PHOSPHINE – AN OVERVIEW OF A UNIQUE 80 YEAR FUMIGANT

Robert F. Ryan[1] and C. P. Francis De Lima[2]

[1]VAPORFAZE, PO Box 4, Sans Souci NSW 2219 Australia; robert.ryan.consultant@gmail.com
[2]Principal Research Entomologist, Department of Agriculture and Food, South Perth WA; francis.delima@agric.wa.gov.au

Summary

Phosphine was patented 80 years ago as a solid formulation for crop protection and continues to be widely used to this day in many new forms for fumigation. This overview summarises the development, use and value to global food production of this unique agricultural chemical over the past eight decades. On farm 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. Phosphine's enduring value to agriculture is due to its unique qualities of relative safety in handling, 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 successfully 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 pests in animal fodder, fresh flowers, vegetables and fruits bringing new and exciting challenges to agricultural research. 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.

Key words: phosphine, fumigant, pest control

INTRODUCTION

The need to control insects in grain and foodstuffs to prevent food losses and to satisfy marketing requirements is an ever present need. Aluminium phosphide, was developed in Germany in 1934 (Freyberg 1935, 1938) as a solid formulation to enable the generation of phosphine gas on exposure to moisture in the atmosphere. This usage was relatively safe because the flammable PH_3 was released slowly over days by dilution with the surrounding air. Widespread practical use began in the mid 1950's when alternatives were required for reasons of safety and portability to ethylene dibromide, ethylene dichloride and carbon tetrachloride in the tropics, and methyl bromide in temperate areas (Munro 1969). Thereafter PH_3 replaced the alternatives because of its relative ease of use under a variety of circumstances, far lower costs, superior efficacy, low residues and low environmental impact. After 80 years of use as a fumigant, PH_3 continues to be used for "Exterminating of Beetles and other Vermin" as envisaged in the original patent application. In the mid 1970's magnesium phosphide formulations were made available and are more commonly used today to treat large and small volumes of produce. PH_3 is widely registered for disinfestation, and is the only MB alternative extensively used for cereals, legumes, dried fruits, nuts, beverages, herbs and spices. PH_3 replaced MB, long before its regulation by parties of the Montreal Protocol, wherever temperature and time were not constraints (Ducom 2006). PH_3 is a naturally occurring gas, albeit short lived because it reacts with the atmosphere forming phosphoric acid (Fluck 1973a) an acid used extensively as a food additive. In the mid 1980's gaseous PH_3 was made available as a fumigant for agriculture in non-flammable gas mixtures in carbon dioxide (CO_2) and nitrogen (N_2) following its supply for decades as 99.3% pure gas to the textile and mining industries for industrial process. Australia exports about 80% of the grains it produces, but to maintain market access its grain must be free from live insects and pesticide residues. For over 50 years the proper use of PH_3 fumigation has enabled the grain industry to meet these requirements. Since the early 1990's the major focus in the grains industry has been on monitoring of PH_3 resistance. Over the past 20 years new technology has enabled PH_3 to be supplied as a liquid under pressure in gas cylinders in pure form or mixed with liquefied CO_2 or N_2 enabling use in fresh produce and timber.

FORMULATIONS

Solid Formulations

The original metallic phosphide ("solid phosphine") formulation patent was lodged in Germany on Nov 6, 1934 and in the USA on May 10, 1938 (Freyberg, 1935, 1938). PH_3 gas is generated from the phosphide by reacting with moisture, but needs to be free of trace levels of diphosphine (P_2H_4) and higher phosphines to avoid being spontaneously flammable (Fluck 1973b). The flammability hazard is minimised by releasing PH_3 slowly to allow safe dilution with the surrounding air. These formulations are sold as pellets, tablets, and sachets of aluminium, calcium or magnesium phosphide mixed with inert ingredients such as ammonium carbonate from which phosphine is slowly evolved by reaction with moisture in the surrounding atmosphere. The major advantages of these formulations are high portability, safety in use, low cost, and versatility of application under a variety of conditions. Negative issues include unreacted powder residues, disposal costs and long exposure times (Gallagher et al. 1995, Ryan and Shore 2012).

