

New aluminium phosphide formulations for controlled generation of phosphine

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Abstract

New formulations of phosphine-generating products have been developed and tested for use with on-site phosphine generators. The formulations are inherently safer during storage and transport before use than current commercial formulations. They are well suited to controlled production of phosphine for continuous application technology such as SIROFLO[®]. However, when used in appropriate generators they allow for controlled phosphine production that is useful in a range of fumigation practice. Patent applications have been lodged on the inventions described in this paper.

Introduction

Phosphine is the most widely used fumigant for disinfecting stored grain. Indeed, it could soon be the only fumigant available for this purpose in many countries. The other commonly used fumigant, methyl bromide, now recognised as a potent ozone depletor, is most likely to be banned or highly restricted by the year 2000. Unless other fumigants are developed and approved, phosphine will become the principal fumigant gas.

Phosphine is a colourless gas, which is odourless when pure, but the technical product has an odour of garlic. The gas can be generated on-site by the hydrolysis of aluminium, magnesium or zinc phosphides. Aluminium phosphide (AIP) is the most commonly used to generate phosphine for disinfection of stored products. Phosphide as tablets, pellets, or as a powder in sachets, slowly reacts with atmospheric moisture to release phosphine. This reaction has been used in several different methods of application. Thus:

- tablets of AIP can be added directly to the commodity;
- tablets of AIP can be placed in removable dispensing containers over the stored product; and/or
- a 'blanket' containing sachets of AIP can be placed over the stored product.

Although these methods, when properly applied, can be very effective, there are some disadvantages, including the following.

- Tablets added directly to the grain leave a residue in the grain, consisting largely of aluminium hydroxide, but with some unreacted phosphide (Bruce et al. 1962; Vardell et al. 1973; Banks 1987).
- In storages without recirculation equipment, distribution and levels of phosphine cannot be controlled once the dose of AIP has been applied.

- Application rates are sometimes increased excessively in the hope this will overcome the reasons for gas loss and maintain levels in leaky storages.
- The most efficient use requires a well-sealed storage structure.

Direct application of phosphine as a gas (rather than by generation from AIP) for fumigation has advantages and methods have been developed recently to exploit these. The introduction of Phosfume[®] gas (2% phosphine in carbon dioxide) and the SIROFLO[®] (Winks 1988) and SIROFUME[®] technologies are examples. SIROFLO[®] is a technique where a low concentration of phosphine is passed through stored grain for sufficient time to ensure that all life stages of an insect infestation are exposed to a lethal dose (concentration × time). SIROFUME[®] is a technique where the level of phosphine in the headspace of a sealed store is monitored and periodically topped up to replace gas lost. For these purposes phosphine can be obtained in cylinders, usually diluted in nitrogen or carbon dioxide. However, there are circumstances where use of cylinders is neither desirable nor warranted. For example, use of phosphine gas for SIROFLO[®] applications in on-farm storages may be better serviced by a phosphine generator. Prototype generators have been constructed (Banks and Waterford 1991) which use commercially available AIP tablets or pellets as a source for the phosphine. While the feasibility of using such devices for continuous phosphine production has been demonstrated, we had concerns about the safety of using currently available formulations of tablets or pellets in this application. Thus, it was decided to investigate alternative formulations of AIP better suited for use in a phosphine generator.

Initial experiments indicated that admixture of AIP with water-immiscible carriers, such as paraffin oil and paraffin wax, produce extrudable pastes or solid formulations. Such formulations are relatively stable in air but produce phosphine when added to water. This paper reports studies to investigate the properties of these formulations, and trials that were used to test the more promising formulations in prototype generators.

Materials and Methods

The AIP used was technical grade, granular 86% AIP (Detia Germany 1988). A fine powder, suitable for making formulations, was made by grinding AIP in an electric blender in air. The phosphide was sieved with a 250 micron mesh in a well-ventilated fumehood after blending for about 30 seconds. The portion that did not pass through the sieve was returned to the blender and topped up with more AIP for further grinding. Using this technique a 1 kg pack of technical grade AIP yielded 950 g (95%) of phosphide with particle size < 250 microns. The formulations produced from this powder were homogeneous, of a smooth consistency and of uniform reactivity.

All subsequent preparation of formulations was also carried out in a well-ventilated fume hood and it was not necessary to provide an inert atmosphere for any of these procedures.

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However, with larger quantities, provision for a blanket of inert gas may be prudent.

The following properties were considered to be important with respect to suitable carriers for the AIP. They should be:

- non-reactive to AIP
- non-flammable
- sufficiently viscose to prevent the phosphide settling out
- of low volatility
- stable in the temperature range -40 to $+60^{\circ}\text{C}$
- non-reactive with packaging material and unable to diffuse through it
- non-reactive with metals such as stainless steel and aluminium
- non-water absorbing.

Paraffin oils and waxes possess many of these properties.

