

## UltraPhos: high purity phosphine – revisited

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### Abstract

The need to control insects in grain and foodstuffs to prevent food losses and to satisfy marketing requirements continues to depend on phosphine (PH<sub>3</sub>) fumigation. The original “solid” PH<sub>3</sub> patent was granted in Germany (1934) for the generation of PH<sub>3</sub> gas from aluminium phosphide on exposure to atmospheric moisture. The compressed 40 bar “liquid” PH<sub>3</sub> in industrial gas cylinders, with benefits of rapid and uniform PH<sub>3</sub> dispensing, was initially investigated as a fumigant for the control of fruit fly in 1976. The CIG patented non-flammable PHOSFUME (PH<sub>3</sub>/CO<sub>2</sub>) supported the CSIRO patented flow-through fumigation process (SIROFLO) developed to fumigate non-gastight grain storage (1986).

The Agriculture Grade PH<sub>3</sub> (99 wt%) was more cost effective as a gaseous fumigant than the high cost Semiconductor Grade PH<sub>3</sub> (99.9999%) required for electronic devices manufacture. Specialty Gases' UltraPhos product is manufactured by reacting white phosphorus (P<sub>4</sub>) with excess caustic soda;  $4P + 3NaOH + 3H_2O = PH_3 + 3NaH_2PO_4$ . The critical impurities are diphosphine (P<sub>2</sub>H<sub>4</sub>) and white phosphorus (P<sub>4</sub>) which are pyrophoric and can cause fires in dispensing equipment. The reaction of P<sub>4</sub> with excess caustic process ensures the elimination of P<sub>4</sub> in the UltraPhos fumigation product resulting in a superior product. The issue of polymer formation created by contact of PH<sub>3</sub> and oxygen (O<sub>2</sub>) can be minimised with pre- and post-purging of PH<sub>3</sub> dispensing equipment. To avoid polymer dust build up in dispensing equipment the on-site mixing of PH<sub>3</sub>/CO<sub>2</sub> requires using CO<sub>2</sub> that has low O<sub>2</sub> levels (less than 100 ppm). The elimination of the reactive incendiary P<sub>4</sub> by the excess caustic UltraPhos manufacturing process avoids the reported pyrophoric incidents and dispensing equipment blockages associated with PH<sub>3</sub> product containing the P<sub>4</sub> impurity.

Keywords: liquid PH<sub>3</sub> gas; PH<sub>3</sub> fumigation, on-site mixing PH<sub>3</sub> with CO<sub>2</sub> or Air, non-flammable PH<sub>3</sub> mixture, flow-through fumigation, metallic phosphides, white phosphorus, PH<sub>3</sub> polymers.

## 1. Introduction

### 1.1. PH<sub>3</sub> history

Dependence on PH<sub>3</sub> fumigation has a long history – the generation of PH<sub>3</sub> gas from “solid” aluminium phosphide (ALP) from moisture in atmospheric air was patented 80 years ago – and continues to be widely used for fumigation. On farm stored grain use of phosphine began in the 1950's in Europe and the USA but as gastight storage structures improved from the 1970's its use was extended world-wide to protect durable produce in storage. The value of PH<sub>3</sub> to agriculture is due to its unique qualities: ease of use, an effective alternative to ozone depleting methyl bromide, and virtually no residues in foodstuffs. In recent years concerns have been raised regarding insect resistance but research has shown that this can be managed with correct application techniques. Since the late 1990's suitable gaseous formulations of phosphine have

enabled its use to be extended for treatment of insect pests in animal fodder, fresh flowers, vegetables and fruits bringing new and exciting challenges to agricultural research. This research shows that insects infesting fresh produce require far higher doses of phosphine, respond in relatively shorter times (hours rather than days) and are killed at far lower temperatures (0-10°C) compared with insects in stored grain.

### 1.2. "Solid" PH<sub>3</sub> formulations

The original "solid phosphine" formulation containing aluminium phosphide (AIP) was patented in USA (Freyberg, 1938). The "solid" formulations are sold as pellets, tablets, and sachets of aluminium, calcium or magnesium phosphide mixed with inert ingredients such as ammonium carbamate from which phosphine is slowly evolved by reaction with moisture in the surrounding atmosphere. To avoid being spontaneously flammable PH<sub>3</sub> needs to be free of white phosphorus (P<sub>4</sub>) and diphosphine (P<sub>2</sub>H<sub>4</sub>) at trace levels (Fluck, 1973). The flammability hazard of PH<sub>3</sub> gas generated from "solid" formulations is minimised by slowly releasing PH<sub>3</sub> to allow safe dilution with the surrounding air. The major advantages of these formulations are portability, low cost, and versatility of application under a variety of conditions. Negative issues include un-reacted powder residues, disposal costs and long exposure times (Ryan and Shore, 2012).