Gaseous Phosphine

Commercial gaseous PH_3 is manufactured in a range of proprietary PH_3 based chemicals for use in textile, mining and electronics industries. It is an intermediate in the synthesis of flame retardants for cotton fabrics, a doping agent for n-type semiconductors, a polymerization initiator, and a condensation catalyst (Ohtiani et al. 1989). In very high purity (99.999% pure) gaseous PH_3 is used in the manufacture of silicon electronics. The commercial manufacture of gaseous PH_3 is either from white phosphorus (reaction with caustic soda: $4P + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2 PO_2$) or from red phosphorus (reaction with steam: $8P + 12H_2O \rightarrow PH_3 + 3H_3 PO_4$). The fumigation grade PH_3 is of lower purity than electronic grade PH_3, however there are critical specifications for impurities such as di-phosphine (P_2H_4) and white phosphorus (P_4) which are pyrophoric (Gallagher et al. 1991, Ryan, 1997). While gaseous PH_3 has a longer history as a dopant in electronic silicon chip technology manufacture, it 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 PH_3 products launched in the early 1980's have been published (Ryan, 1997; Cavasin et al., 2000; McSwigan et al., 2004; Cavasin et al., 2006; Cavasin et al., 2008; Tumambing et al., 2012).

PH3 has a wide flammable range in air and various mixtures with CO2 and/or N2 have been patented to overcome this problem (Ryan 1997, Ryan and Latif 1989). The flammable PH3 formulation VAPORPH3OS® (99.3% PH3 CYTEC Industries) can be dispensed onsite by rapid dilution in turbulent air flow to less than 16,000 ppm (ca. 22g PH3/m3) in air (Ryan and Shore, 2005) or onsite mixing with inert gases. Gaseous PH3 generated onsite from the "solid PH3" formulations can release in excess of 5 kg PH3/h (Navarro 2006). The Horn Diluphos System™ supplies 10,000 ppm (ca. 14g PH3/m3) at rates of 19 to 200 g/min in air (Horn and Horn 2006). Although more expensive, the non-flammable compressed gaseous PH3 mixtures have benefits over the solid metal phosphide formulations inasmuch as they eliminate the PH3 spontaneous flammability hazard, allow accurate control of PH3 concentration, deliver PH3 gas more rapidly, achieve better distribution in the grain mass without disturbing grain, allow controlled flow and dosage maintenance for long periods. While gaseous PH3 eliminates handling and disposal of the "spent" metallic phosphide tablets and requires less labour it reacts with oxygen to produce a polymer dust and oily phosphoric acid which affects control valves and has other OH&S issues (Schonstein et al. 1994, Ryan and Shore 2012). The reaction of PH3 with oxygen to form polymers is an issue which requires pre- & post-purging of PH3 dispensing systems.

DOSAGE AND EFFICACY

Phosphine doses have been dramatically reduced from the 10,000ppm (14g/m^3) used in the 1950's (Annis 2001) to the current recommendations of 1-3g PH_3/m^3 (718 - 2,154 ppm) or as low as ~100ppm (0.14 g/m^3) in a continuous flow system (Anon. 1992). The critical requirement of a successful fumigation is to provide an adequate concentration (C) for a sufficient period of time (T). With most fumigants the CxT product is a constant ("Habers Rule") (Miller et al. 2000), but the response of insects to PH_3 is far more effective if the exposure time is lengthened because PH_3 is a slow acting poison. High concentrations do not increase toxicity unless the exposure time is increased (Bond et al. 1969, Howe 1974, Hole et al. 1976, Winks 1986, Winks and Hyne 1994). Annis (2001) examined >3,000 records of reliable data of all stored product psocids moths and beetles (excluding *Trogoderma* spp.) from the 1950's to 2000 and found that >99% mortality was achieved by applying PH_3 in the range of 10,000 ppm for 1.5 days to 10 ppm for 30 days. Issues of PH_3 specific insect toxicity thresholds and of narcosis induced in insects at very high doses of PH_3 and the potential for inducing resistance in technically unfounded low dosages have been reported by Nakakita et al. 1974, Reichmuth 1994, and Winks 1984, 1987).