Paste formulations

Paraffin oil admixed with ground AIP powder in the ratio of 73% AIP/27% paraffin oil produced a paste which could be readily extruded from a syringe or canister with an orifice > 3 mm. The basic formulation was modified to eliminate settling or separation by substituting a proportion of the paraffin oil in the carrier with petroleum jelly. The modifications included, 50% paraffin oil–50% petroleum jelly, and petroleum jelly alone. These formulations increased the viscosity of the carrier and in turn the viscosity of the final paste mixture.

Solid formulation

A solid formulation (27% wax, 73% powder) was made by suspending finely divided phosphide in molten paraffin (BDH Ltd, paraffin wax with ceresin, congealing point ca 60°C), and allowing the mixture to cool. The wax was heated to about 90°C so that the powder could be admixed before the wax congealed.

Evolution of phosphine from formulations in water

Samples of phosphide formulation (ca 1.0 g) were weighed into a 150 mL flask fitted with a connection to a gas burette. The flask was flushed with nitrogen then 100 mL of reactant, usually water, was added and the flask sealed. The reaction vessel was held in a water bath to maintain a constant temperature of either 23 or 40°C ($\pm 1^{\circ}\text{C}$). Evolution of phosphine was followed by recording gas burette readings with time. Measurements were made for the first 30 minutes without stirring the mixture. Thereafter, the mixture was agitated using a magnetic stirrer. For comparison unformulated AIP powder, ground to the same particle size, was also used.

Additives chosen from a variety of readily available detergents and surfactants were assessed as possible means to further control the release of phosphine from formulations and included:

- Teepol® — Shell, household detergent
- BP Comprox® — British Petroleum (BP), general purpose detergent
- PEG 600 — ICI, polyethylene glycol, surfactant
- Heptane — May & Baker, laboratory solvent
- Dishwashing powder — alkaline non-foaming detergent.

The materials sold as Teepol® and Comprox® are mixtures of anionic and non-ionic detergents and are subject to changes in formulation depending on availability of materials. In the present work the Teepol® was newly acquired material whereas the Comprox® was taken from a drum of material that had been in store for some years.

Evolution of phosphine from paste formulations in air

Phosphide paste formulations were placed in shallow containers and the exposed surface area measured. A container of paste was placed in a glass vessel fitted with an inlet line providing air of known humidity at 100 mL/minute, and an outlet line fitted with a sampling septum. The humidifier was a glass gas-washing bottle containing either water or an appropriate water/glycerol solution. The reaction vessel and the humidifier could be maintained separately at any given temperature from 23 to 40°C (Fig. 1). Phosphine evolution was calculated from concentrations measured at intervals by gas chromatographic analysis (FPD) of the outlet gas stream.

Conditions were changed to test the effects on the evolution of phosphine from the paste formulation of:

- exposed surface area,
- humidity, and
- temperature.

Analysis of phosphide residues and evolved phosphine gas

Spent formulation samples were recovered from reactions where the paste was stirred with water for 48 hours and then allowed to stand for 24 hours. Samples were analysed for unreacted phosphide by a modification of the method of Bruce et al. (1962) using mercuric chloride to trap released phosphine. A known amount of phosphine gas and a sample taken from a spent sachet containing AIP were analysed for comparison. The latter was taken from a Detia AIP 'blanket'.

Gas samples were taken at random from the phosphine generated from the paste formulations and analysed on a gas chromatograph fitted with a gas density balance.

Phosphine production from prototype generators

A prototype generator was constructed to evaluate selected formulations at rates sufficient to fumigate a 2000 t bin of grain. For a bin of this size, SIROFLO® protocol requires a supply of phosphine of about 1.5 g/hour. The major components of the generator are shown in Figure 2. They include:

- a 20 L reaction vessel with a stirrer
- ability for the headspace of the reaction vessel to be flushed with air or an inert gas
- ability to pass this same gas through the water to produce extra agitation
- a port for the introduction of the paste
- a port to extract phosphine produced and any gas used for stirring or flushing
- a delivery mechanism for the formulation.

The phosphine generated was swept from the headspace with air from a small diaphragm pump. It was piped into a measured air flow of a standard SIROFL® system fitted to a 40 t farm bin filled with wheat. The concentration of phosphine produced in the air flow was measured with a CiTicel® phosphine sensor, and the output recorded on a chart recorder. The response of the sensor was calibrated periodically by using an analysed phosphine gas standard (20 ppm from The Commonwealth Industrial Gases Ltd, Australia).

A second generator (Fig. 3) was constructed to evaluate the generation of phosphine from an exposed surface area of formulation.

A prototype dispenser (Fig. 4) was used to evaluate the solid formulation, where plugs (4.5×2 cm) were dispensed, one at a time, from the bottom of an upright canister containing a total of 12 plugs.