### 1.3. "Liquid" PH<sub>3</sub> formulations

Commercial "liquid" PH<sub>3</sub> is manufactured into a range of proprietary chemicals for use in textile, mining and electronics industries. In very high purity (99.9999% pure) PH<sub>3</sub> is used in the manufacture of silicon electronics. The reaction of PH<sub>3</sub> with oxygen (O<sub>2</sub>) to form polymers is an issue, which requires pre- & post-purging of dispensing systems. The commercial manufacture of gaseous phosphine is either from white phosphorus (reaction with caustic soda:  $4P + 3NaOH + 3H_2O = PH_3 + 3NaH_2PO_4$ ) or from red phosphorus (reaction with steam:  $8P + 12H_2O = PH_3 + 3H_3PO_4$ ). Fumigation grade phosphine is of lower purity than electronic grade; however there are critical specifications for impurities such as diphosphine (P<sub>2</sub>H<sub>4</sub>) and white phosphorus (P<sub>4</sub>) which are pyrophoric (Ryan, 1997). While gaseous phosphine has a longer history as a dopant in electronic silicon chip technology manufacture, PH<sub>3</sub> was initially investigated as a fumigant for the control of fruit fly in 1976 (Ryan, 1997). A number of regular updates of the history of the commercial gaseous phosphine products launched in the early 1980's have been published (Ryan, 1997). While pure phosphine is not spontaneously flammable, it has a wide flammable range in air (1.6% to 100%). Non-flammable gaseous mixtures of 2% PH<sub>3</sub> in CO<sub>2</sub>; 2% PH<sub>3</sub> in N<sub>2</sub>; and 2.4% PH<sub>3</sub>+60% CO<sub>2</sub> in N<sub>2</sub> eliminate PH<sub>3</sub> flammability hazard (Ryan 1997, Ryan and Latif, 1989). Current "liquid" PH<sub>3</sub> products include non-flammable ECO<sub>2</sub>FUME<sup>®</sup> (2wt% phosphine in CO<sub>2</sub>: BOC Gases) and FRISIN<sup>®</sup> (1.7vol% PH<sub>3</sub> in N<sub>2</sub>- S&A Service und Anwendungstechnik GmbH). Flammable PH<sub>3</sub> [VAPORPH<sub>3</sub>OS<sup>®</sup> – CYTEC Industries & UltraPhos<sup>®</sup> – Specialty Gases Pty Ltd) can be dispensed on-site by rapid dilution in turbulent air flow to less than 16,000 ppm / 22g PH<sub>3</sub>/m<sup>3</sup> or with inert gases (Ryan and Shore, 2005). Although more expensive, "liquid" PH<sub>3</sub> has benefits over the "solid" PH<sub>3</sub> as on-site mixing eliminates the spontaneous flammability hazard, allows accurate control of PH<sub>3</sub> concentration, deliver PH<sub>3</sub> more rapidly, achieve better distribution in the grain mass without disturbing grain, and allows controlled flow and dosage maintenance for long periods. Also "liquid" PH<sub>3</sub> eliminates handling and the cost of disposal of the "spent" metallic phosphide tablets and the associated high labour costs.

## 2. Materials and Methods

### 2.1. *PH<sub>3</sub>* efficacy

Phosphine doses have been dramatically reduced from the 10,000ppm (14g/m<sup>3</sup>) used in the 1950's (Annis, 2001) to the current recommendations of 1 to 3g/m<sup>3</sup> (718ppm to 2,154 ppm) or as low as ~100ppm (0.14 g/m<sup>3</sup>) in the continuous flow-through fumigation (Anonymous, 1992). The critical requirement of a successful fumigation is to provide an adequate concentration for a sufficient period of time. A unique characteristic of phosphine is that it is not absorbed in the absence of oxygen (O<sub>2</sub>) and thus is not toxic to insects in a low O<sub>2</sub> atmosphere (Bond et al. 1967). Kashi and Bond (1975) showed that in the presence of 4% CO<sub>2</sub> there was a 20% increase in the uptake of oxygen and a 3-fold increase in the toxicity of phosphine to insects. The action of phosphine is potentiated by carbon dioxide and the concentration of PH<sub>3</sub> and exposure time can be reduced when both CO<sub>2</sub> and O<sub>2</sub> are present. The optimum CO<sub>2</sub> concentration is in the range of 5-35%. At 5% CO<sub>2</sub> the PH<sub>3</sub> LC<sub>90</sub> can be reduced by ~50% (Kashi and Bond 1975; Bond and Buckland 1978). Australian recommendations are 1g to 3g PH<sub>3</sub>/m<sup>3</sup> for 7 to 21 days depending on temperature, commodity, insect species and storage type (Anonymous, 1989; Anonymous, 1992). Over the past 20 years phosphine have been successfully developed against insects in flowers, fruits and vegetables at relatively high doses of >1.4g PH<sub>3</sub>/m<sup>3</sup> for relatively short exposure period (6-24h) at low temperatures (<15°C) on adults and immature stages of a number of insect and mite species (Karunaratne et al. 1997).

