Controlled release of phosphine — an update

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Abstract

The controlled release techniques possible with cylinders containing phosphine in carbon dioxide in minimising selection and controlling resistant strains were initially reported at the last International Working Conference on Stored-Products Protection at Bordeaux (Winks and Ryan, 1990). The benefit of controlled release has led to the growing international acceptance of Phosfume®, the patented non-flammable mixture of 2% wt. phosphine in carbon dioxide. The safe and accurate metering of the universal grain fumigant, phosphine, has revolutionised stored-product disinfestation. Innovations adopting this technology include;

- SIROFLO®, the flow-through fumigation application for phosphine in leaky silos developed by CSIRO;
- recirculation fumigation at export terminals developed by Western Australia Cooperative Bulk Handling (WACBH);
- low-dose (0.3 g/t) fumigation of pad storage by GRAINCO, Qld;
- long-term storage of peanuts in concrete silos by the Peanut Marketing Board (PMB), Qld;
- continuous low dose fumigation by the Ministry of Agriculture Fisheries and Food (MAFF), U.K.

CIG's provisional patented LoDose® regulator has the capability of dispensing a range of gas flow-rates from 0–100 L/minute at pressures as low as 0.1 kPa direct from the high pressure (5000 kPa) Phosfume® cylinder. The LoDose® phosphine dispensers have been proven in applications as diverse as bulk grain and on-farm fumigations.

Introduction

Australia currently enjoys a reputation for exporting grain that has one of the highest levels of insect freedom (Winks and Ryan 1993). This 'insect-free' status was achieved using residual pesticides, but during the last decade pesticide residues in grain have featured prominently as a concern of overseas customers. The market's demand for insect-free and pesticide residue-free food should ensure that residual pesticide grain protectants will be phased out.

The safe, accurate and controlled metering of the universal grain fumigant, phosphine, has revolutionised stored-product disinfestation. Gaseous phosphine [PH_3] fumigation is a proven cost-effective alternative to residual pesticides. Phosphine is an extremely flammable gas, and existing commercial metallic phosphide formulations do not eliminate this hazard. The slow release of the phosphine from metallic phosphide formulations allows the phosphine to dissipate into the surrounding air and minimise explosive concentration levels. Phosfume™ is a patented (U.S. Patent No: 4889708) non-flammable mixture of phosphine (2% in weight) in carbon dioxide marketed by the international BOC Group, which can be easily, accurately and safely dispensed into all types of grain storage using gastight pipeline.

Innovations adopting this technology include:

- SIROFLO®
- recirculation fumigation
- pad/bunker fumigation
- continuous dose.

SIROFLO®

An exception to the gaseous grain fumigation's requirement of appropriate sealed storage is the CSIRO flow-through SIROFLO® fumigation technique. SIROFLO® is an innovative patented fumigation technique developed by Dr R.G. Winks of the CSIRO Stored Grain Research Laboratory, Canberra (Winks 1983). The traditional fumigant phosphine is used in a revolutionary way which makes it far more effective. The system is quite simple. A low concentration of phosphine gas from Phosfume™ cylinders is mixed with an air stream. The air–gas mixture is pumped into the base of the storage facility. The airstream produces a small positive pressure that causes the gas to spread evenly through the entire grain mass.

SIROFLO® obviates the need for expensive sealing ($3–5/t) and offers effective, essentially residue-free treatment at low cost; say 10–50 ¢/t depending on whether the treatment is short or long term plus $1/ t installation cost (Evans 1988).

CSIRO research suggests a solution to overcome the traditional problem of insect resistance in the case of phosphine by showing that phosphine-resistant strains succumb to the gas provided the exposure period is long enough. This can be achieved in gastight storage or by using the flow-through SIROFLO® fumigation technique (Winks and Ryan 1990).

For a minimum exposure period of 28 days, the recommended SIROFLO® minimum concentration is 10–22 ppm PH_3 with a continuous flow equivalent of approximately one volume change/day.

Developing Phosfume™ dispensing systems to provide the continuous long-term flow-through requirement of SIROFLO® involved an extended effort between CIG, CSIRO and the Bulk Grain Authorities. The equipment selection was complicated because Phosfume™ is dispensed as a liquid and early successful prototypes were later plagued by inherent impurity problems associated with phosphorus products. While phosphine's chemistry is not fully understood, it reacts with oxygen producing a polymer dust and oily phosphoric acid. Gas regulators and fine orifices in control valves are particularly vulnerable to the paste formed from these contaminants.

