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THE USE OF GASEOUS PHOSPHINE BY ONSITE MIXING

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ABSTRACT

The use of liquid carbon dioxide (CO_2) as a solvent / propellant resulted in the development of a nonflammable compressed gaseous phosphine (2% PH_3) in liquid CO_2 mixture which progressed to the onsite mixing of pure flammable 99% PH_3. Prior to compressed gaseous PH_3 in industrial gas cylinders, metallic phosphide "solid phosphine" (e.g. AlP) was the only PH_3 source. Issues of flammability, OH&S and disposal cost of the spent AlP formulations has seen a continuing growth in the use of compressed gaseous PH_3 (currently some 40 tonne/year is used in Australia). The early PH_3/CO_2 mixture has been overtaken by the use of pure gaseous PH_3 mixed with CO_2 or air on-site. The onsite mixing of PH_3/CO_2 eliminates flammability issues and currently fumigated some 2 million tonne/year of grain in Australia. The on-site mixing technology can treat grain storage that is not gastight using the SIROFLO® flow through technique. This flow through technology maintains a low concentration of PH_3 over an extended period of weeks (e.g. 140 ppm x 21 days exposure). The external control of dispensing the gaseous PH_3 outside the grain storage eliminates the need for confined space entry to apply fumigant or retrieve spent solid waste. The precise control and instant dispensing of gaseous PH_3 from a high pressure industrial gas cylinder are reasons for its continued acceptance. The use of gaseous PH_3 also avoids the time and cost involved in disposal of the spent AlP formulations. Proprietary dispensing equipment has been developed that is capable of 24/7 dispensing a PH_3/CO_2 mixture unattended for a period of over 4 weeks.

Keywords: non-flammable, liquid CO_2 fumigant mixture, gaseous PH_3, metallic phosphide, cereal grain fumigation, on-site mixing, non gastight storages, gas dispensing equipment, long exposure period

INTRODUCTION

"Golden Age of Malathion and Tin Sheds":
The quality standard for stored grain has undergone a quantum leap over the last 50 years. In Australia prior to 1963 insects were accepted components of stored grain. The issues were "visible" insects (approximately 2000 insects/tonne which at 30°C can multiply to 200,000 insects/tonne in one month [Rees, 1998]) or if significant losses from heating or mould occurred. Because of excessive financial penalties paid in compensation for infested 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 and during this "golden age of malathion and tin sheds" period insect-free status was achieved using residual pesticides, however, eventually concern of pesticide residues contamination was raised as important marketing issue.

Pesticide residue-free grain is achieved using gas fumigation to eliminate insect infestations however sealed storage is required. The solution adopted to treat the large number of non-gastight storage was SIROFLO®, the flow through fumigation system developed by CSIRO's Stored Grain Research Laboratory (Winks, 1986).

Phosphine (PH_3) – the fumigant of choice:

There has always been a need to control insects in grain and foodstuffs to prevent food losses and to satisfy marketing requirements. The traditional preferred fumigants were methyl bromide (MeBr) and phosphine (PH_3) with the latter the fumigant of choice because of cost considerations, superior efficacy and environmental acceptance (MeBr is listed on the Montreal Protocol as an ozone depletor). PH_3 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_3 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_3 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_3 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_3 over days to allow dilution with the surrounding air to avoid ignition and fires. While a very low cost PH_3 source there are other issues with the "solid" PH_3 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 (Scudamore and Goodship, 1986) PH_3 was the preferred fumigant to attain insect-free and residue-free foodstuffs; however PH_3 is an extremely flammable gas with a lower explosion limit in air of 1.6%. Discounting its flammability hazard, PH_3 is a very effective fumigant being some fifty times more toxic to insects than MeBr. After a lapsed Fruit Fly project in1976 involving Gosford Postharvest Horticultural Laboratory, CIG Ltd (now BOC/The LINDE Group) patented PHOSFUME® [now ECO_2FUME®] a non-flammable gaseous mixture of 2 wt% PH_3 in liquid CO_2 (Ryan and Latif, 1989). In August 1999, the gaseous PH_3 products ECO_2FUME (2% PH_3/CO_2) and $VAPORPH_3OS$ (99% PH_3) 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 gaseous PH_3 has many benefits over the traditional metallic phosphide formulations:

- Mixing with CO_2 eliminates PH_3 spontaneous flammability hazard
- Compressed PH_3 allows accurate control to maintain the required PH_3 concentration
- Quick gas release reduces the long exposure times of the "solid" PH_3 formulations.
- Gaseous PH_3 allows quick distribution in the grain mass without disturbing the grain;
- Regulated PH_3 allows controlled flow for long periods e.g. 28 days SIROFLO exposure
- Piped gas system contains the PH_3 and minimises OH&S concerns.

