CAF2020 Paper No. P-1-9-9

Ryan RF (2021) Phosphine fumigation: quo vadis? Pp. 25-31. In: Jayas DS, Jian F (eds) Proceedings of the 11th International Conference on Controlled Atmosphere and Fumigation in Stored Products (CAF2020), CAF Permanent Committee Secretariat, Winnipeg, Canada.

Phosphine fumigation: quo vadis?

Robert Francis Ryan

Principal Consultant, VAPORFAZE, Sans Souci NSW 2219, Australia
Corresponding author's email: robert.ryan.consultant@gmail.com

Abstract

Effective fumigation is required to control all life stages of stored product pests, achieve "pesticide-free" status, and avoid insect resistance. The current preferred global fumigant, phosphine (PH_3), initially patented in the 1930's as a solid metallic (aluminum) phosphide formulation, has evolved over the decades. The slow-release (2^+ d) solid formulations dominate the global fumigation market which has increasing contributions from solid quick release formulations and PH_3 gas / PH_3 mixtures in high-pressure industrial gas cylinders. Developments of PH_3 gas in cylinders include on-site mixing of 99% PH_3 with carbon dioxide or atmospheric air.

An advantage of the solid formulations is lower cost. Disadvantages of the solid formulations include inability to control/maintain optimum PH_3 concentration; operator safety with PH_3 exposure on handling; disposal of unreacted residues; flammability issues; and longer exposure times (2^+ d to generate and extended time to achieve uniform distribution). Advantages of gaseous PH_3 include rapid uniform gas distribution; reduced exposure times; ability to maintain/control optimum concentration; avoid operator exposure; and effective fumigation of non-gastight storage using flow-through PH_3 fumigation. A disadvantage of the gaseous PH_3 is higher cost.

The proven way to prevent resistance is to use PH_3 correctly in a gas-tight sealed storage by achieving the minimum Concentration x time (Ct) product to ensure effective fumigation. The majority of global grain storages are not "gastight". The Australian Standard, AS2628 (2010), states that sealable storage must perform a 5-min, half-life pressure test. Modern "bunker" storage can be sealed for fumigation. Specialist bulk grain storage sealing companies can achieve gastight status in many storages. Most "non-sealed" storage can be partially sealed and adapted to flow-through fumigation which uses low PH_3 levels (~150 ppm) with extended exposure times (3 wk). Flow-through PH_3 fumigation has been used in Australia for over 25 yr with tall vertical silos having the lowest treatment cost (~3 g/tonne).

Keywords: Phosphine fumigation, Aluminum phosphide fumigant, Cylindered phosphine fumigant, Sealed storages for fumigation, Flow-through fumigation, Pest control

Introduction

After 85 yr usage as a fumigant, PH_3 is the dominant global fumigant because of its low cost, efficacy, and environmental acceptance. Methyl bromide (MBr), first reported by Le Goupil (1932), is being phased out because of its ozone depleting effect. Actually, PH_3 replaced MBr long before its regulation by parties of the Montreal Protocol, wherever temperature and time were not constraints for PH_3 fumigation (Ducom, 2006). Because of its common use in global food production, the cereal grain industry is determined to maintain PH_3 as the priority grain fumigant. The major threat to the on-going use of PH_3 is the outbreaks of strong insect resistance. Fumigation needs to control insects, prevent food losses, and satisfy marketing requirements. Australia exports about 80% of the grains it produces, and in order to maintain market access, the grain must be free of live insects and pesticide residues. Insect control was initially achieved using grain protectants, but insect resistance and the requirement for insect and pesticide-free product led to increased use of phosphine (PH_3) fumigation. The solid aluminum phosphide (AlP) formulation developed in Germany (Freyberg, 1935) generates PH_3 gas on exposure to moisture in the atmosphere. This usage is relatively safe because the flammable PH_3 is released slowly over days by diffusion and dilution in the surrounding air. Phosphine is widely registered for disinfestation and is the only MBr alternative extensively used for cereals, legumes, dried fruits, nuts, beverages, herbs and spices. Widespread practical use began in the mid-1950s 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). Phosphine 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-1980s, 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). Over the past 20 years, new technology has enabled pure PH_3 to be supplied as a liquid under pressure in gas cylinders and mixed on-site with atmospheric air.

Flammability

Most historical and current fumigants are flammable including MBr (flammability ranges 10 to 16%); however, there is no reported fire incident associated with MBr while dust explosions in grain storage are well documented. All PH_3 products are manufactured from white phosphorus P_4 which is pyrophoric (any unreacted P_4 is a flammability hazard). The flammability issue of the pure PH_3 gas is resolved by formulating a non-flammable mixture in 2.6% CO_2, 2.0% N_2, or by rapid on-site dilution in atmospheric air to less than 1.8% flammability limit, prior to dispensing into the storage structure being fumigated.