#### 2.1.1. *PH<sub>3</sub>* efficacy on grain insects

Since the 1950's the primary method of PH<sub>3</sub> application was through the use of tablets, pellets and sachets in farm silos, freight trains, bulk vehicles, in warehouse under fumigation sheets, etc. However because of the long exposure period required for PH<sub>3</sub> the preference was to use methyl bromide (Bond 1989). With the development of better gastight silos dosage of PH<sub>3</sub> of 1.5g /m<sup>3</sup> is now recommended with a minimum of 300 ppm for 7 days or 200 ppm for 10 days in Australia (Anonymous, 2013). In most overseas countries EPP0 standards (EPP0 2012) of 3g PH<sub>3</sub>/m<sup>3</sup> for 7days at 20°C increasing to 12days at 10°C are observed, often requiring a minimum of 300 ppm (0.4g /m<sup>3</sup>) for 7 days to be successful. PH<sub>3</sub> supplied in gaseous form is instantly available (as opposed to the slow release of "solid" PH<sub>3</sub> formulations) and is applied at lower dosages to reduce costs, but to be effective, fumigations should be carried out in gastight storage structures to the appropriate standards (Banks and Annis, 1984; Anonymous, 1980). The first applications of the non-flammable, gaseous PH<sub>3</sub>/CO<sub>2</sub> mixture were conducted by Cooperative Bulk Handling (Western Australia) in gastight 2,000tonne vertical and 15,000 tonne horizontal bulk grain storage (Ryan, 1988). The 0.17g/tonne PH<sub>3</sub> dose was evenly distributed by natural convection in the 15,000 tonne sealed storage within 44 hours and a concentration in excess of 100ppm was maintained for 260 hours (treatment cost AUD 0.05/tonne). The 30,000t bunker storages in Queensland (Ryan; 1990, 1992) used 0.3g PH<sub>3</sub>/tonne with treatment cost of AUD 0.10/tonne. By combining treatments of PH<sub>3</sub>+CO<sub>2</sub> (Carmi et al., 1990, 1994) and PH<sub>3</sub>+CO<sub>2</sub>+heat (Mueller, 1994) successful fumigations were achieved in large silos and flour mills. Recirculation of phosphine in gastight structures (Cook, 1984) was done under various conditions including: the closed-loop system in the USA (Noyes and Kenkel, 1994); the circumfluent system in China (Sun et al., 1993); the PHYTO-EXPLO<sup>®</sup> (Chakrabarti et al., 1994); and the Degesch J-SYSTEM<sup>®</sup> (Zettler et al., 1984). These technologies reduce the dosage of PH<sub>3</sub> required to produce a lethal concentration (C) x time (T) product in grain pests and thus improve the efficiency of conventional types of fumigations (Zettler, 1997). In the PH<sub>3</sub>+CO<sub>2</sub> recirculation fumigation at

the Xizui Grain Terminal, Dalian, China (Dalian site capacity = 1.4 million tonnes), multiple 30,000 tonne gastight vertical grain storages were fumigated mixing PH<sub>3</sub> gas from cylinders with CO<sub>2</sub> from a bulk refrigerated liquid tank (Ryan and Shore, 2010). Fumigation of wheat in a 300,000 tonne sealed horizontal shed at Cooperative Bulk Handling, Kwinana, Western Australia successfully used 0.45 g/tonne PH<sub>3</sub> with onsite mixing of gaseous phosphine in air (Thornton et al., 2006).

### 2.1.2. efficacy of PH<sub>3</sub>FloThru<sup>®</sup>: Continuous flow-through application in leaky storage

For effective fumigation it is critical that the storage is gastight to ensure PH<sub>3</sub> concentration is sufficient to kill all stages of all species present in an infested commodity. However grain storage structures in Australia and other countries often fall well short of the specified standards of gas tightness for PH<sub>3</sub> (Anonymous, 1980; Winks, 1987). Many Australian grain storages that fail the gas tightness test are fumigated using the SIROFLO<sup>®</sup> continuous flow-through technique (Winks, 1993). Flow through fumigation techniques rely on susceptibility of pest species to a continuous supply of low level (ca. 120 ppm) PH<sub>3</sub> concentrations maintained in a pressure of 500 Pa throughout the grain mass for up to 28 days to kill all stages of insects (Winks and Ryan, 1990, 1995; Winks, 1993, Winks and Russell, 1994, Winks and Russell, 1997, Varnava et al., 1998). This flow through technique provides a method for fumigating grain in leaky storage and has resulted in many old silos being useful storage and has enabled grain handlers to decrease their reliance on grain protectants in eastern Australia (Collins 2010).

### 2.2. PH<sub>3</sub> residues

Baking studies showed that there were no PH<sub>3</sub> residues in baked products even when “solid” PH<sub>3</sub> metallic phosphides were added to the flour immediately before baking (Bruce et al. 1962). In tests using <sup>32</sup>P to assess the presence of phosphorus residues after PH<sub>3</sub> treatment of wheat and flour, the radioactive residue was not removed by aeration or by heating at baking temperature, but was largely water-soluble consisting mainly of hypophosphite and phosphite. At practical PH<sub>3</sub> concentrations, residues of the order of 0.04 ppm to 1.2 ppm (calculated as PH<sub>3</sub>) on flour and wheat were indicated (Robinson and Bond, 1970). In organoleptic evaluation of cooked products, prepared from wheat, maize and sorghum fumigated with aluminium phosphide at 1.5 and 3 g/m<sup>3</sup> (3 days exposure), Kavadia (1984) found no effect of phosphine residue on any of the sensory characteristics except “softness” in wheat chapatti, “colour” in maize chapatti and “doneness” in maize dahlia prepared out of the fumigated grains and all residues of phosphine were below the tolerance limit (0.02 mg/kg) within 2 days. Dumas (1980) fumigated whole cereal grains with CxT product up to 190 g.h/m<sup>3</sup> (for 4, 7 and 14 days) and after 1 day all residues were less than 0.02 mg/kg. Scudamore & Goodship (1986) recorded residue levels of 0.001 ppm phosphine in several fumigated foodstuffs. Hazelnuts and brazilnuts fumigated with CxT products, up to 125 g.h/m<sup>3</sup> for 4 and 7 days, resulted in initial residues >0.2 mg/kg and required 14 days to drop below the WHO/FAO Codex limit of 0.1 mg/kg. There was no significant increase in residues between fumigations at 10 and 25°C (Scudamore & Goodship, 1986).

