulation of the high pressure (50 bar) “liquid” PH<sub>3</sub>/CO<sub>2</sub> mixture and dispensing vaporised gas mixture (100 L/min / 12 kg/h) for periods up to a month; low volume manifold using dual 3 mm SS tubing ensures efficient purging to eliminate polymer formation and avoid PH<sub>3</sub> diffusion through traditional SS Teflon-lined flexible hoses; Auto/Manual motorised Flow Control Metering Valves; higher capacity PH<sub>3</sub>/CO<sub>2</sub> vaporiser for

global customers. Customised PH<sub>3</sub>/CO<sub>2</sub> dispensers have been the outcome of joint development between GasApps Australia and Bulk Handling Companies.

### 2.1.2. On-Site Mixing PH<sub>3</sub>/CO<sub>2</sub> dispensing equipment:

The development of onsite of PH<sub>3</sub> and CO<sub>2</sub> was made possible by the innovation of novel mixing equipment. The initial trials used a purpose built piston mixer which incorporated a pressure equaliser to ensure each piston received the exact amount of gas. The pressure equaliser was itself further developed into a simple low cost mixer, and further developed into the high-pressure construction used in the 1.1 million tonne grain storage facility at Dalian, China. The development of specialised equipment for the dispensing of gaseous PH<sub>3</sub> continued to evolve. The range was extended from the non-flammable PH<sub>3</sub>/CO<sub>2</sub> mixture to the on-site mixing of the flammable 99% PH<sub>3</sub> with CO<sub>2</sub> to produce a non-flammable mixture [2.6 vol% PH<sub>3</sub>/CO<sub>2</sub>].

### 2.1.3. On-Site Mixing PH<sub>3</sub>/Air dispensing equipment:

Early development of mixing PH<sub>3</sub> with Air for “one-shot” dump of non-flammable PH<sub>3</sub>/Air (<10,000ppm PH<sub>3</sub>) mixture was proven with prototypes tested by CBH WA (2000). This was not commercialized as at that time the “solid” AIP was the preferred PH<sub>3</sub> source. Currently large quantities of “liquid” 99% PH<sub>3</sub> is mixed on-site by dilution with Air to dispense a non-flammable PH<sub>3</sub>/Air mixture. However the development of safe, rugged, reliable on-site PH<sub>3</sub>/Air dispensing equipment to operate unmanned in remote rural sites 24/7 for over 4 weeks is still ‘work in progress’. The current ongoing requirement of delivering insect and pesticide free grain for export continues to be achieved using PH<sub>3</sub> fumigation even in non gastight grain storage. The insect free status is independently verified. Government regulations mandate that export grain from Australia is “insect-free” and this is enforced by thorough inspection at grain export terminals. Grain in non gastight storages is fumigated using the flow through fumigation technique. The types of storage vary with a mixture of vertical and horizontal storage. The cost of treatment varies with the storage type, as vertical storage is much cheaper to fumigate than horizontal storage – a greater height of grain is treated with the same gas flow in a vertical storage. Costs also vary with exposure time as longer exposure time allows lower PH<sub>3</sub> concentration (CxT product). The other significant variable is labour and consumable costs. The fumigation cost of flow through fumigation are also more expensive than “one-shot” fumigation however the horrendous cost of modification or replacement of existing non gastight storage is not a financial option in the short term. Taking into account all the expenses the fumigation cost of non-gastight storage is in the range of AUD 0.5 to AUD 2/tonne (treatment cost of PH<sub>3</sub> fumigation of gastight storage can be as low as AUD 0.1/tonne).

The PH<sub>3</sub> dosage for flow through fumigation has increased fourfold (4x) from the dose recommended in 1996 (Ryan, 1997) this is due to the ongoing increases in insect tolerance to PH<sub>3</sub>. A major concern of bulk grain handlers is the increase in insect resistance to PH<sub>3</sub>. The immediate problem is the PH<sub>3</sub> resistant *Cryptolestes* [flat grain beetle] in NE Australia where existing PH<sub>3</sub> label rates are not effective.