- Compressed PH_3 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_3 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 (SCA Technical Report, 1980). Many Australian grain storages fail this test however they can be fumigated using the SIROFLO flow through fumigation technique.

SIROFLO is a flow-through fumigation technique that maintains a small positive pressure throughout the grain mass to ensure a uniform low concentration of PH_3 and can control phosphine-resistant insect's strains in non-gastight storage (Winks and Ryan, 1990). The low PH_3 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 gaseous PH_3 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 (both concentration and time);
- increases 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_3 and CO_2 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_3 and CO_2 is carried out using a unique and very simple mixing system developed by GasApps Pty Ltd, Australia which incorporates no moving parts. Liquid CO_2 was delivered by bulk road-tanker and stored at low temperature in a 5 tonne cryogenic tank. The PH_3 was dispensed from 50 L industrial gas cylinders (holding up to 22 kg of the liquefied PH_3 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_3 contains the same quantity of PH_3 as 35 x 31 kg cylinders of the PH_3/CO_2 premix.
Cyprus:
Following the installation of PH_3/CO_2 demonstration unit at Larnaca, the Cyprus Grain Commission installed flow through fumigation SIROFLO technology in all steel vertical grain silos. In addition demonstration PH_3/CO_2 trials were carried out New Zealand, Bahrain, Qatar, Vietnam, Thailand and Indonesia.

Dispensing Equipment

Pre-Mix PH_3/CO_2 dispensing equipment:

Specialised PH_3/CO_2 dispensing equipment was developed to satisfy the requirements of SIROFLO flow through technology. Innovations include: regulation of the high pressure (70,000 kPa) liquid PH_3/CO_2 mixture and dispensing vaporised gas mixture (100 L/min / 12 kg/h) for periods up to a month; "Spider" manifold using dual 3 mm SS tubing allow purging to eliminate polymer formation and avoid PH_3 diffusion associated with traditional SS Teflon-lined flexible hoses; Auto/Manual motorised Flow Control Metering Valves; higher capacity PH_3/CO_2 vaporiser for global customers. Customised PH_3/CO_2 dispensers have been the outcome of joint development between GasApps Australia and Bulk Handling Companies.

On-Site Mixing PH_3/CO_2 dispensing equipment:

The development of onsite of PH_3 and CO_2 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_3 continued to evolve. The range was extended from the non-flammable PH_3/CO_2 mixture to include the flammable 99% PH_3 which can be mixed onsite with CO_2 to produce a non-flammable mixture [2.6 v/v% PH_3/CO_2].

MATERIALS AND METHODS

The onsite mixing of PH_3 and CO_2 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 the SIROFLO flow-through technique. The treatment of unsealed grain storage fitted with a SIROFLO 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_3/CO_2/Air mixture at a calibrated low pressure to the individual grain storage. Orifice plates installed in the pipe work meter the diluted PH_3/CO_2 in air mixture to ensure the individual storage or sections of the same storage receives the target PH_3 concentration. The SIROFLO system is designed to ensure the treated storage has approximately one air volume change each day to ensure the PH_3 concentration is maintained for the duration of the fumigation exposure period (up to 25 days).

GasApps supply the required quantity of PH_3 and CO_2 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_3 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_3 and CO_2 mixture through the storage.

The external control of dispensing the gaseous PH_3 outside the grain storage eliminates the need for fumigation space entry. The precise control and instant dispensing of gaseous PH_3 from a high pressure industrial gas cylinder are reasons for the continued acceptance of gaseous PH_3. Proprietary dispensing equipment has been developed that is capable of 24/7 dispensing a PH_3/CO_2 mixture unattended over 4 week's exposure period.

RESULTS AND DISCUSSION

The current ongoing requirement of delivering insect and pesticide free grain for export continues to be achieved using PH_3 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 SIROFLO flow through 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_3 concentration (*ct*-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_3 fumigation of gastight storage can be as low as AUD 0.1/tonne).

The PH_3 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_3. A major concern of bulk grain handlers is the increase in insect resistance to PH_3. The immediate problem is the PH_3 resistant *Cryptolestes* [flat grain beetle] in NE Australia where existing PH_3 label rates are not effective.

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