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CIG responded by implementing a program ensuring that oxygen was excluded from the Phosfume™ cylinders and developing the LoDose™ regulator. The initial response of analysing individual cylinder for oxygen contamination before filling is being superseded by the fitting of Minimum Pressure Relief [MPR] cylinder valves. The MPR valves used are identical to those proven in ultra high purity gas cylinders and exclude atmospheric air by maintaining a higher than ambient pressure of gas in the cylinder even if the cylinder valve is left open. The LoDose™ regulator was developed to accept liquid gas input and accommodate any polymer dust and phosphoric acid contaminants.

A schematic of the SIROFLO® technique using a LoDose™ regulator is shown in Figure 1. The high pressure liquid Phosfume™ mixture is vaporised to a low pressure gas and diluted ~1000 times in an air stream (i.e. ~26 ppm) before being dispensed into the base of the on-farm storage bin. The vaporisation and pressure reduction is achieved using the LoDose™ regulator. The LoDose™ regulator has the pressure reduction capability of ~50,000 i.e. it could reduce the 5000 kPa Phosfume™ to 0.1 kPa. The LoDose™ ambient-heat regulator shown in Figure 1 has a maximum continuous output flow of 3 L/minute (ie sufficient to treat a ~5000 m^3 storage using SIROFLO®).

The LoDose™ heater regulator shown in Figure 2 has a temperature controlled heater block inserted between the regulator's orifice seat and diaphragm controller. This regulator has a maximum continuous output of 25 L/minute (i.e. sufficient to treat a ~40,000 m^3 storage using SIROFLO®).

Both the LoDose™ ambient-heat and LoDose™ heater regulators have been successfully trailed by Bulk Grain Authorities dispensing Phosfume™ in SIROFLO® fumigation, and more than 200 units have been requested by the Bulk Grain Authorities to date. The LoDose™ heater regulator

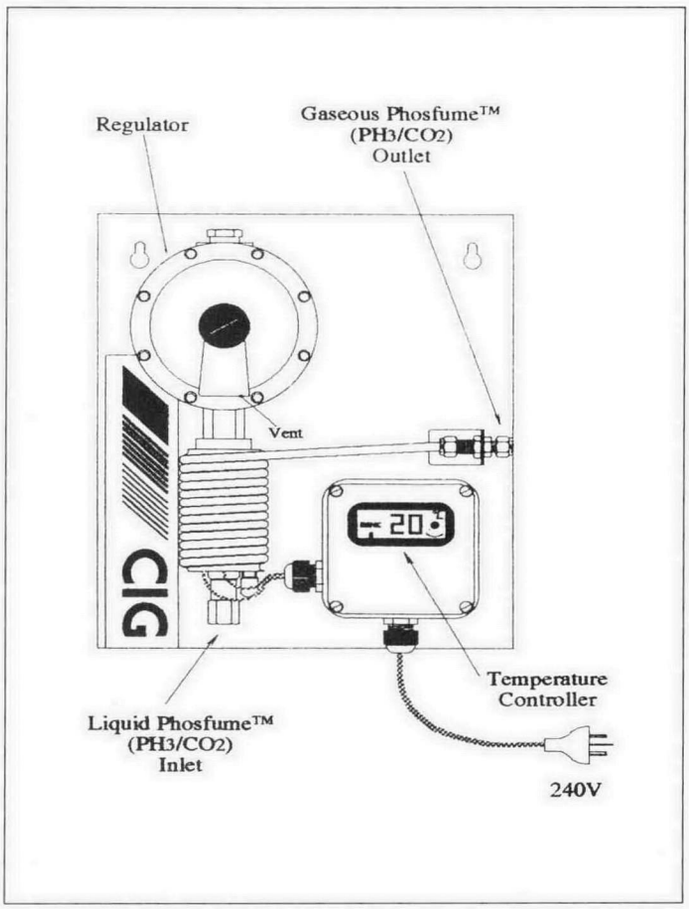

Fig. 2. LoDose™ heater regulator.