A unique characteristic of PH_3 is that it is not absorbed in the absence of oxygen and is not toxic to insects (Bond et al. 1967, 1969, Cherfuka et al. 1976). Kashi and Bond (1975) showed that in the presence of 4% CO_2 there was a 20% increase in the uptake of oxygen and a 3-fold increase in the toxicity of PH_3 to insects. The action of phosphine is potentiated by carbon dioxide and the concentration and exposure time can be reduced when both CO_2 and O_2 are present. The optimum CO_2 concentration is in the range of 5-35%. At 5% CO_2 the PH_3 dose for LC_{90} efficacy can be reduced by ~50% (Kashi and Bond 1975, Bond and Buckland 1978). Over the past 20 years PH_3 have been successfully developed against insects in flowers, fruits and vegetables at relatively high doses of >1.4g PH_3/m^3 for relatively short exposure periods of 6-24h at low temperatures <15°C on adults and immature stages of a number of insect and mite species (Karunaratne et al. 1997a, De Lima

2001, Horn and Horn 2004, Liu 2008, and Jamieson et al. 2012).

GRAINS

Solid PH_3 applications

Since the 1950's the primary method of PH_3 application has been through the use of tablets, pellets and sachets in farm silos, freight trains, bulk vehicles, in warehouse under fumigation sheets, etc. However, because of its small molecular size, PH_3 gas was difficult to retain for the required long exposure period, and the preference was to use methyl bromide (Bond 1989). With the development of better gas-tight silos, the dosage of PH_3 in solid form of 1.5g PH_3/m^3 is now recommended with a minimum of 300ppm for 7 days or 200ppm for 10 days in Australia (Anon. 2013).). In most overseas countries EPPO standards of 3g PH_3/m^3 for 7d at 20°C (or 12d at 10°C) are observed, with a minimum of 300ppm (0.4g PH_3/m^3) required for 7 days for the fumigation to be successful (EPPO 2012). If *Trogoderma granarium* is present the rate is increased to 5g PH_3/m^3 for 4d at >25°C (or 9g PH_3/m^3 for 20d at 10°C for diapausing larvae) (EPPO 2012a). Australian recommendations are 1g - 3g PH_3/m^3 for 7 - 21 days depending on temperature, commodity, insect species and storage type (Anon 1989, Anon. 1992). In commercial fumigations shorter exposure periods of less than 5 days have been used to control adults only (Zettler 1993, Rajendran and Navasimhan 1994).

Gaseous PH_3 applications in gas-tight structures

Phosphine supplied in gaseous form is available immediately, in contrast to the slow release of solid formulations, but must be carried out in gastight storage structures sealed to the appropriate standards (Banks and Annis 1984, Anon. 1980). The first applications of the non-flammable gaseous PH_3/CO_2 mixture (PHOSFUME®) were successfully completed in gastight horizontal bulk grain storages of 15,000t and 30,000t using 0.17 or 0.3g PH3 per tonne (Ryan, 1988, 1990, 1992). The dose was evenly distributed by natural convection and exceeded 100ppm for 260 hours. Treatment costs were between \$0.05 and \$0.10 per tonne. By combining treatments of PH_3 with CO_2 (Carmi et al. 1990, 1994) and PH_3 with CO_2 plus heat (Mueller, 1994), successful fumigations were achieved in large silos and flour mills. CO_2 helps the movement of PH_3 through commodities and the addition of heat lowers the effective dose of PH_3 required for a lethal CxT product (Zettler, 1997). Recirculation of PH_3 in gastight structures (Cook, 1984) was done under various conditions including: the closed-loop system in the USA (Kenkel et al. 1993, Noyes and Kenkel 1994); the circumfluent system in China (Sun et al. 1993, Lu et al. 1994); the PHYTO-EXPLO® (Chakrabarti et al. 1994, Vaquer et al. 1993a, b); and the J-SYSTEM® (Degesch) (Zettler et al. 1984, and Leesch et al. 1986). These technologies reduce the dosage of PH_3 required to produce a lethal CxT product in grain pests and thus improve the efficiency of conventional types of PH_3 fumigations (Zettler 1997). A grain terminal in China with capacity 1.4m tonnes comprising multiple 30,000 tonne gastight vertical grain storages was successfully treated with gaseous PH_3 mixed with CO_2 from a bulk refrigerated liquid tank (Ryan and Shore (2010). Fumigation of wheat in a 300,000t sealed horizontal shed at Cooperative Bulk Handling, Kwinana, Western Australia successfully used 0.45 g/t PH_3 recirculation with onsite mixing of gaseous PH_3 in air (Thornton et al. 2006).