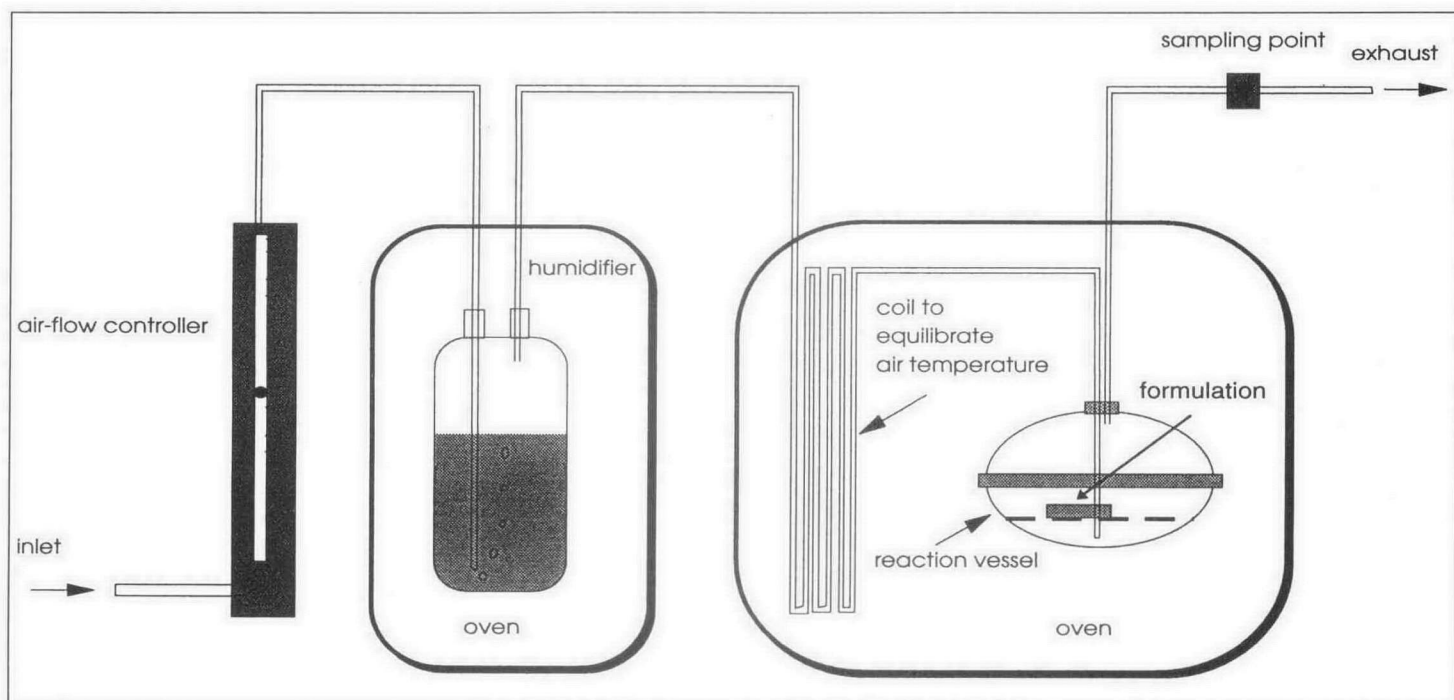


Fig. 1. Diagram of apparatus used to assess phosphine output from a range of surface areas of paste formulations at various temperatures and relative humidities.

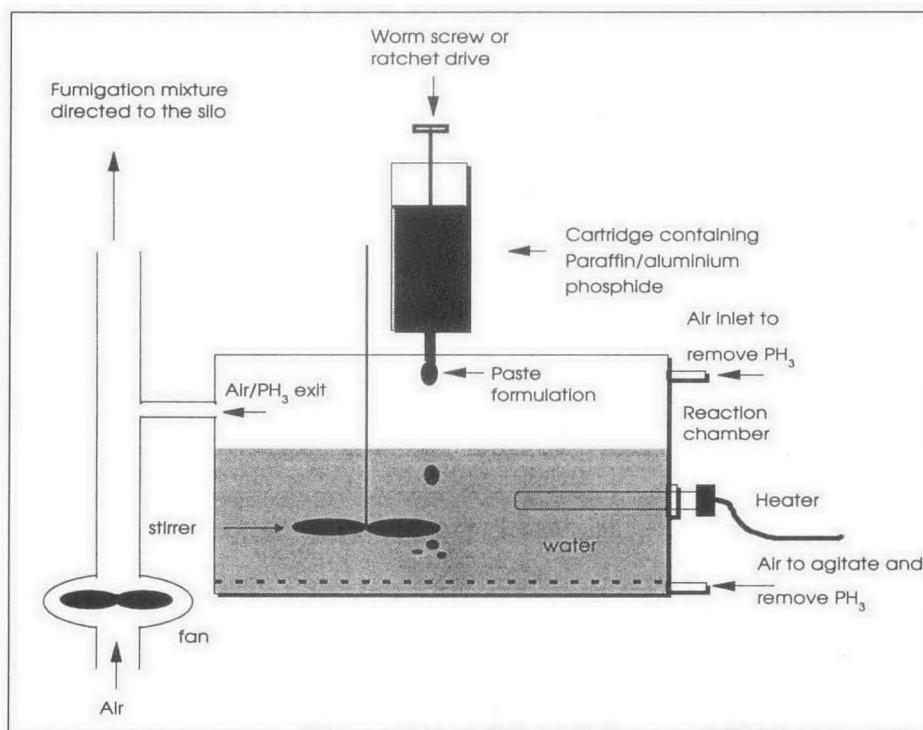


Fig. 2. Diagram of phosphine generator used to assess phosphine-generating paste formulations.