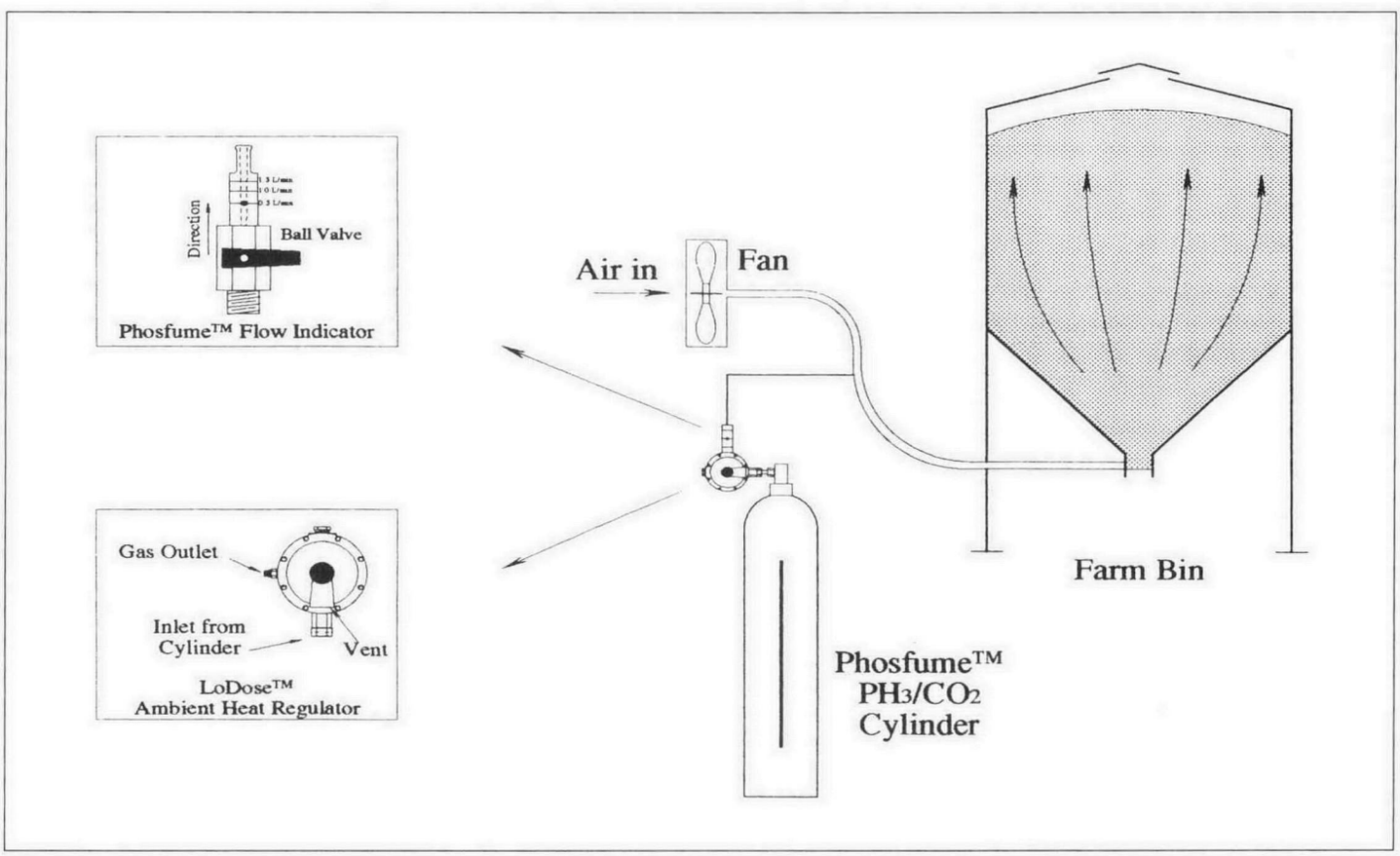

Fig. 1. SIROFLO® flow-through fumigation.

upgrade of the NSW GrainCorp SIROFLO® dispenser is shown in Figure 3.

SIROFLO® adoption by the Bulk Grain Authorities continues to grow and more than 6 million t of grain will be treated by this technique using Phosfume™ in 1994 (Winks and Ryan 1993).

Recirculation Fumigation

Cooperative Bulk Handling (CBH), the Western Australian grain handling authority, continues to use Phosfume™ at its ~1.5 Mt capacity Kwinana Grain Terminal. WACBH inject Phosfume™ into the forced air recirculation system of the 2200 t vertical storage (a total capacity of 912000 t is held in the 144 vertical cell which have individual dimensions of 11 m diameter and 30 m high).

The initial dispensing was achieved using a capillary tube restrictor to ensure the Phosfume™ was dispensed at a uniform rate over the time period required for the air blower to achieve one volume change. The LoDose™ heater regulator shown in Figure 2 is capable of uniformly dispensing the Phosfume™ dose required to treat the 2000 t vertical cells in the 5 hours required for one volume change. A schematic for a Phosfume™ recirculation system is shown in Figure 4.

CBH has access to low-cost metallic phosphide, but the 2 day saving in time using Phosfume™ is more critical than any increased costs over pellets [note: the cost of the Phosfume™ treatment is a low ~5¢ / t]. The additional benefits of eliminating occupational health and safety concerns associated with handling (pellets instantaneous generate PH_3 on exposure to atmospheric moisture) and disposal of spent pellets are an additional bonus (spent pellets can have ~5% unreacted metallic phosphide).