Non flammability of PH_3 is important especially in the fumigation of large structures. It is critical to ensure that the PH_3 level being dosed into the storages is below the lower level of flammability to avoid fire or explosion. Explosions that can destroy the structure are relatively common in grain storage as there is always a “source of ignition” and high levels of dust which can lead to dust explosions. The reasoning behind the slow release of “solid” PH_3 formulations is to allow the flammable PH_3 to dissipate and dilute quickly into the surrounding air.

Phosphine products

The "solid" formulation refers to the solid tablets and plates which mainly consist of aluminum phosphide (e.g., AlP tablets), while the "liquid" is in high pressure industrial gas cylinders. The gaseous PH_3 is similar to gaseous CO_2 as both gases liquefy when compressed to high pressure (4MPa). The solid aluminum phosphide formulation developed in Germany and patented in the USA (Freyberg, 1935; 1938) generates PH_3 gas on exposure to moisture in the atmosphere. This usage is relatively safe because the flammable PH_3 is released slowly over days by diffusion and dilution in the surrounding air. The major advantages of the solid 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.

The use of "liquid" PH_3 is made commercially available with the patented non-flammable PH_3 and CO_2 mixture (Ryan and Latif, 1989). This progresses to the onsite mixing patent of PH_3 and air (Ryan and Shore, 2005). The advantage of these gaseous PH_3 products is reduced exposure time as uniform distribution of the PH_3 is achieved in hours, not days. Other advantages of the gaseous PH_3 products include accurate control of PH_3 concentration, a more rapid delivery of PH_3 gas, better distribution in the grain mass without disturbing grain, and a controlled flow and dosage maintenance for long periods. Liquid PH_3 eliminates handling and disposal of the "spent" metallic phosphide tablets and requires less labour. The reaction of PH_3 with oxygen to form polymers is an issue which requires pre- and post- purging of PH_3 dispensing systems. Phosphine gas needs to be free of trace levels of diphosphine (P_2H_4) and higher phosphines to avoid being spontaneously flammable (Fluck, 1973b). The fumigation grade PH_3 has critical specifications for impurities such as P_2H_4 and P_4 which are pyrophoric (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 the fruit fly in 1976 (Ryan, 1997). A series of regular updates of the history of the commercial gaseous PH_3 products launched in the early 1980s have been published (Ryan, 1997). Phosphine has a wide flammable range in air, so various mixtures with CO_2 and/or N_2 have been patented to overcome this problem (Ryan, 1997; Ryan and Latif, 1989).

Significant timelines include: the original patented solid formulation (Detia, 1935); initial gaseous PH_3 (CIG, 1976); liquid PH_3/CO_2 mix (CIG, 1984); PH_3/CO_2 supported flow-through fumigation (CSIRO, 1986); PH_3/CO_2 (BOC, 1989); PH_3/N_2 (S&A, 1998); PH_3/Air mixing (GasApps, 1999); Solvay (CYTEC, 1999); PH_3/Air (Horn, 2001); PH_3/Air mixing (Solvay, 2005); UltraPhos 99% PH_3 (Specialty Gases, 2014).

Fumigation storage

Effective fumigations should be carried out in validated gastight storage. The Australian Standard, AS 2628 (2010), details the use of a decaying pressure test ($P_{0.5}$ > 5 min from 25 mm to 12 mm using a U-tube liquid manometer). Most grain storages fail this test; however, all can be fumigated using PH_3 flow-through fumigation. The liquid PH_3 formulations supported CSIRO's flow-through fumigation process, SIROFLO (24/7 flow and 28 d exposure), used in non-gastight grain storages (Winks, 1987). The flow-through fumigation enables the fumigation of grain in "leaky" (non-gastight) storage; achieves pesticide residue-free and insect-free status for grain in "leaky" storage; makes old silos useful storage facilities; overcomes air ingress via small positive pressure and prevents fumigation failure; improves efficacy by achieving Ct product; uses low concentrations for long exposure periods; increases workers' safety by using low PH_3 levels and constant low emissions levels. Any released PH_3 is short lived because it reacts with the atmosphere forming phosphoric acid. As flow-through fumigation equipment is used at unmanned rural sites, robust reliable design is required for rural "road" transport. The SIROFLO flow-through fumigation maintains a small positive pressure throughout the grain mass to ensure a uniform low concentration of PH_3 and can control PH_3 resistant insect strains in non-gastight storage (Winks and Ryan, 1990). The low PH_3 concentration (~100 ppm) if maintained up to 28 d will kill all stages of insects in non-gastight storages (these can be effectively "sealed" in critical areas).