Results

Formulations in water

The results from unstirred reactions are presented in Figure 5. The reaction rate of the unstirred formulation in water is very much less than that observed for the powder, even when the reaction mixture was heated to 40°C. The reaction rate of all formulations in water when not stirred was very low com-

pared with the reaction rate of the unformulated powder. With one notable exception, addition of materials intended to aid the dispersal of the formulation in water had no effect on unstirred reactions (Fig. 6). The addition of Teepol® to the water promoted a marked increase in the reaction rate, in striking contrast to other detergents, surfactants and solvents, which did not.

When the paste formulations were continuously stirred in water the reaction rates in general were observed to be signifi-

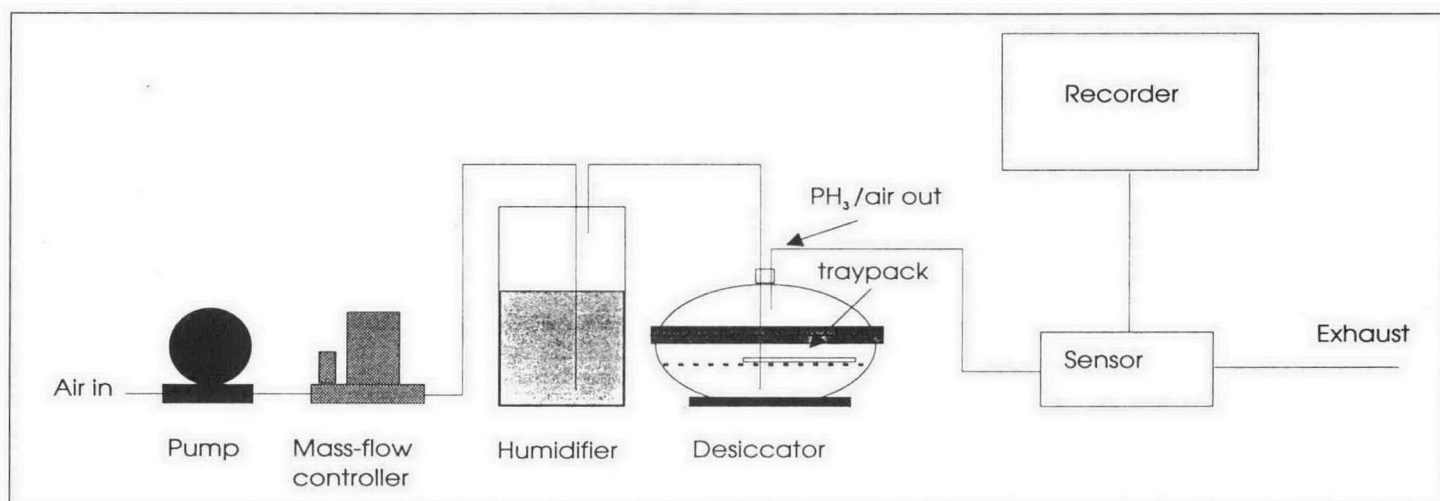


Fig. 3. Diagram of apparatus used to assess production of phosphine from tray packs using paste formulations based on 20 and 27% paraffin with the balance aluminium phosphide.