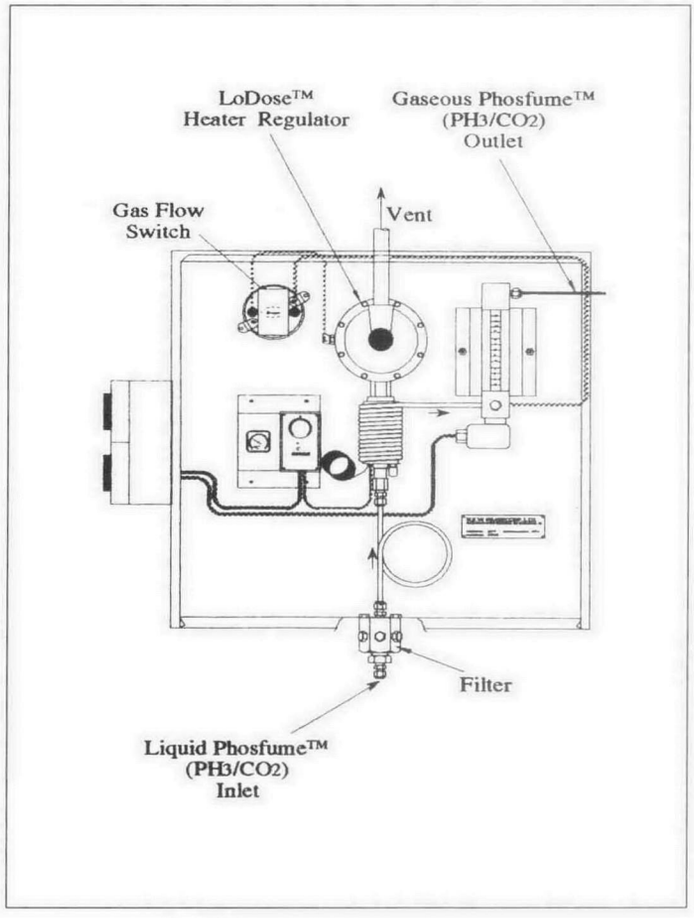

Fig. 3. GrainCorp SIROFLO® upgrade.

Western Australia commenced a program of sealing grain storage in the 1980s to enable grain to be fumigated with PH_3 effectively and today no residual pesticide grain protectants are used by the CBH.

Pad / Bunker Fumigation

Fumigation of pad or bunker storages using Phosfume™ has been perfected by GRAINCO, Qld (Ryan 1992). The tarpaulin-covered grain, typically ~30,000 t (Figure 5) is probed using a 9 mm diameter, 2 m stainless steel tube (with a 1.5 mm exit hole) connected to the Phosfume™ cylinder using a 30 metre length of teflon lined, stainless steel high pressure flexible hose. The dose rate of 0.3 g PH_3 / m^3 pioneered by GRAINCO has been recommended for addition to the Phosfume™ label. The innovative GRAINCO technique ensures quick release of phosphine, achieves peak phosphine concentration some four times that from metallic phosphide formulations, ensures rapid distribution (~140 ppm in 24 hours) and results in entomologically effective concentrations even after exposures of more than 3 months (daily loss of ~1.5 ppm in well constructed pad / bunker storage).

Continuous Dose

Requirement for low cost and 'nil electrics' fumigation equipment resulted in trials using LoDose™ regulators to dispense Phosfume™ in the fumigation of peanuts in long-term storage (Peanut Marketing Board [PMB], Kingaroy, Queensland) and fumigation of isolated on-farm grain storage (Blairgowrie Pastoral Company, Mendooran, NSW). The PMB used a LoDose™ heater regulator connected to the Phosfume™ cylinder supply and each silo (43 silos in group) was fitted with an individual low cost 0–1.5 L/minute Flow Indicator machined from clear acrylic tube and a low pressure ball valve (Fig. 1, inset). Measured phosphine level achieved in 'non-gastight' storage indicated entomologically effective concentrations are obtainable with continuous dosing. Results to date are encouraging enough to warrant additional trials.