Continuous flow PH_3 applications in leaky structures

Many older Australian grain storages fail to meet the specified standards of gas tightness for phosphine application (Anon. 1980, Winks, 1987). However with appropriate modifications to the silo, flow-through technologies such as SIROFLO® (Winks 1993) or other systems using PH_3/CO_2 mixtures can be used (Bell et al. 1993, Chakrabarti et al. 1994). In the SIROFLO® technique a continuous flow of low concentration (eg 120ppm) for an extended time (eg 21-28d) is introduced at the base of a vertical silo and allowed to rise through the bulk to emerge from the surface. The technique is effective because insect eggs and pupae, which are naturally tolerant to phosphine, continue to develop to larvae and adults while the bulk is still under fumigation (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 used for storage again and has enabled grain handlers to decrease their reliance on protectants in eastern Australia (Collins 2010). However, in the European Union this method is not acceptable because the resulting PH_3 emissions exceed clean air standards (Reichmuth 1999) while Pratt (1998) found a high frequency of emissions exceeded the 1ppb EU emission limit even though he applied PH_3 at low levels.

Small scale PH_3 applications for subsistence grain storage

The application of phosphine has been of invaluable benefit in preventing food losses at the subsistence level where grain is stored in structures such as well-sealed gourds, small metal containers and poly-lined mud bins (De Lima 1976, 1978a, 1978b, 1983, 1988). Subsistence maize, millet, sorghum, beans, cowpeas, groundnuts, has been successfully stored in many African countries, as well as in wheat, maize and rice in Pakistan (De Lima 1985). When used as part of an integrated program (De Lima 1976, 1978a), dosage of between 2 and 6 g/m^3 over a 3 week period killed *Oryzaephilus surinamensis* (L.), *Lasioderma serricorne* (F.), *Ephestia elutella* (Hubner), *Plodia interpunctella* (Hubner), *Acanthoscelides obtectus* (Say), *Callosobruchus maculatus* (F.), *Sitophilus zeamais* (Motsch.), *Sitophilus oryzae* (L.), *Rhyzopertha dominica* (F.), *Sitotroga cerealella* (Olivier), *Tribolium spp*., *Cryptolestes spp. Prostephanus truncatus* (Horn), and psocids. By using phosphine sold in pellet form (0.2g/m^3) human toxicity issues were avoided and since the volume of product treated was very small and leakage low (De Lima 1983, 1985) the application in small air-tight containers effectively protected the fraction of grain intended for consumption later in the season crucially in the 3-6 months after the main harvest.