### 2.3. Insect resistance to PH<sub>3</sub>

Resistance to phosphine has occurred in every insect species tested (Winks and Ryan, 1990). There is also considerable variation in susceptibility of different stages in the insect's life cycle (Winks and Hyne, 1994). By using long fumigation exposure periods, the more tolerant stages (eggs and pupae) will in general develop to susceptible ones (larvae and adults respectively) and succumb (Lindgren and Vincent, 1966; Winks and Ryan, 1990). In early work, Price and Bell

(1981) reported that PH<sub>3</sub> did not alter the development period of eggs of the tropical warehouse moth *Ephesia cautella* treated at 0.8g/m<sup>3</sup> for 24h while Pike (1994) found no development inhibition in psocids *Liposcelis entomophila* at 0.8g/m<sup>3</sup> for 120h. However, Rajendran and Muthu (1991) observed inhibition in hatching of 1 to 3 day-old eggs of *Tribolium castaneum* following a 24 h exposure to PH<sub>3</sub>. Rajendran (2000) reported a significant delay in hatching in phosphine fumigated insects compared with untreated controls for a susceptible strain treated at 30 ppm for 120h as well as a resistant strain treated at 300 ppm for 72h. These data indicated that PH<sub>3</sub> induced inhibition of hatching has serious consequences for the development of resistance when fumigations are shorter than 7 to 21 days. Wang et al. (2010) examined several strains of *Sitophilus oryzae* (L.) having varying tolerance to PH<sub>3</sub> and found that while fumigation for 5 days was sufficient for pupae and eggs of susceptible insects, 9 days was required to control eggs and pupae of resistant strains. Collins et al. (2001) found that egg hatch was delayed in psocids *Liposcelis bostrychophila* in eggs exposed to PH<sub>3</sub> compared with controls, with delay increasing as PH<sub>3</sub> concentrations increased e.g. hatching in eggs exposed to 0.05 g/m<sup>3</sup> for 6 days was delayed by 7 days whereas eggs exposed to 1g/m<sup>3</sup> the delay was 14 days. The differential toxicity of phosphine among insect species can be the result of certain mechanisms: in some species an active exclusion mechanism seems to operate reducing the uptake of phosphine e.g. in resistant *Ryzopertha dominica* strains (Price, 1984); while in *Tribolium castaneum*, concentrations between 0.5 to 1 g/m<sup>3</sup> phosphine have been found to induce a kind of narcosis whereby some insects become inactive and reduce their uptake of gas, surviving longer than at higher or lower concentrations (Winks, 1984). When assessment of resistance is uncertain, a more meaningful method for resistance is to use data from mixed cultures, enabling recommendations to be made for better phosphine fumigation in the field (Winks and Hyne 1994). In Australia resistance to phosphine has become a widespread problem in most commercial grain storage and claims of resistance are increasing in other parts of the world. There is considerable evidence demonstrating that the development of PH<sub>3</sub> resistance is associated with inadequate fumigation (Price, 1984; Banks, 1994). Proper use of phosphine fumigation in on-farm sealed storage in Australia has issues since many of these specially built silos are poorly maintained (Newman, 1994). Emery (1994) found that inefficient use of sealed silos, rather than fumigation in unsealed silos, posed a greater threat, through facilitating the development of higher levels of resistance. Collins et al. (1997) reported that a very poor fumigation will not select for resistance as quickly as a fumigation that is close to successful. Research has established two levels of resistance to PH<sub>3</sub> ('weak' and 'strong') and it has been suggested that once the frequency of 'weak' resistance reaches 80% in populations there is a strong possibility of development of strong resistance in that species (Collins and Emery, 2002) and illustrated in the development of strong resistance in *Tribolium castaneum* (Herbst) in Western Australia in 2010 (Emery et al., 2011). Development of strong resistance (875x) to phosphine in flat grain beetles *Cryptolestes ferrugineus* in large bulk storages in Australia poses a serious threat. At 1 g/m<sup>3</sup> phosphine *C. ferrugineus* requires a fumigation period of 24 d compared with current recommended periods of 10 d and 12 d for the control of strongly resistant populations of lesser grain borer and psocids. Collins (2010) considers that the evolution of strong resistance in *C. ferrugineus* is the greatest challenge since this resistance is several times greater than in any other stored product pest to date. The Australian National Phosphine Management Strategy holistic approach (Nayak, 2012) has shown encouraging results in the effective management of strongly resistant *C. ferrugineus* populations in bulk storages through use of sulfuryl fluoride as an alternative fumigant and in the implementation of resistant *C. ferrugineus* eradication plan. However, Winks and Hyne (1994)

have questioned claims for resistance based on short discriminating doses emphasising that they are to be treated with caution until properly verified through extensive testing.

### 3. Results and Discussions

#### 3.1. Phosphine alternatives

The current industry trend is the substitution of the traditional “solid” PH<sub>3</sub> formulations with the more sophisticated, versatile and controllable “liquid” PH<sub>3</sub> supplied in industrial gas cylinders. In some regions there is a dominance of the “liquid” PH<sub>3</sub> which is the only option for the fumigation of leaky storage requiring the flow-through fumigation technique. Most global grain storage are “leaky” i.e. they are unable to reach the minimum positive pressure (500Pa) required to conduct the half-pressure test (P<sub>0.5</sub>: 50% pressure reduction must be greater than 5 minutes) which is the universal minimum requirement to pass the gastight test. In sealed storage (e.g. bunker/pad storage) it is possible with ‘liquid’ PH<sub>3</sub> to maintain the optimum concentration with regular additions to compensate for minor PH<sub>3</sub> leaks and sorption by the grain.