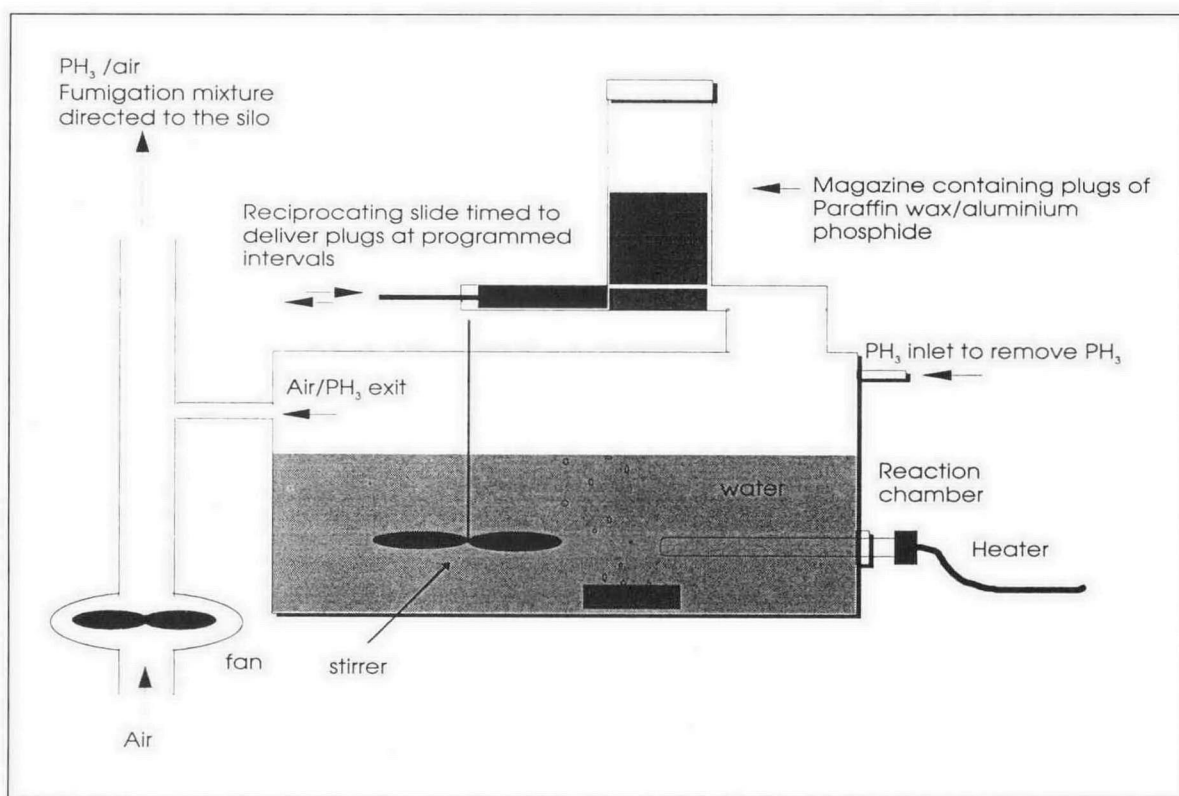


Fig. 4. Schematic of phosphine generator fitted with a mechanism to deliver wax plugs of a phosphine-generating formulation.

cantly faster than the unstirred reactions. Raising the temperature to 40°C increased the reaction rate (Fig. 7) and increasing the viscosity of the formulation reduced the reaction rate (Fig. 8) but, with one exception, the changes were not large. The behaviour of the solid preparation made with paraffin wax differed markedly in two respects. Firstly, this formulation was not greatly affected by stirring and secondly, the reaction rate over the period of digestion was found to be remarkably steady. A 5 mm × 12 mm sample of solid formulation retained its form but became thinner with time during the course of the reaction.

Addition of dispersal agents to the stirred reactions gave unexpected results. Heptane or 3% Comprox®, the latter a

non-foaming detergent, caused a significant decrease in the reaction rate for the stirred mixture. Teepol® caused an increased reaction for the unstirred mixture which was not altered by subsequent stirring. None of the remaining additives was effective in significantly increasing the reaction rate over that observed in water alone.

Paste formulations in air

The effect of change of humidity and temperature on the release rate of phosphine from exposed formulation is shown in Figure 9. Initially the air was at 23°C with a relative humidity of >90%. After 24 hours the temperature of the reaction

vessel was raised to 40°C while the humidifier was maintained at 23°C, which kept the absolute moisture content of the air constant. Apart from a minor excursion due to disturbance of the apparatus, the rate of evolution of phosphine was not altered by the increase in temperature. However, the evolution rate doubled when the humidifier was also heated to 40°C, restoring the relative humidity to >90%, thus increasing the absolute moisture content of the air passing over the paste.

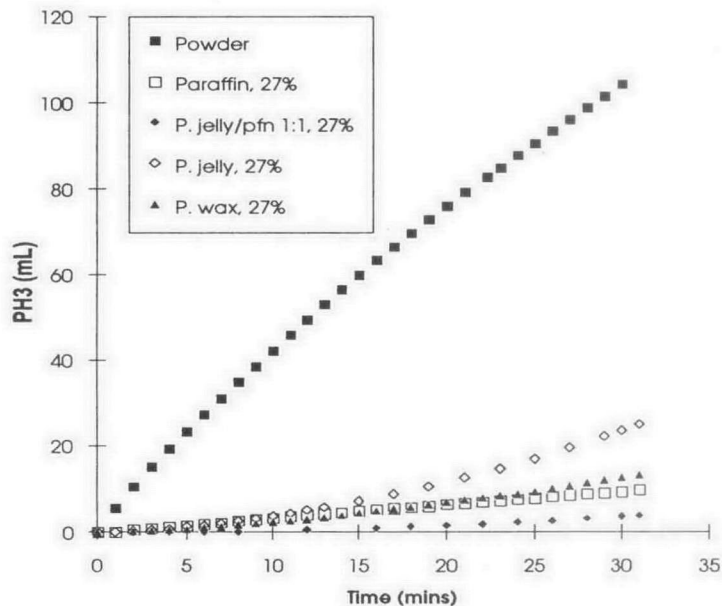


Fig. 5. Phosphine released from aluminium phosphide formulations (1.0 g) in unstirred water, compared with release from aluminium phosphide powder. Formulations were made from aluminium phosphide powder and 27% paraffin oil, 27% of a 1:1 petroleum jelly/paraffin oil mixture, 27% petroleum jelly, and 27% paraffin wax.