PH_3 applications for large-scale long term hermetic grain storage for food security

Grain can be stored in good quality for many years as a famine reserve if preserved in air-tight structures (De Lima 1980a, 1980b, 1982). However because hermetic storage alone cannot control insects because of insufficient reduction in oxygen levels in insect free grain, De Lima (1984) applied and maintained PH_3 at very low dosages of 0.03-0.07g/m^3 (20-50ppm) over several months in 68 x 1,000 m^3 hermetic bins. In this way he achieved effective protection of over a million tonnes of maize and wheat in continuous storage from 1972 to 1984. Over a period of >10 years, grain for famine reserve was continuously stored in individual bins for periods of 4 years with losses due to all factors (handling, insect damage, fungal spoilage, heating, etc.) of less than 0.8% (De Lima 1984, 1990). De Lima (1984, 1990) showed that the presence of >6% oxygen in the air-tight bins made phosphine more effective in killing insects.

FODDER

The world-wide trade in fodder for animal feed requires disinfestation for many insect pests of quarantine concern. Yokoyama et al. (1993, 1996, 2001) used PH_3 alone or in combination with physical treatments including bale compression to disinfest hay from Hessian fly *Mayetiola destructor* (Say) and cereal leaf beetle *Oulema melanopus* (L) using 2.2g/m^3 (1,500ppm) for 7 days at >15.5°C. Quarantine treatments using PH_3 for a range of insects found in oaten hay fodder were developed (De Lima et al. 1994, De Lima 2000) in 40ft 67m^3 shipping containers. Treatments were successfully done at container loadings of up to 0.45 tonnes/m^3 using gaseous PH_3 against adults of several species present in exported baled hay including: *Ahasverus advena*, *Anacharis spp.*, Anthicidae, *Anthicus floralis*, *Carpophilus spp.*, *Cryptolestes spp.*, *Desiantha diversipes*, Lauxaniidae, Lygaeidae, Sciaridae, Staphylibidae, *Tribolium castaneum*, *Typhaea stercorea* (De Lima 1994).

TIMBER

Phosphine trials of 200ppm PH_3 (0.3g/m^3) for 10 days on radiata pine logs and sawn timber in New Zealand (Brash and Page 2009) successfully controlled six pests of quarantine importance: bark-borne burnt pine longhorn *Arhopalus ferus* (Mulsant), black pinebark beetle *Hylastes ater* (Paykull), goldenhaired barkbeetle *Hylurgus ligniperda* (Fabricius), Sirex wasp *Sirex noctilio* (F.), huhu *Prionoplus reticularis* (White) and New Zealand drywood termite *Kalotermes brouni* (Froggatt). Shorter times and higher doses e.g. 2,100 ppm (3g/m^3) PH_3 for 72 hours killed adult stages of most species and juveniles of *Kalotermes brouni,* but the mortality of eggs and larvae were less than 100% (Zhang et al. 2006, Cavasin et al. 2006).

CUT FLOWERS

Kangroo paw *Anigozanthos manglesii* Hook, was not damaged when exposed to PH_3 as high as 11.2g/m^3 for 6h Karunaratne et al. (1997a) whereas PH_3 at 5.6g/m^3 for 4h reduced shelf life of King Protea *Protea cynaroides* L., tulip *Tulipina gesneriana* and Geraldton Wax *Chamelaucium unicinatum*. PH_3 at 0.4g/m^3 at 24°C killed adult greenhouse thrips (*Heliothrips haemorrhoidalis* Bouche) within 18h (Karunaratne et al. 1997b) while adult aphids (*Myzus persicae* Sulzer) required 1.4g/m^3 PH_3 + 33% CO_2 for 4h at 24°C. Williams et al. (1998) found no damage at 1.1g/m^3 for 5h in *Tryptomene spp*., *Leucadendron spp*., *Chamelaicum spp*., and *Dianthus spp*. after 7 days after treatment, however they found that while 0.3g/m^3 PH_3 for 4.5h was sufficient to kill *Myzus persicae*, the fumigation needed to be extended to 15.5h to kill a related species *M. ornatus*. PH_3 at 1g/m^3 for 5h at 15°C was not phytotoxic to Protea `Pink Ice' (Weller and van S. Graver, 1998) but did not kill all life stages of psocids (*Liposcelis bostrichophila*), non-diapausing two spotted mite (*Tetranychus urticae*), cotton whitefly Type B (*Bemisia tabaci*) rice weevils (*Sitophilus oryzae*) and ants (*Iridomyrex purpureus*). De Lima (2001) applied 2.2 g/m^3 PH_3 at 10°C for 24h against adults of western flower thrips (*Frankliniella occidentalis* Pergande) in Geraldton wax *Chamelaucium uncinatum* and obtained 100% mortality without damage to flowers. Zhang et al. (2013) used PH_3 fumigation for 6h with dosages as high as 12.2g/m^3 at 24°C and found no adverse effects on chrysanthemum, carnation, rose, and Chinese rose flowers but damage occurred at 2°C for 12d fumigation. Park et al. (2010) showed that PH_3 at 2-4g/m^3 for 24h at 8°C controlled eggs and adults of *Tetranychus uriticae*, larvae and adults of *Aphis gossypii* and *Frankliniella occidentalis* in cut flowers without damaging roses, chrysanthemums and lily. Liu (2011a, b) found efficacy of PH_3 1.4g/m^3 for 5h at 5°C against western flower thrips *Frankliniella occidentalis* increased significantly from 79.5 to 97.7% when oxygen was increased from 20.9 to 40% and reached 99.3% using 80% O_2 oxygenated PH_3