The capability of the “liquid” PH<sub>3</sub> to maintain the required concentration even in leaky storage using flow-through fumigation is an important capability in the control of PH<sub>3</sub> resistant insects. Often increasing the CxT by extending the exposure time can achieve control of PH<sub>3</sub> resistant insects. A potential candidate to counter PH<sub>3</sub>resistance insects is methyl-phosphine which is efficacious against PH<sub>3</sub> resistant insects but not so effective against PH<sub>3</sub> susceptible insects (Chaudhry et al., 1997).

Other possible PH<sub>3</sub> alternative option is the occasional use of other “break” fumigants however there are some issues. Possible other fumigants include: sulfuryl fluoride (SF)<sub>2</sub>– however SF<sub>2</sub> has poor efficacy against the egg stage of storage pests; high pressure CO<sub>2</sub>- has excellent potential for rapid disinfestation but only at high pressure (20 bar) and there are high costs associated with the construction and operation of high pressure chambers; carbonyl sulphide (COS) - has efficacy issues with *S. oryzae* and leaves off odours; ethyl formate (EF) - can be effective against a range of insects when combined with CO<sub>2</sub>; hydrogen cyanide (HCN) -has limited use on grain due to its highly sorptive nature; EthaneDiNitrile (C<sub>2</sub>N<sub>2</sub>) - is a broad spectrum fumigant but is also sorptive; modified atmospheres involving elevated CO<sub>2</sub> or low O<sub>2</sub> has shown excellent effects but has issues of cost effectiveness and the need for long exposure times (Nayak et al., 2010).The elimination of the reactive incendiary P<sub>4</sub> by the excess caustic UltraPhos manufacturing process avoids the reported pyrophoric incidents and dispensing equipment blockages associated with PH<sub>3</sub> product containing the P<sub>4</sub> impurity.

### 4. Conclusions

The growth of PH<sub>3</sub> as the preferred fumigant for stored products is due to the benefits of high pressure compressed “liquid” PH<sub>3</sub> marketed in industrial gas cylinders. The flammability issue of the pure 99wt% PH<sub>3</sub> is eliminated using on-site dilution / mixing with CO<sub>2</sub> or Air. The reliable and proven on-site PH<sub>3</sub>/CO<sub>2</sub> mixing technology was the forerunner for on-site mixing of PH<sub>3</sub>/Air. This mixing/dispensing equipment allows accurate controlled flow to fumigate gastight and leaky storage. The issue of failed fumigations with “leaky” storage is overcome by using PH<sub>3</sub>FloThru<sup>®</sup>, the continuous flow-through fumigation. The PH<sub>3</sub>FloThru<sup>®</sup> requires long exposure time of accurately controlled low flow PH<sub>3</sub> dosing which is only possible using “liquid” PH<sub>3</sub> cylinders control equipment.

In addition to ensuring non-flammability by adequate dilution of PH<sub>3</sub> in air (a conservative limit is 16,000 ppm i.e. 1.6% PH<sub>3</sub>) other issues are impurities and pre- / post-purging of the equipment. The critical impurities are diphosphine (P<sub>2</sub>H<sub>4</sub>) and white phosphorus (P<sub>4</sub>) which are pyrophoric and can cause fires in dispensing equipment. The reaction of P<sub>4</sub> with excess caustic process ensures the elimination of P<sub>4</sub> in the UltraPhos fumigation product resulting in a superior product. The issue of polymer formation created by contact of PH<sub>3</sub> and oxygen (O<sub>2</sub>) can be minimised with pre- and post-purging of PH<sub>3</sub> dispensing equipment. The elimination of the reactive incendiary P<sub>4</sub> by the excess caustic UltraPhos manufacturing process avoids the reported pyrophoric incidents and dispensing equipment blockages associated with PH<sub>3</sub> product containing the P<sub>4</sub> impurity.

## References

- Annis, P.C., 2001. Phosphine dosage regimes required for high mortality: A data-base approach. Donahaye, E.J., Navarro, S. and Leesch J.G. [Eds.] (2001) Proceeding International Conference Controlled Atmosphere and Fumigation in Stored Products, Fresno, CA. 29 Oct. - 3 Nov. 2000, Executive Printing Services, Clovis, CA, U.S.A. pp. 45-55.
- Anonymous, 1989. Suggested Recommendations for the Fumigation of Grain in the ASEAN Region. Part I. Principles and General Practice. AFHB/ACIAR, Canberra, Kuala Lumpur.
- Anonymous, 1992. Phosphine-Generating Products: Guidelines for Use Directions and Similar Requirements for Registration. Agricultural Chemicals Advisory Committee, Canberra. Revision of document PB 441. Bailey, S.W.
- Anonymous, 2013. DAFF Queensland <http://www.daff.qld.gov.au/plants/field-crops-and-pastures/broadacre-field-crops/grain-storage/fumigation>.
- Banks, H.J., 1994. Fumigation an endangered technology? In: Highley, E., Wright, E.J., Banks, H.J., Champ, B.R. (Eds.), Stored Product Protection. Proceedings of the 6th International Working Conference on Stored-Product Protection. Canberra, Australia, 1994, CAB International, pp. 2-6.
- Bond, E.J., Buckland, C.T., 1978. Control of insects with fumigants at a low temperature: toxicity of fumigants in atmospheres of carbon dioxide. *Journal of Economic Entomology* 71, 307-309
- Bruce, R.B., Robbins, J., Tuff, T.O., 1962. Phosphine residues from Phostoxin treated grain, *Journal of Agricultural and Food Chemistry* 10, 18-21.
- Carmi, Y., Golani, Y., Frandji, H., 1990. Fumigation of a silo bin with a mixture of magnesium phosphide and carbon dioxide by surface application. In: Proceedings of 5<sup>th</sup> International Working Conference on Stored-Product Protection (Edited by Fleurat-Lessard, F. and Ducom, P.), Bordeaux, France, 9-14 September 1990, 767-773.
- Carmi, Y., Golani, Y., Frandji, H., Shaaya, E., 1994. The feasibility of increasing the penetration of phosphine in concrete silos by means of carbon dioxide. In: Proceedings of 6<sup>th</sup> International Working Conference on Stored Product Protection (Edited by Highley, E., Wright, E.J. Banks, H.J. and Champ, B.R.), Canberra, Australia, 17-23 April, 1994, CAB International, Wallingford, Oxon, UK, 48-49.