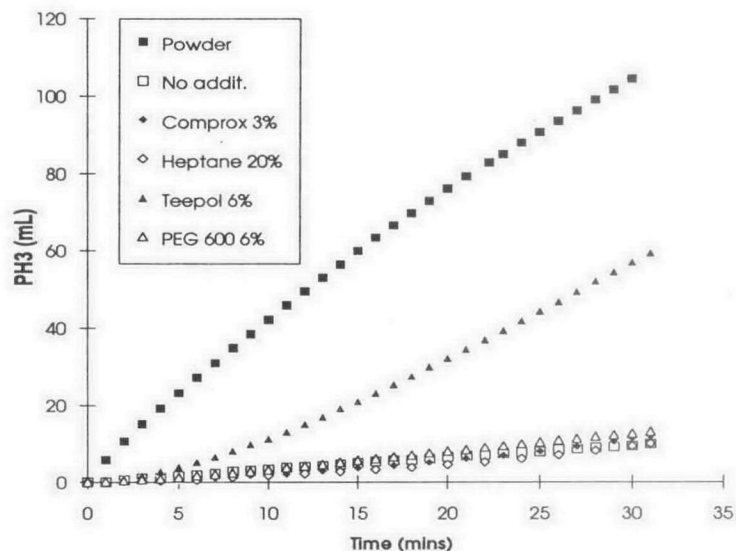


Fig. 6. Phosphine released from 73/27 aluminium phosphide/paraffin oil formulation (1.0 g) when placed in unstirred water with various additives, compared with unformulated aluminium phosphide powder in water and the formulation with no additives.

Analysis of phosphide residues and evolved phosphine gas

The results of phosphide analysis are presented in Table 1. The amount of unreacted phosphide in the used formulation samples was found to be very low, even in a freshly obtained sample. By contrast the sachet sample contained 4–5% unreacted phosphide, a typical result for preparations that use exposure to air to generate phosphine (Banks 1987).

Table 2 shows the composition of the gas produced by reaction of the formulations with water. The small amounts of air that were present in the samples can be attributed to diffusion during sampling and the water over which the gas was stored. The methane could have resulted from the reaction of aluminium carbide with water. The method used to produce technical grade AIP is known to produce small amounts of the carbide as a contaminant.

Table 1. Phosphine residue analyses

Substrate	Condition	Residue analysis ^a
Phosphine (control) ^b	Gas 0.61 mg	0.63 mg
Celphos® sachet	Used	4.2–4.6% ^c
AIP/paraffin 73/27	10 weeks after reaction in water	10 ppm ^c
AIP/paraffin 73/27	Stirred in water 48 hours, stand 24 hours, N ₂ 4 hours	28 ppm ^c

^a Bruce et al. (1962)

^b Known amount of phosphine injected into analytical apparatus and analysed as if released from a substrate.

^c Expressed as AIP remaining in spent product (w/w)

Table 2. Concentration of phosphine in samples of gas produced by the reaction of paste with water.

Component	Concentration (mole%)	Retention time (minutes) ^a
Air ^b	2.7	1.35
	2.3	1.41
	2.4	1.40
	2.36	1.39
	2.36	1.39
Methane ^c	1.27	1.69
	1.28	1.75
	1.22	1.75
	1.39	1.73
	1.39	1.73
Phosphine	96.07	4.11
	96.42	4.18
	96.39	4.15
	96.25	4.12

^a Analysed by GC using a Gowmac Gas Density Balance detector on a Tracor MT150 GC fitted with a 6 ft × 1/4 inch stainless steel column packed with 80–100 mesh Porapak Q.

^b The air comes partly from diffusion during sampling and partly from the water over which the gas was stored.

^c Aluminium carbide in the technical grade AIP is the source for the small percentage of methane.

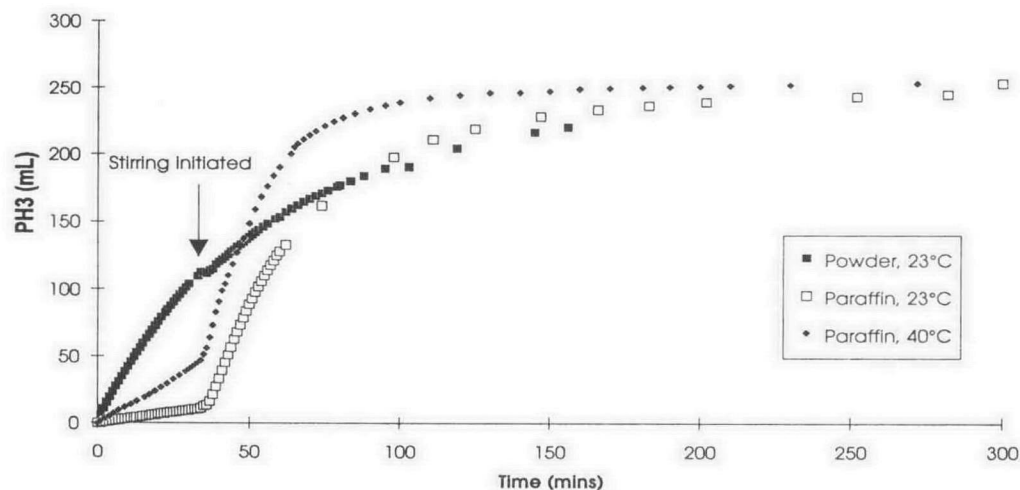


Fig. 7. Phosphine released by 73/27 aluminium phosphide/paraffin oil formulation (1.0 g) in water at 23 and 40°C, compared with aluminium phosphide powder. Stirring commenced at 31 minutes.