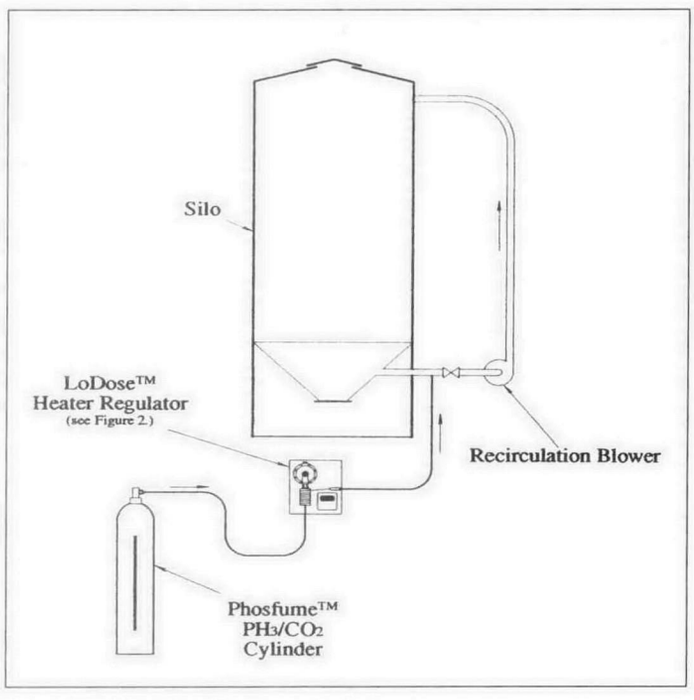

Fig. 4. Phosfume™ recirculation system.

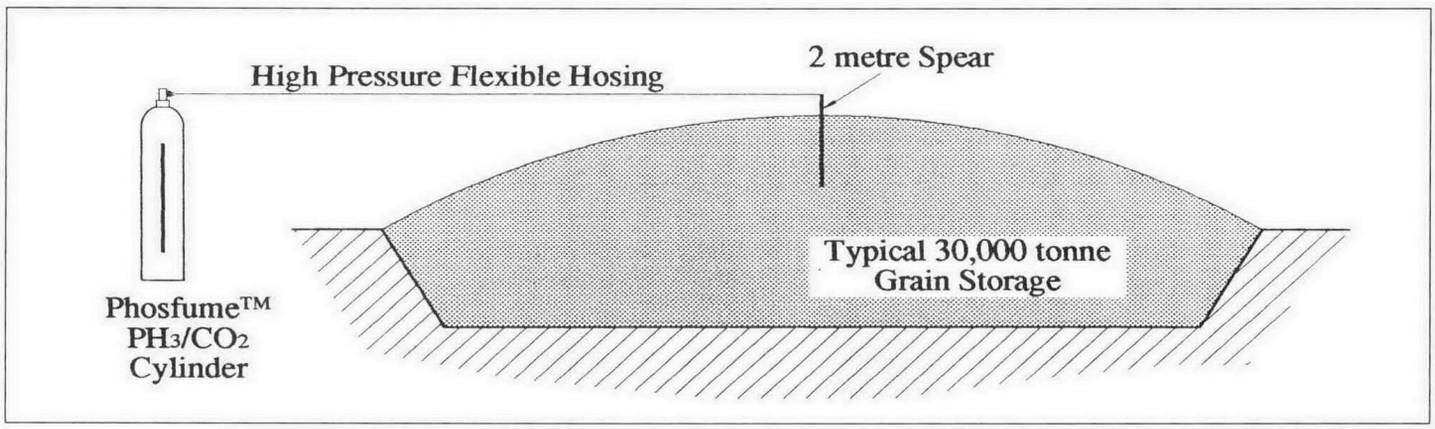

Fig. 5. Pad/bunker fumigation.

This technique using Phosfume™ was initially reported in a U.K. report (Bell et al. 1991) as a 'continuous flow system'. The difficulty of controlling gas flow experienced in the U.K. work was overcome using the LoDose™ regulators, although absence of appreciable back pressure required the inclusion of a restriction in the gas delivery line.

Conclusion

Phosfume™ capability to provide a controlled source of phosphine allows concentrations to be adjusted during a fumigation to compensate for unforseen air ingress. This adds an order of sophistication to grain fumigation. This, combined with the non-flammability and occupational health and safety benefits of Phosfume™, give significant advantages over alternatives. The new LoDose™ regulator provides long-term continuous flows required for techniques such as SIROFLO®. These techniques ensure that grain stored in non-gastight storages can be treated to achieve 'insect-free and residue-free' status and eliminate the need for traditional residual pesticide grain protectants.

The BOC Group Companies continues to develop a 'grain protection package' to include additional gases [eg carbon dioxide, nitrogen, Envirosol™ gas mixtures], gastight sealing of grain storage and dispensing equipment [e.g. SIROFLO®, non-cryogenic on-site nitrogen gas generators] to satisfy the need for cost effective 'residue-free' grain protection. With the deregulation of grain markets the BOC Group is focusing on the needs of on-farm fumigation.

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