SWEET CORN

Phosphine alone and in combination with 25% CO_2 at 10°C was effective (De Lima 2003, 2011) against corn earworm, *Helicoverpa armigera*, Australian bollworm, *H. punctigera*, two spotted spider mite *Tetranychus urticae*, plague thrips *Thrips imaginis*, western flower thrips *Frankliniella occidentalis*, green peach aphid *Myzus persicae* and corn aphid *Rhopalosiphum maidis*. All insects were controlled at 4g/m^3 phosphine in 72h exposures but required only 3g/m^3 in 25% CO_2. Fumigation in a 20ft refrigerated shipping container for 48h with 4g/m^3 PH_3 in N_2 and 4.1% loading gave 100% control of all insects at 5°C. The treated produce did not show any phytotoxic symptoms even after further storage for 20 days at 5°C.

KIWIFRUIT

Jamieson et al. (2012) fumigated kiwifruit infested with oleander scale insects for 48h and long-tailed mealybug for 12h at 1.7–4.6°C with 4.6 to 8.8g/m^3 PH_3 and achieved 100% mortality of all life stages. They required 3.8 to 6.1g/m^3 PH_3 for 36h at 2.5–3.3°C to achieve 100% mortality of all greedy scale insect life stages. Diapausing two spotted spider mite adults required 1.6 to 5.1g/m^3 PH_3 for 96h and 48h respectively at 1–15°C to achieve 91.3–100% mortality. The quality of kiwifruit was affected at doses >2.8g/m^3 PH_3 with metallic aromas detected.

