

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 (PH₃) fumigation. The original “solid” PH₃ patent was granted in Germany (1934) for the generation of PH₃ gas from aluminium phosphide on exposure to atmospheric moisture. The compressed 40 bar “liquid” PH₃ in industrial gas cylinders, with benefits of rapid and uniform PH₃ dispensing, was initially investigated as a fumigant for the control of fruit fly in 1976. The CIG patented non-flammable PHOSFUME (PH₃/CO₂) supported the CSIRO patented flow-through fumigation process (SIROFLO) developed to fumigate non-gastight grain storage (1986). The Agriculture Grade PH₃ (99 wt%) was more cost effective as a gaseous fumigant than the high cost Semiconductor Grade PH₃ (99.9999%) required for electronic devices manufacture. Specialty Gases’ UltraPhos product is manufactured by reacting white phosphorus (P₄) with excess caustic soda; $4P + 3NaOH + 3H_2O = PH_3 + 3NaH_2PO_4$. The critical impurities are diphosphine (P₂H₄) and white phosphorus (P₄) which are pyrophoric and can cause fires in dispensing equipment. The reaction of P₄ with excess caustic process ensures the elimination of P₄ in the UltraPhos fumigation product resulting in a superior product. The issue of polymer formation created by contact of PH₃ and oxygen (O₂) can be minimised with pre- and post-purging of PH₃ dispensing equipment. To avoid polymer dust build up in dispensing equipment the on-site mixing of PH₃/CO₂ requires using CO₂ that has low O₂ levels (less than 100 ppm). The elimination of the reactive incendiary P₄ by the excess caustic UltraPhos manufacturing process avoids the reported pyrophoric incidents and dispensing equipment blockages associated with PH₃ product containing the P₄ impurity.

Keywords: liquid PH₃ gas, PH₃ fumigation, on-site mixing PH₃ with CO₂ or Air, non-flammable PH₃ mixture, flow-through fumigation, metallic phosphides, white phosphorus, PH₃ polymers

1. Introduction

1.1. PH₃ history

Dependence on PH₃ fumigation has a long history – the generation of PH₃ gas from “solid” aluminium phosphide (AIP) 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 PH₃ 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” PH₃ formulations

The original “solid phosphine” formulation containing aluminium phosphide (AlP) 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 PH₃ needs to be free of white phosphorus (P₄) and diphosphine (P₂H₄) at trace levels (Fluck, 1973). The flammability hazard of PH₃ gas generated from “solid” formulations is minimised by slowly releasing PH₃ 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” PH₃ formulations

Commercial “liquid” PH₃ is manufactured into a range of proprietary chemicals for use in textile, mining and electronics industries. In very high purity (99.9999% pure) PH₃ is used in the manufacture of silicon electronics. The reaction of PH₃ with oxygen (O₂) 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 (P₂H₄) and white phosphorus (P₄) which are pyrophoric (Ryan, 1997). While gaseous phosphine has a longer history as a dopant in electronic silicon chip technology manufacture, PH₃ 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% PH₃ in CO₂; 2% PH₃ in N₂; and 2.4% PH₃+60% CO₂ in N₂ eliminate PH₃ flammability hazard (Ryan, 1997; Ryan and Latif, 1989). Current “liquid” PH₃ products include non-flammable ECO₂FUME[®] (2wt% phosphine in CO₂: BOC Gases) and FRISIN[®] (1.7vol% PH₃ in N₂- S&A Service und Anwendungstechnik GmbH). Flammable PH₃ [VAPORPH₃OS[®] – CYTEC Industries & UltraPhos[®] – Specialty Gases Pty Ltd] can be dispensed on-site by rapid dilution in turbulent air flow to less than 16,000 ppm/22 g PH₃/m³ or with inert gases (Ryan and Shore, 2005). Although more expensive, “liquid” PH₃ has benefits over the “solid” PH₃ as on-site mixing eliminates the spontaneous flammability hazard, allows accurate control of PH₃ concentration, deliver PH₃ more rapidly, achieve better distribution in the grain mass without disturbing grain, and allows controlled flow and dosage maintenance for long periods. Also “liquid” PH₃ 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. *PH₃* efficacy

Phosphine doses have been dramatically reduced from the 10,000 ppm (14 g/m³) used in the 1950's (Annis, 2001) to the current recommendations of 1 to 3g/m³ (718 ppm to 2,154 ppm) or as low as ~100 ppm (0.14 g/m³) 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 (O₂) and thus is not toxic to insects in a low O₂ atmosphere (Bond et al., 1967). Kashi and Bond (1975) showed that in the presence of 4% CO₂ 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 PH₃ and exposure time can be reduced when both CO₂ and O₂ are present. The optimum CO₂ concentration is in the range of 5-35%. At 5% CO₂ the PH₃ LC₉₀ can be reduced by ~50% (Kashi and Bond, 1975; Bond and Buckland, 1978). Australian recommendations are 1g to 3g PH₃/m³ for 7 to 21 days depending on temperature, commodity, insect species and storage type (Anonymous, 1989, 1992). Over the past 20 years phosphine have been successfully developed against insects in flowers, fruits and vegetables at relatively high doses of >1.4 g PH₃/m³ for relatively short exposure period (6-24 h) 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. *PH₃* efficacy on grain insects