### 3. Results and Discussion

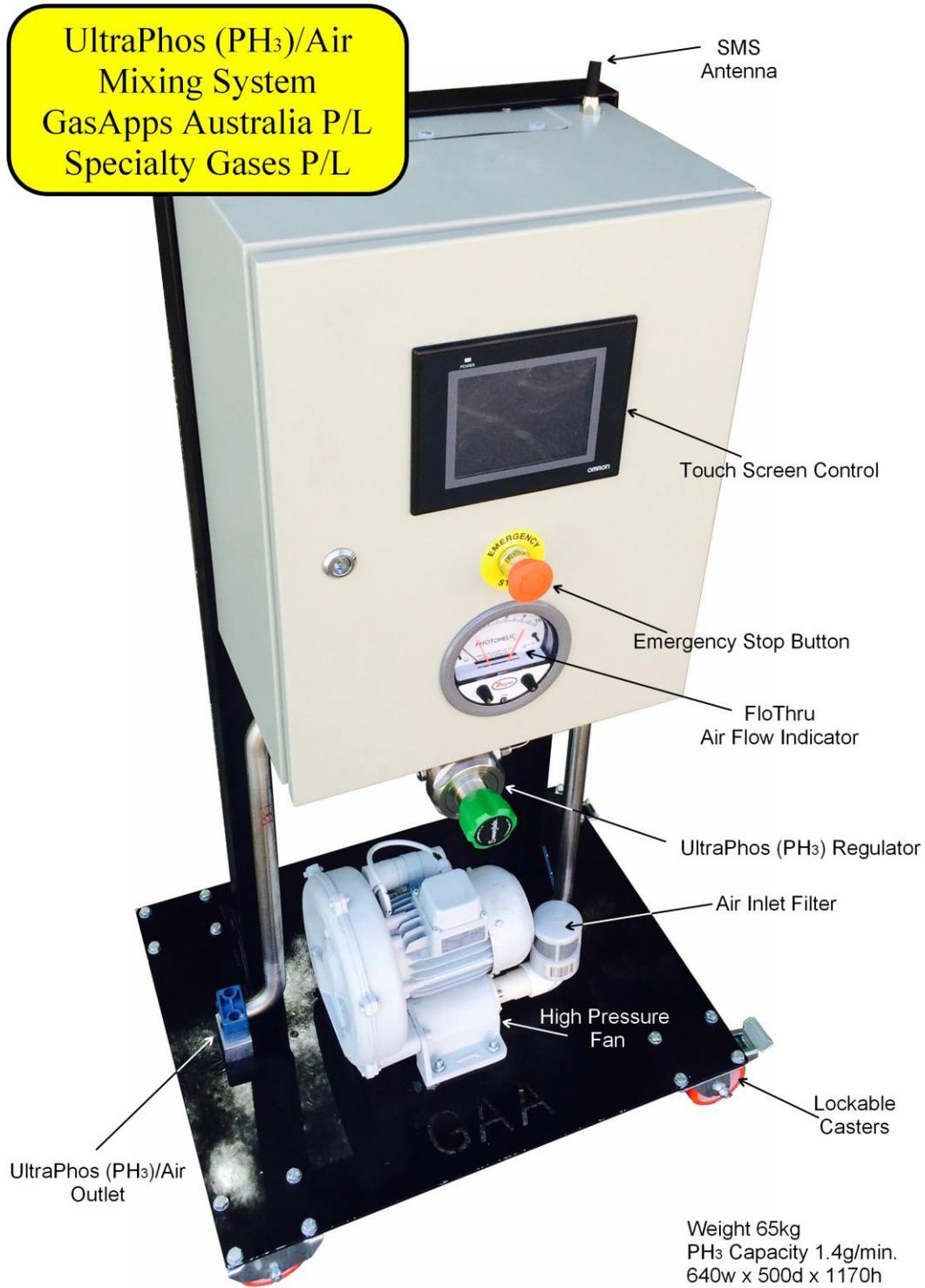
#### 3.1. Dispensing PH<sub>3</sub>/Air issues

The current challenge is the development of a safe, rugged, reliable on-site PH<sub>3</sub>/Air dispensing equipment to operate unmanned in remote rural sites 24/7 for up to 4 weeks exposure time required for FloThru fumigation. Most grain storages are located in the rural areas have issue such as unmanned sites, regular transport of equipment between grain storages on unsealed “bumpy” roads and extremes of temperatures. The prototype UltraPhos Air Mixing System (PH<sub>3</sub>/Air) has benefited from the successful design of the early rugged/reliable PH<sub>3</sub>/CO<sub>2</sub> mixer. The UltraPhos Air Mixing System prototype incorporates a proprietary high capacity mixer and includes multiple fail safe devices that have been the subject of independent HAZOP/CHAZOP reviews and external approvals.

Following the finalization of the design and independent review, the UltraPhos Air Mixing System is currently being evaluated in laboratory test and field fumigation bulk grain trials. The rugged/reliable UltraPhos Air Mixing System incorporates ultra reliable rapid mixing technology which guarantees no ignition issues when the highly flammable PH<sub>3</sub> is mixed with Air. Automatic pre- and post purging also ensures the absence of any polymer dust issues.

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UltraPhos (PH<sub>3</sub>)/Air Mixing System  
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