OTHER FRUITS, VEGETABLES AND NURSERY PLANTS

Liu (2008) fumigated western flower thrips *Frankliniella occidentalis* using 0.7 and 1.4g/m^3 PH_3 for 24h at 2°C to obtain 100% mortality in lettuce, broccoli, asparagus and strawberry without causing any damage. However, 2.8g/m^3 PH_3 for 6h at 2°C obtained only 98.8% mortality demonstrating that the longer exposure time was more important to obtain complete kill of insects than the higher PH_3 dose. Liu (2012) found that 2.8g/m^3 PH_3 for 72h under normal atmosphere (20.9% O_2) and an oxygenated (60% O_2) 1.4g/m^3 PH_3 for 48h at 3°C both achieved complete control of the aphid, *Nasonovia ribisnigri* (Mosley) on romaine and head lettuce with less phytotoxicity under the shorter fumigation. Phosphine tolerant light brown apple moth *Epiphyas postvittana* eggs were controlled (Liu et al. 2013) using 60% oxygenated PH_3 for 72h at 5 and 10°C. Horn and Horn (2004) used 2.1g/m^3 PH_3 at <0ºC for 62.5h and to achieve 100% control in adults and crawlers and 99.7% control of eggs of *Pseudococcus viburni* and 100% control of larvae of codling moth *Cydia pomonella* in apples. Horn et al. (2005) and Horn (2012) found that 3.5g/m^3 PH_3 (2% PH_3 in N_2) for 72h at 6ºC was not sufficient to control false Chilean mite (*Brevipalpus chilensis*) but the addition of cold treatment for 10 days at 0ºC was an effective combined treatment. Klementz et al. (2005) fumigated table grapes at 2g/m^3 PH_3 at 0°C for 48 hours and did not find any significant loss in quality of fruits. Brash et al. (2009) controlled 5th instar codling moth in apples at 0.5ºC using 1.4g/m^3 PH_3 for 96h. Fumigation of imported nursery plants at 2g/m^3 PH_3 at 15°C for 24 hours controlled the egg stage of *Planococcus citri* (citrus mealy bug) without phytotoxic effects to dracaena and palm trees (Moon et al. 2012). Cuthbertson *et al*. (2013) fumigated rooted and cut chrysanthemum plants containing all stages of *Bemisia tabaci*, *Liriomyza huidobrensis* and *Frankliniella occidentalis* at 15ºC for 24h and found that 2g/m^3 PH_3 in a large scale test achieved 100% kill in *L. huidobrensis* eggs and pupae but only, 98.5% in *B. tabaci* eggs and 86% in *F. occidentalis* eggs with no significant effect on plant growth.

RESIDUES

Baking studies showed no phosphine residues in baked products even when metallic phosphides were added to the flour immediately before baking (Bruce et al. 1962). In tests using ^{32}P to assess the presence of phosphorus residues after PH_3 treatment of wheat and flour, the radioactive residue consisted mainly of water soluble fractions of hypophosphite and phosphite and was not removed by aeration or by heating at baking temperature. At practical PH_3 concentrations, residues of the order of 0·04-1·2 ppm calculated as PH_3 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 $3g/m^3$ (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. All residues of phosphine were below the tolerance limit (0.02mg/kg) within 2 days. Dumas (1980) fumigated whole cereal grains with CxT product up to $190g.h/m^3$ (for 4, 7 and 14 days) and found after 1 day all residues were less than 0.02mg/kg. Scudamore & Goodship (1986) recorded residue levels of 0.001 ppm PH_3 in several fumigated foodstuffs, but hazelnuts and brazilnuts fumigated with CxT products up to $125g.h/m^3$ for 4 and 7 days resulted in initial residues >0.2mg/kg and required 14 days to drop below the WHO/FAO Codex limit of 0.1mg/kg. There was no significant increase in residues between fumigations at 10 and $25^{\circ}C$ (Scudamore et al. 1986). Flingelli et al. (2010) fumigated kiwifruit at $3.5g/m^3$ PH_3 for 4 days at 15°C and found that residues did not exceed the European Minimum Residue Limit for fruits of 50 µg PH_3/kg after a waiting period of less than 12h. Brash et al. (2009) found that PH_3 residues in apples fumigated for 48 h at 5°C were below the detection limit of 0.01 mg/kg.

RESISTANCE

Resistance to phosphine has occurred in every insect species tested (Winks and Ryan, 1990) and there is considerable variation in susceptibility of different stages in the insect's life cycle (Howe 1973, 1974, Hole 1976, Bell 1976, Winks and Hyne, 1994, 1997). By using long treatment exposure periods, the more tolerant stages of eggs and pupae will in general develop to susceptible larvae and adults and succumb to fumigation if the concentration has been maintained (Lindgren and Vincent 1966, Nakakita and Winks 1981, Winks and Ryan, 1990, Bell et al. 1997). In early work, Price and Bell (1981) reported that PH_3 did not alter the development period of eggs of the tropical warehouse moth *Ephestia cautella* treated at PH_3 $0.8g/m^3$ for 24h while Pike (1994) found no development inhibition in psocids *Liposcelis entomophila* at $0.8g/m^3$ 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_3, and Rajendran (2000) reported a delay in hatching in PH_3 fumigated insects compared with untreated controls. He showed that hatching was delayed in both a susceptible and a resistant strain, and would have 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_3 and found that while PH_3 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, 2002) found that egg hatch was delayed in psocid eggs of *Liposcelis bostrychophila* exposed to PH_3, and the delay increased from 7d to 14d when the concentration increasedfrom0.05 g/m^3 to $1g/m^3$.