Future

To predict the future, it is useful to review the past history of fumigants. The two significant issues with PH_3 are ineffective fumigation and insect tolerance / resistance. The expression "If you are not measuring, you are not fumigating" has been quoted for decades. This is still an issue and the major cause is non-gastight storage and/or failure to top-up the PH_3 concentrations. Effective fumigations should be carried out in validated gastight storage (AS 2628, 2010) using a decaying pressure test ($P_{0.5}$ > 5 min from 25mm to 12mm using a U-tube liquid manometer). Grain storages that fail this test should be candidates for PH_3 flow-through fumigation. The flow-through fumigation enables the fumigation of grain in "leaky" (non-gastight) storage and can achieve the required Ct product by maintaining low concentrations for long exposure periods.

Another major threat to the on-going use of PH_3 is outbreaks of strong insect resistance. Insect resistance to PH_3 fumigation is a critical issue for planning the future of this valued fumigant. Resistance issues detailed in a review by Ryan and DeLima (2014) include reported PH_3 resistance occurring in every insect species tested; variation in susceptibility of different life stages; improved efficacy by extending exposure periods; induced narcosis at high concentrations; widespread problems in most commercial storages; associated resistance with inadequate fumigation; and critical attainment of Ct product. The review also noted three levels of resistance ('weak' and strong' and 'very strong'). The development of very strong resistance (875x) in flat grain beetles *Cryptolestes ferrugineus* (Stephens) in large bulk storages in Australia poses a serious threat, however, an effective management of *this* strain through the use of sulfuryl fluoride as an alternative fumigant has been implemented. Also, PH_3 tolerant insects have been controlled using flow-through fumigation by extending the exposure period.

Of course, the last resort is to identify alternatives. The application of ethyl 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. Among the alternatives, a broad-spectrum fumigant known as sulfuryl fluoride (SF) is the most promising. Although sulfuryl fluoride is being used in the effective management of strong resistant *C. ferrugineus* populations in bulk storage, SF does have an issue with efficacy against the egg stage of storage pests, particularly at lower temperatures. Carbon dioxide (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 commercialized although it has generally good efficacy, and ethyl formate (EF) can be effective against a range of insects when combined with CO_2. Hydrogen cyanide (HCN) has been used in a limited way on grain despite its high sorption, and ethanedinitrile (C_2N_2) is a new broad-spectrum fumigant. 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).

Discussion

There have been significant changes from the high PH_3 doses of 10,000 ppm (14 g/m^3) used in the 1950s (Annis, 2001) to the current recommendations of 1-3 g PH_3/m^3 (718 - 2,154 ppm) or as low as ~100 ppm (0.14 g/m^3) in a continuous flow system (Anonymous, 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 Ct product is a constant (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 also increased (Bond et al., 1969; Howe, 1974; Hole et al., 1976; Winks, 1986; Winks and Hyne, 1994). 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 (Nakakita et al., 1974; Reichmuth, 1994; Winks, 1984, 1987). A unique characteristic of PH_3 is that in the absence of oxygen it is not absorbed and is therefore 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).

In summary, the critical requirement of a successful fumigation is to provide an adequate Ct product. This needs a gastight storage or flow-through fumigation, especially in order to maintain the concentration, but the response of insects to PH_3 is also far more effective if the exposure time is lengthened. As a case history, in 1960, the Australian Government reacted to a crisis / customer revolt demanding a change to the "relaxed" attitude of regular shipments of infested grain being exported from Australia. The Export (Grain) Regulations at that time, prohibited the export of grain from Australia unless it was found to be free from insect pests. These days, the Australian $7 billion grain export revenue industry has ongoing independent government overview focusing on nil-insect and Maximum Residue Levels (MRL) requirements. In many global jurisdictions, changes are needed to improve the quality of fumigation, but this is unlikely to happen unless customers revolt or governments propagate and enforce regulations. The solutions are known: however, there is not a "burning platform" to initiate global change. The future of PH_3 as a fumigant may have a different outcome in individual countries. Reflecting on the long list of former insecticides, now discontinued due to insect pesticide resistance issues, should highlight the potential stark outcome.

References

Annis PC (2001) Phosphine dosage regimes required for high mortality: A data-base approach. Pp.45-55. In: Donahaye EJ, Navarro S, Leesch JG (eds) Proc 6th Intern Conf Controlled Atm Fumi Stored Prod, Fresno, USA.

AS 2628 (2010) Standards Australia, Sealed grain-storage silos for insect control, 03-11-2010.

Bond EJ, Robinson JR, Buckland CT (1969) The toxic action of phosphine absorption and symptoms of poisoning in insects. J Stored Prod Res **5**: 289–292.

Chaudhry MQ, MacNicoll AD, Mills KA, Price NR (1997). The potential of ethyl phosphine as a fumigant for the control of phosphine resistant strains of four species of stored-product insects. Pp45–57. Proc 5th Intern Conf Controlled Atm Fumi in Stored Prod, Nicosia, Cyprus. Pp. 45–57.