Since the 1950's the primary method of PH₃ 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 PH₃ the preference was to use methyl bromide (Bond, 1989). With the development of better gastight silos dosage of PH₃ of 1.5 g/m³ 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 EPPO standards (EPPO, 2012) of 3 g PH₃/m³ for 7days at 20°C increasing to 12 days at 10°C are observed, often requiring a minimum of 300 ppm (0.4 g/m³) for 7 days to be successful. PH₃ supplied in gaseous form is instantly available (as opposed to the slow release of "solid" PH₃ 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 PH₃/CO₂ mixture were conducted by Cooperative Bulk Handling (Western Australia) in gastight 2,000 tonne vertical and 15,000 tonne horizontal bulk grain storage (Ryan, 1988). The 0.17 g/tonne PH₃ dose was evenly distributed by natural convection in the 15,000 tonne sealed storage within 44 hours and a concentration in excess of 100 ppm was maintained for 260 hours (treatment cost AUD 0.05/tonne). The 30,000 t bunker storages in Queensland (Ryan; 1990, 1992) used 0.3 g PH₃/tonne with treatment cost of AUD 0.10/tonne. By combining treatments of PH₃+CO₂ (Carmi et al., 1990, 1994) and PH₃+CO₂+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[®] (Chakrabarti et al., 1994); and the Degesch J-SYSTEM[®] (Zettler et al., 1984). These technologies reduce the dosage of PH₃ 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 PH₃+CO₂ 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 PH₃ gas from cylinders with CO₂ 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 PH₃ with onsite mixing of gaseous phosphine in air (Thornton et al., 2006).

2.1.2. efficacy of PH₃FloThru[®]: Continuous flow-through application in leaky storage

For effective fumigation it is critical that the storage is gastight to ensure PH₃ 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 PH₃ (Anonymous, 1980; Winks, 1987). Many Australian grain storages that fail the gas tightness test are fumigated using the SIROFLO[®] 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) PH₃ 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. PH₃ residues

Baking studies showed that there were no PH₃ residues in baked products even when “solid” PH₃ metallic phosphides were added to the flour immediately before baking (Bruce et al., 1962). In tests using ³²P to assess the presence of phosphorus residues after PH₃ 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 PH₃ concentrations, residues of the order of 0.04 ppm to 1.2 ppm (calculated as PH₃) 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/m³ (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/m³ (for 4, 7 and 14 days) and after 1 day all residues were less than 0.02 mg/kg. Scudamore and 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/m³ 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 and Goodship, 1986).

2.3. Insect resistance to PH₃

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 PH₃ did not alter the development period of eggs of the tropical warehouse moth *Ephesia cautella* treated at 0.8 g/m³ for 24 h while Pike (1994) found no development inhibition in psocids *Liposcelis entomophila* at 0.8 g/m³ 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 PH₃. 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 120 h as well as a resistant strain treated at 300 ppm for 72 h. These data indicated that PH₃ 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 PH₃ 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 PH₃ compared with controls, with delay increasing as PH₃ concentrations increased e.g. hatching in eggs exposed to 0.05 g/m³ for 6 days was delayed by 7 days whereas eggs exposed to 1 g/m³ 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/m³ 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 PH₃ 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 PH₃ ('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 *T. 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/m³ 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 Discussion

3.1. Phosphine alternatives

The current industry trend is the substitution of the traditional “solid” PH₃ formulations with the more sophisticated, versatile and controllable “liquid” PH₃ supplied in industrial gas cylinders. In some regions there is a dominance of the “liquid” PH₃ 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_{0.5}: 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’ PH₃ to maintain the optimum concentration with regular additions to compensate for minor PH₃ leaks and sorption by the grain.

The capability of the “liquid” PH₃ to maintain the required concentration even in leaky storage using flow-through fumigation is an important capability in the control of PH₃ resistant insects. Often increasing the CxT by extending the exposure time can achieve control of PH₃ resistant insects. A potential candidate to counter PH₃ resistance insects is methyl-phosphine which is efficacious against PH₃ resistant insects but not so effective against PH₃ susceptible insects (Chaudhry et al., 1997).

Other possible PH₃ alternative option is the occasional use of other “break” fumigants however there are some issues. Possible other fumigants include: sulfuryl fluoride (SF)₂ – however SF₂ has poor efficacy against the egg stage of storage pests; high pressure CO₂ – 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 CO₂; hydrogen cyanide (HCN) – has limited use on grain due to its highly sorptive nature; EthaneDiNitrile (C₂N₂) – is a broad spectrum fumigant but is also sorptive; modified atmospheres involving elevated CO₂ or low O₂ 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 P₄ by the excess caustic UltraPhos manufacturing process avoids the reported pyrophoric incidents and dispensing equipment blockages associated with PH₃ product containing the P₄ impurity.

4. Conclusions

The growth of PH₃ as the preferred fumigant for stored products is due to the benefits of high pressure compressed “liquid” PH₃ marketed in industrial gas cylinders. The flammability issue of the pure 99wt% PH₃ is eliminated using on-site dilution/mixing with CO₂ or Air. The reliable and proven on-site PH₃/CO₂ mixing technology was the forerunner for on-site mixing of PH₃/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 PH₃FloThru[®], the continuous flow-through fumigation. The PH₃FloThru[®] requires long exposure time of accurately controlled low flow PH₃ dosing which is only possible using “liquid” PH₃ cylinders control equipment.

In addition to ensuring non-flammability by adequate dilution of PH₃ in air (a conservative limit is 16,000 ppm i.e. 1.6% PH₃) other issues are impurities and pre- /post-purging of the equipment. The critical impurities are diphosphine (P₂H₄) and white phosphorus (P₄) which are pyrophoric and can cause fires in dispensing equipment. The reaction of P₄ with excess caustic process ensures the elimination of P₄ in the UltraPhos fumigation product resulting in a superior product. The issue of polymer formation created by contact of PH₃ and oxygen (O₂) can be minimised with pre- and post-purging of PH₃ dispensing equipment. The elimination of the reactive incendiary P₄ by the excess caustic UltraPhos manufacturing process avoids the reported pyrophoric incidents and dispensing equipment blockages associated with PH₃ product containing the P₄ impurity.

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