- Chakrabarti, B., Watson, C.R., Bell, C.H. Wontner-Smith, T.J., Rogerson, J., 1994. Fumigation of a 7000t bulk of wheat with phosphine using the PHYTO-EXPLO<sup>®</sup> system to assist gas circulation. In: Proceedings of 6<sup>th</sup> International Working Conference on Stored Product Protection (Edited by Highley, E., Wright, E.J. Banks, H.J. and Champ, B.R.), Canberra, Australia, 17-23 April, 1994, CAB International, Wallingford, Oxon, UK, 64-67.
- Chaudhry, M.Q., MacNicoll, A.D., Mills, K.A., Price, N.R., 1997. The potential of methyl phosphine as a fumigant for the control of phosphine resistant strains of four species of stored-product insects. (Eds. Donahaye, E.J., Navarro, S. and Varnava, A.), Nicosia, Cyprus. 21-26 April 1996. Printco Ltd, Nicosia, Cyprus, pp 45-57.
- Collins, P.J., Darglish, G.J., Nayak, M.K., Ebert, P.R., Schlipalius, D., Chen, W., Pavic, H., Lambkin, T.M., Kopittke, R., Bridgeman, B.W., 2001. Combating resistance to phosphine in Australia. Donahaye, E.J., Navarro, S. and Leesch J.G. [Eds.] (2001) Proc. Int. Conf. Controlled Atmosphere and Fumigation in Stored Products, Fresno, CA. 29 Oct. - 3 Nov. 2000, Executive Printing Services, Clovis, CA, U.S.A. pp. 593-607.
- Collins, P.J., Lambkin, T.A., Haddrell, R.L., Lambkin, T.A., Bond, L.A., 1997. Does under dosing select for resistance to phosphine? In: Proceedings of International Conference on Controlled Atmosphere and Fumigation in Stored Products (Ed. by Donahaye, E.J., Navarro, S. and Varnava, A.), 21-26 April 1996, Printco Ltd, Nicosia, Cyprus, pp. 493-502.
- Collins, P.J., Emery, R.N., Wallbank, B.E., 2002. Two decades of monitoring and managing phosphine resistance in Australia, In: Credland, P.F., Armitage, D., Bell, C.H., Cogan, P.M., Highley, E. (Eds.), Proceedings of the 8th International Working Conference on Stored-product Protection. CAB International, York, United Kingdom, pp. 570-575.
- Collins, P.J., 2010. Research on stored product protection in Australia: a review of past, present and future directions, In: Carvalho, M.O., Fields, P.G., Adler, C.S., Arthur, F.H., Athanassiou, C.G., Campbell, J.F., Fleurat-Lessard, F., Flinn, P.W., Hodges, R.J., Isikber, A.A., Navarro, S., Noyes, R.T., Riudavets, J., Sinha, K.K., Thorpe, G.R., Timlick, B.H., Trematerra, P., White, N.D.G. (Eds.), Proceedings of the 10th International Working Conference on Stored-product Protection. Julius Kuhn-Institut, Estoril, Portugal, pp. 3-13.
- Cook, J.S., 1984. The use of controlled air to increase the effectiveness of fumigation of stationary grain storages. In: Developments in Agricultural Engineering V: Controlled Atmosphere and Fumigation in Grain Storages (Edited by Ripp, B.E.), Elsevier Science Publishers, New York, 419-424.
- Dumas, T., 1980. Phosphine sorption and desorption by stored wheat and corn. Journal of Agricultural and Food Chemistry 28, 337-339.
- Emery, R.N., 1994. A Western Australian farm survey for phosphine-resistant grain beetles, In: Highley, E., Wright, E.J., Banks, H.J., Champ, B.R. (Eds.), Proceedings of the 6th International Working Conference on Stored-Product Protection. CAB International, Canberra, Australia, pp. 98-103.
- Emery, R.N., Nayak, M.K., Holloway, J.C., 2011. Lessons learned from phosphine resistance monitoring in Australia. Stewart Postharvest Review. 3: 8.