Ducom PJF (2006) The Return of the fumigants. Pp. 510-516. In: Lorini I, Bacaltchuk B, Beckel H, Deckers D, Sundfeld E, dos Santos JP, Biagi JD, Celaro JC, D'A Faroni LR, Bortolini LOF, Sartori MR, Elias MC, Guedes RNC, da Fonseca RG, Scussel VM, (eds) Proc 9th Intern Working Conf Stored-Prod Prot, Campinas, São Paulo, Brazil.

Fluck E (1973a). The chemistry of phosphine. Page 22. In: Topics in Current Chemistry. Vol 35. Springer Vertag N.Y.

Fluck E (1973b) The chemistry of phosphine. Page 18. In: Topics in Current Chemistry. Vol 35. Springer Vertag N.Y.

Freyberg W (1935) Protection of stored goods with phosphine. Technical Bulletin Detia GmbH, 3 p.

Freyberg W (1938) Chemische Fabrik, US Patent 2,117,158: Method of exterminating corn beetles and other vermin, May 10.

Hole BD, Bell CH, Mills KA, Goodship G (1976) The toxicity of phosphine to all developmental stages of thirteen species of stored product beetles. J Stored Prod Res **12**: 235–244.

Howe RW (1974) Problems in the laboratory investigation of the toxicity of phosphine to stored products insects. J Stored Prod Res **10**: 167-181.

Le Goupil (1932) Les proprietes insecticides du bromure de methyle. Rev Path **19**: 167-172.

Munro HAU (1969) Manual of Fumigation, 2nd Edition, FAO Agriculture Studies, No. 79, Rome, Italy.

Miller FJ, Schlosser PM, Janszen DB (2000) Haber's rule: a special case in a family of curves relating concentration and duration of exposure to a fixed level of response for a given endpoint. Toxicology **149**: 21–34.

Nakakita H, Saito T, Iyatomi K (1974) Effect of phosphine on the respiration of adult *Sitophilus zeamais* Motsch (Coleoptera: Curculionidae). J Stored Prod Res **10**: 87-92.

Nayak M, Holloway J, Pavic H, Head, M, Reid R, Collins PJ (2010) Developing strategies to manage highly resistant phosphine populations of flat grain beetles in large bulk storages in Australia. Pp. 396-401. In: Carvalho MO, Fields PG, Adler CS, Arthur FH, Athanassiou CG, Campbell JF, Fleurat-Lessard F, Flinn PW, Hodges RJ, Isikber AA, Navarro S, Noyes RT, Riudavets J, Sinha KK, Thorpe GR, Timlick BH, Trematerra P, White NDG (eds) Proc 10th Intern Working Conf Stored-Prod Prot, Estoril, Portugal.

Reichmuth CH (1994) Uptake of phosphine by stored-product pest insects during fumigation. Pp. 157-162. In: Highley E, Wright EJ, Banks HJ, Champ BR (eds) Proc 6th Intern Working Conf Stored-Prod Prot, Canberra, Australia.

Ryan RF (1997) Gaseous phosphine - a revitalized fumigant. Pp. 305- 310. In: Donahaye ED, Navarro S, Varnava A (eds), Proc 5th Intern Conf Controlled Atm Fumi Stored Prod, Nicosia, Cyprus.

Ryan RF, DeLima CPF (2014) Phosphine - an overview of a unique 80-year fumigant. Gena Appl Entomol **42**:31-42.

Ryan RF, Latif S (1989) Fumigant System. US Patent 4,889,708. 26 Dec 1989.

Ryan RF, Shore WP (2005) Process and Apparatus for Supplying a Gaseous Mixture, US Patent 6,840,256 B1.

Winks RG (1984) The toxicity of phosphine to adults of *Tribolium castaneum* (Herbst): Time as a dosage factor. J Stored Prod Res **20**: 45-56.

Winks RG (1986) The effect of phosphine on resistant insects. Pp. 105-118. In: Proc GASGA Sem Fumi Tech Dev Countries. TDRI, London, UK.

Winks RG (1987) Strategies for effective use of phosphine as a grain fumigant and the implications of resistance. Pp. 335-344. In: Donahaye J, Navarro S (eds) Proc 4th Intern Working Conf Stored-Prod Prot, Tel Aviv, Israel.

Winks RG, Ryan RF (1990) Recent developments in the fumigation of grain with phosphine. Pp. 935-943. In: Fleurat-Lessard F, Ducom P (eds) Proc 5th Intern Working Conf Stored-Prod Prot, Bordeaux, France.

Winks RG, Hyne EA (1994) Measurement of resistance to grain fumigants with particular reference to phosphine. Pp. 244-250. In: Highley E, Wright EJ, Banks HJ, Champ BR (eds) Proc 6th Intern Working Conf Stored-Prod Prot, Canberra, Australia.