The differential toxicity of PH_3 among insect species can be the result of an active exclusion mechanism which seems to reduce the uptake of PH_3 in resistant *Ryzopertha dominica* strains (Price, 1984, Chaudhry and Price 1992, Daglish 2004), while in *Tribolium castaneum*, a kind of narcosis is induced at concentrations between 0.5 to 1 g/m^3 PH_3. These insects become inactive and reduce their uptake of gas, thereby surviving longer than at higher or lower concentrations (Winks 1984). Other metabolic mechanisms may also be involved. When assessment of resistance is uncertain, a more meaningful method is to use data from mixed cultures, enabling recommendations to be made for better PH_3 fumigation in the field (Winks and Hyne 1994, 1997). These authors 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.

In Australia resistance has become a widespread problem in most commercial storages, while claims of resistance are increasing in other parts of the world. There is considerable evidence that the development of PH_3 resistance is associated with inadequate fumigation (Price 1984, 1986; Tyler et al. 1983; Taylor, 1989; Banks, 1994), including poorly maintained on-farm sealed storage in Australia (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, and 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 three levels of resistance to PH_3 ('weak' and 'strong' and 'very strong'), and it has been suggested that once the frequency of 'weak' resistance reaches about 80% in a population there is a strong possibility of development of strong resistance in that species (Collins and Emery, 2002). This was illustrated in the development of strong resistance in *Tribolium castaneum* (Herbst) in

Western Australia in 2010 (Emery et al. 2011). Development of very strong resistance (875x) to PH_3 in flat grain beetles *Cryptolestes ferrugineus* in large bulk storages in Australia poses a serious threat. At $1g/m^3$ PH_3 *C. ferrugineus* requires a fumigation period of 24d compared with current recommended periods of 10d and 12d 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 facing the Australian grain industry since this resistance is several times greater than in any other species. The Australian National Phosphine Management Strategy holistic approach (Nayak 2012) has shown encouraging results in the effective management of this strain through use of sulfuryl fluoride as an alternative fumigant and in the implementation of an eradication plan.

ALTERNATIVES TO PHOSPHINE

Approaches to combat resistance can include use of oxygenated PH_3 fumigations since these are significantly more effective than fumigations under normal atmospheric pressure O_2. The application of methyl-phosphine (Chaudhry et al. 1997) has the potential to counter PH_3 resistance in insects. Other alternatives may have potential in particular situations but phosphine remains the most effective treatment at present. Sulfuryl fluoride (SF) is likely to have a role with control of psocids but it has poor efficacy against the egg stage of storage pests. CO_2 is well accepted as a treatment for organic grain and has excellent potential for rapid disinfestation at high pressure but there are high costs associated with the construction and operation of high-pressure chambers. Carbonyl sulphide (COS) has not been commercialised although it had generally good efficacy except for *S. oryzae*, and ethyl formate (EF) can be effective against a range of insects when combined with CO_2. Hydrogen cyanide (HCN) had been used in a limited way on grain despite its high sorption, but is no longer registered, and ethanedinitrile (C_2N_2) is a new broad-spectrum fumigant but is phytotoxic. Modified atmospheres involving elevated CO_2 or low O_2 have shown excellent effects but issues of cost effectiveness and the need for long exposure times may be significant (Nayak et al. 2010). Nitrogen can be generated using the pressure swing absorption technique on site and has been shown to have good potential in large sealed storages by excluding oxygen (Cassells, Banks and Allanson 1994).

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