- EPPO, 2012. Phosphine fumigation of stored products to control stored product insects in general. Bulletin OEPP/EPPO (2012) 42 (3), 498–500. ISSN 0250-8052. DOI: 10.1111/epp.2622.
- Fluck, E., 1973. The Chemistry of Phosphine in Topics in Current Chemistry. Vol 35 (Springer Verlag N.Y 1973) p. 18.
- Freyberg, W., 1938. Chemische Fabrik, US Patent 2,117,158: Method of Exterminating Corn Beetles and other Vermin, 10 May.
- Karunaratne, C., Moore, G.A., Jones, R., Ryan, R., 1997. Vase life of some cut flowers following fumigation with phosphine. Hort Science 32, 900-902.
- Kashi, K.P., Bond, E.J., 1975. The toxic action of phosphine: Role of carbon dioxide on the toxicity of phosphine to *Sitophilus granaries* (L.) and *Tribolium confusum* DuVal. Journal of Stored Products Research 11, 9-15.
- Kavadia, V.S., 1984. Studies on the organoleptic qualities of cereals fumigated with aluminium phosphide. The Indian Journal of nutrition and dietetics 21:14.
- Lindgren, D.L., Vincent, L.E., 1966. Relative toxicity of hydrogen phosphide to various stored-product insects. Journal of Stored Products Research 2, 141-146.
- Mueller, D.K., 1994. A new method of using low levels of phosphine in combination with heat and carbon dioxide. In: Proceedings of International Conference on Controlled Atmosphere and Fumigation in Stored-Product (Edited by Highley, E., Wright, E.J. Banks, H.J. and Champ, B.R.), Canberra, Australia, 17-23 April, 1994, CAB International, Wallingford, Oxon, UK, 1, 123-125.
- Nayak, M., Holloway, J., Pavic, H., Head, M., Reid, R., Collins, P.J., 2010. Developing strategies to manage highly phosphine resistant populations of flat grain beetles in large bulk storages in Australia, In: Carvalho, M.O., Fields, P.G., Adler, C.S., Arthur, F.H., Athanassiou, C.G., Campbell, J.F., Fleurat-Lessard, F., Flinn, P.W., Hodges, R.J., Isikber, A.A., Navarro, S., Noyes, R.T., Riudavets, J., Sinha, K.K., Thorpe, G.R., Timlick, B.H., Trematerra, P., White, N.D.G. (Eds.), Proceedings of the 10th International Working Conference on Stored-product Protection. Julius Kuhn-Institut, Estoril, Portugal, pp. 396-401.
- Nayak, M.K., 2012. Managing resistance to phosphine in storage pests: challenges and opportunities. In: Navarro, S., Banks, H.J., Jayas, D.S., Bell, C.H., Noyes, R.T., Ferizli, A.G., Emekci, M., Isikber, A.A., Alagusundaram, K. [Eds.]. Proceeding 9<sup>th</sup> International Conference on Controlled Atmosphere and Fumigation in Stored Products, Antalya, Turkey. 15-19 October 2012, ARBER Professional Congress Services, Turkey pp: 609-619.
- Newman, C., 1994. Western Australia fumigation practice survey. In: Proceedings of International Conference on Controlled Atmosphere and Fumigation in Stored-Product (Edited by Highley, E., Wright, E.J. Banks, H.J. and Champ, B.R.), Canberra, Australia, 17-23 April, 1994, CAB International, Wallingford, Oxon, UK, 139-143.

- Noyes, R.T., Kenkel, P., 1994. Closed loop fumigation systems in the south-western United States. In: Proceedings of International Conference on Controlled Atmosphere and Fumigation in Stored-Product (Edited by Highley, E., Wright, E.J. Banks, H.J. and Champ, B.R.), Canberra, Australia, 17-23 April, 1994, CAB International, Wallingford, Oxon, UK, 335-341.
- Pike, V., 1994. Laboratory assessment of the efficacy of phosphine and methyl bromide fumigation against all stages of *Liposcelis entomophilus* (Enderlein). *Crop Protection* 13, 141-145.
- Price, N.R., Bell, C.H., 1981. Structure and development of embryos of *Ephestia cautella* (Walker) during anoxia and phosphine treatment. *International Journal of Invertebrate Reproduction* 3, 17-25.
- Price, N.R., 1984. Active exclusion of phosphine as a mechanism of resistance in *Ryzopertha dominica* (F.) (Coleoptera: Bostrychidae). *Journal of Stored Products Research* 21, 163-168.
- Rajendran, S., Muthu, M., 1991. Effect of fumigants on the hatchability of eggs of *Tribolium castaneum* Herbst. *Bulletin of Grain Technology* 29, 117-120.
- Rajendran, S., 2000. Inhibition of hatching of *Tribolium castaneum* by phosphine *Journal of Stored Products Research* 36, 101-106.
- Robinson, J.R., Bond, E.J., 1970. The toxic action of phosphine: Studies with <sup>32</sup>PH<sub>3</sub> terminal residues in biological materials. *Journal of Stored Products Research* 6, 133-146.
- Ryan, R.F., 1988. Pesticide Boosts Export Opportunity. *Process & Control Engineering, PACE*, Volume 41, Issue 4, April 1988, p8.
- Ryan, R.F., Latif, S., 1989. Fumigant System. US Patent 4,889,708, 26Dec. 1989.
- Ryan, R.F., 1997. Gaseous Phosphine - A Revitalised Fumigant. In: Proceedings of International Conference on Controlled Atmosphere and Fumigation in Stored Products (Edited by Donahaye, E.J., Navarro, S. and Varnava, A.), 21-26 April 1996, Printco Ltd, Nicosia, Cyprus, pp. 305- 310.
- Ryan, R.F., 1990. PHOSFUME<sup>®</sup> - A Gaseous Phosphine Grain Protectant. *Chemistry in Australia, Proceedings of the Royal Australian Chemical Institute* Volume 57, No. 6, June 1990, pp. 184.
- Ryan, R.F., 1992. Attaining insect-free and residue-free status in Foods. *Food Aust.* 1992, 44 (12) pp. 556.
- Ryan, R.F and Shore, W.P., 2005. Process and Apparatus for Supplying a Gaseous Mixture, U.S. Patent 6,840,256 B1.
- Ryan, R.F., Shore, W.P., 2010. Pre-Mix and on-site mixing of fumigants. 10th International Working Conference on Stored Product Protection. *Julius-Kühn-Archiv*, 425, 2010 pp. 419-422.
- Ryan, R.F., Shore, W.P., 2012. The use of Gaseous Phosphine by Onsite Mixing. In: Navarro, S., Banks, H.J., Jayas, D.S., Bell, C.H., Noyes, R.T., Ferizli, A.G., Emekci, M., Isikber, A.A., Alagusundaram, K. [Eds.]. *Proc. 9<sup>th</sup> Int. Conf. on Controlled Atmosphere and Fumigation in Stored Products*, Antalya, Turkey. 15-19 October 2012, ARBER Professional Congress Services, Turkey pp: 358-362.