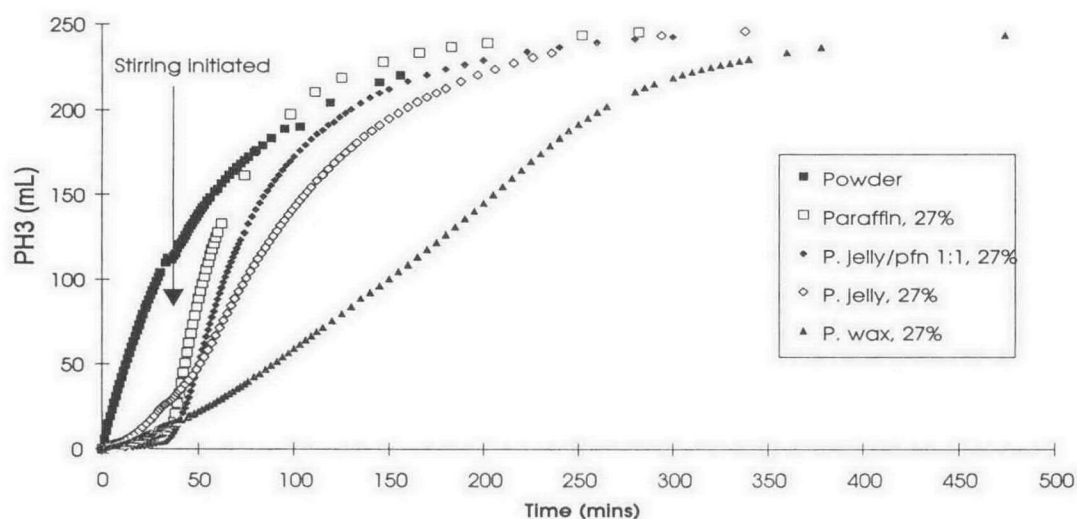


Fig. 8. Phosphine released from formulations (1.0 g) in water with stirring after 31 minutes, compared with release from aluminium phosphide powder. Formulations were made from 27% paraffin oil, 27% of a 1:1 mixture of petroleum jelly and paraffin oil, 27% petroleum jelly, and 27% paraffin wax.

Performance of paste formulations in a prototype generator

The phosphine production rate for a typical trial is presented in Figure 10. In most cases the reaction rate came to an equilibrium and then declined when addition of the formulation ceased. Generally, the reaction commenced more rapidly when detergent was included with the water.

Performance of paste formulations when used as 'tray-packs'

One novel aspect of the work suggested a method of generating phosphine by exposing a thin layer of formulation to moist air in what has been loosely termed a tray-pack. Figure 11 shows evolution of phosphine from paste when used as a tray-pack where the formulation contained 20% paraffin. The output tracked the ambient temperature and hence the available moisture provided by the humidifier held at ambient conditions. The output of phosphine ranged from about 100–300 µg/hour/cm² for the exposed surface area. At this rate the exposed surface area of a tray-pack required to provide 1 g/hour output would be

about 0.5 m². However, the increased volume of the reaction products of the formulation absorbed some of the paraffin oil, which together produced an increased surface area and reaction rate towards the end of the time over which phosphine was produced. Some means of steadily reducing the available surface area during the reaction would prevent this.

Performance of solid formulation in prototype generators

A typical production profile for the solid formulation from a plug of 4.4 cm radius and 1.8 cm depth, with all surfaces available for reaction, is shown in Figure 12. The plug was suspended in the reaction vessel of the generator. The water, containing 5% Teepol®, was heated to approximately 28°C. This single addition produced phosphine at an average rate of approximately 1 g/hour over 38 hours.

By increasing in the depth of formulation and restricting the reaction to one surface only phosphine production was extended to 7 days (Fig. 13). The plugs had a radius of 2.7 cm and were 4.5 cm deep. The plug was removed and examined on two occasions during the trial in an attempt to correlate production rates with the progress and nature of the digestion of the