- Scudamore, K.A., Goodship, G., 1986. Determination of Phosphine Residues in Fumigated Cereals and other Foodstuffs, *Pesticide Science* 37, 385-395.
- Sun, R., Guan, L., Zhang, C., Liu, C., Lui, J., 1993. Ducting Systems for Silo Fumigations in Tianjin Municipality, China. In: *Proc. Int. Conf. on Controlled Atmospheres and Fumigation in Grain Storages* (Edited by Navarro, S. and Donahaye, E.) Winnipeg, Canada, 11-13 June 1992. Caspit Press Ltd., Jerusalem, 343-351.
- Thornton, H., Kostas, E., Feineler, G., Tumaming, J., 2006. Commercial applications of the Horn Diluphos System and VAPORPH<sub>3</sub>PHOSPHINEOS<sup>®</sup> Phosphine Fumigant for sealed storage fumigation at CBH. Australian Postharvest Technical Conference, 2006, 16 - 18 July 2006, Perth, Western Australia.
- Varnava, A., Potsos, J., Russel, G., Ryan, R.F., 1998. New phosphine grain fumigation technology in Cyprus using SIROFLO/ECO<sub>2</sub>FUME flow-through method. In: *Proceedings of the 7<sup>th</sup> International Working Conference on Stored-Product Protection*. Jin, Z., Liang, Q., Liang, Y., Tan, X., and Guan, L [Eds]. 14-19 October, 1998. Beijing, China. Sichuan Publishing House of Science and Technology, Chengdu, China, pp. 409-415
- Wang, D.X., Ma, X.H., Bian, K., 2010. Mortality time of immature stages of susceptible and resistant strains of *Sitophilus oryzae* (L.) exposed to different phosphine concentrations. 10th International Working Conference on Stored Product Protection. 452-458
- Winks, R.G., 1987. Strategies for effective use of phosphine as a grain fumigant and the implications of resistance. In: Donahaye, E., Navarro, S. (Eds.), *Proceedings of the 4th International Working Conference on Stored Product Protection*, Tel Aviv, Israel, 1986, pp. 335-344.
- Winks, R.G., 1993. The Development of SIROFLO in Australia. In: *Proceedings of International Conference on Controlled Atmosphere and Fumigation in Grain Storages* (Edited by Navarro, S. and Donahaye, E.), Winnipeg, Canada, 11-13 June 1992, Caspit Press Ltd., Jerusalem, 399-410.
- Winks, R.G., Hyne, E.A., 1994. Measurement of resistance to grain fumigants with particular reference to phosphine. In: *Proceedings of 6<sup>th</sup> International Working Conference on Stored Product Protection* (Edited by Highley, E., Wright, E.J. Banks, H.J. and Champ, B.R.), Canberra, Australia, 17-23 April, 1994, CAB International, Wallingford, Oxon, UK, 244-250.
- Winks, R.G., Ryan, R.F., 1990. Recent Developments in the Fumigation of Grain with Phosphine. In: *Proceedings of 5<sup>th</sup> International Working Conference on Stored-Product Protection* (Edited by Fleurat-Lessard, F. and Ducom, P.), Bordeaux, France, 9-14 September 1990, 935-943.
- Winks, R.G., Russell, G.F., 1994. Effectiveness of SIROFLO<sup>®</sup> in vertical silos. In: *Proceedings of 6<sup>th</sup> International Working Conference on Stored-Product Protection*, (Edited by Highley, E., Wright, E.J., Banks, H.J. and Champ, B.R.). Canberra, Australia 17-23 April, 1994, CAB International, Wallingford, Oxon, UK, 244-250.

- Winks, R.G., Russell, G.F. (1997). Active Fumigation Systems: Better Ways to Fumigate Grain. In: Proceedings of International Conference on Controlled Atmosphere and Fumigation in Stored Products (Edited by Donahaye, E.J., Navarro, S. and Varnava, A.), 21-26 April 1996, Printco Ltd, Nicosia, Cyprus, pp. 293-303.
- Winks, R.G., Whittle, C.P., Ryan, R.F., 1995. Improved methods of application for fumigating grain with phosphine and the associated benefits. In: Proc.45<sup>th</sup> RACI Cereal Chem. Conf., Adelaide Australia, 10-14 September, 1995.
- Zettler, J.L., Gillenwater, H.B., Redlinger, L.M., Leesch, J.G., Davis, R., McDonald, L.L., Zehner, J.M., 1984. Efficacy of perforated tubing in assisting phosphine distribution for in-transit fumigation of export corn. *Journal of Economic Entomology* **77**, 675-679.
- Zettler, J.L., 1997. Influence of resistance on future fumigation technology. In: Proceedings of International Conference on Controlled Atmosphere and Fumigation in Stored Products (Edited by Donahaye, E.J., Navarro, S. and Varnava, A.), 21-26 April 1996, Nicosia, Cyprus, pp. 445-454.