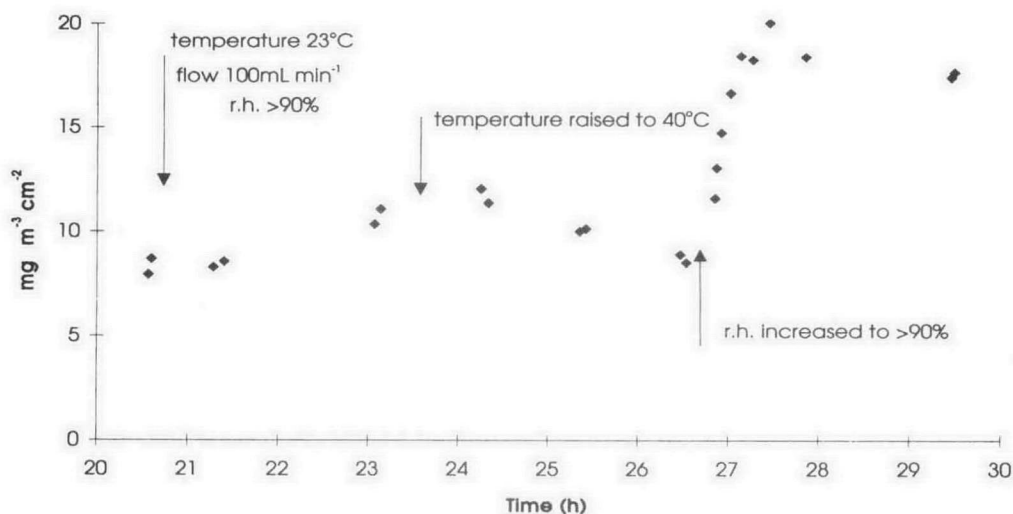


Fig. 9. Phosphine released from the surface of a 73/27 aluminium phosphide/paraffin oil paste formulation on exposure to air at differing temperatures and humidities.

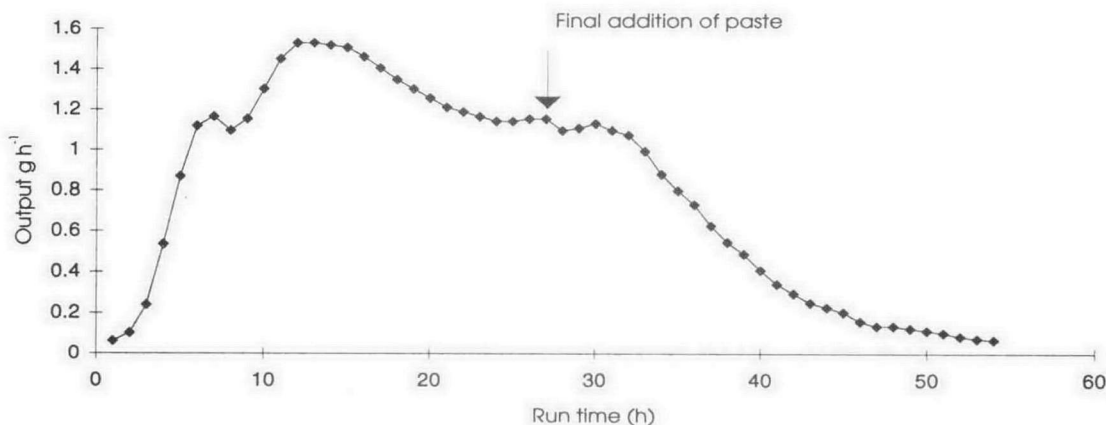


Fig. 10. Phosphine output from 73/27 aluminium phosphide/petroleum jelly paste formulation. Nominal addition rate of 6 g paste/hour. No air stirring.

plug. On the first inspection, the face of the plug was distorted down one side, the effect of which was to increase the surface area available for reaction. This increased surface area would explain the level of reaction rate just before the inspection. A large sliver of spent formulation above the reactive face, which had split off the plug, may have caused the higher reaction rate some hours earlier by doubling of the reactive surface. The plug was replaced in the generator and the reaction continued. The second inspection towards the end of the reaction indicated that the sloughing off or splitting from the face of the plug had continued. Passage of water to the unreacted face of the plug and the escape of phosphine gas may have been slowed by the increasing depth of reacted residue towards the end. This may explain the rise and fall of the rate about the expected rate for this evaluation.

Assessed also were four identical plugs (36 g each, 73% AIP) in which the base and sides of each plug were coated with an additional layer of wax (1–2 mm) so that only the top surface remained reactive. One was reacted with unstirred water at a constant temperature of 30°C. The generated phosphine was extracted with air and monitored as previously described. The sample produced phosphine over a period of 45 hours.

The second was reacted at ambient temperature (12–25°C). The recorder trace from this trial was very noisy, the average reaction rate was generally lower and the plug took about 10 hours longer than the first plug to digest. The third was reacted in the same way as the second, with the concentration recorded at a point within the grain in order to assess the damping effect that the grain would have on the pulses of phosphine production. The recorder trace showed that the time to complete digestion of the plug was similar to the second plug and significant damping of the concentration had occurred over the reaction period once the gas had passed into the grain.

The fourth was left exposed to air of about 40% r.h. Signs of a slow reaction with the surface changing from greenish to grey were apparent after a day. The reaction proceeded slowly over several months producing a 'growth' of reacted material on the surface. However, the surfaces coated with the layer of extra wax did not react.

A dispenser (Fig. 4) with the capacity to add plugs to a generator at a predetermined rate was also evaluated. The rate chosen was one plug a day. Phosphine was produced for 8 days. Conditions were changed during the trial to assess the effect on output. The first two plugs were reacted at ambient

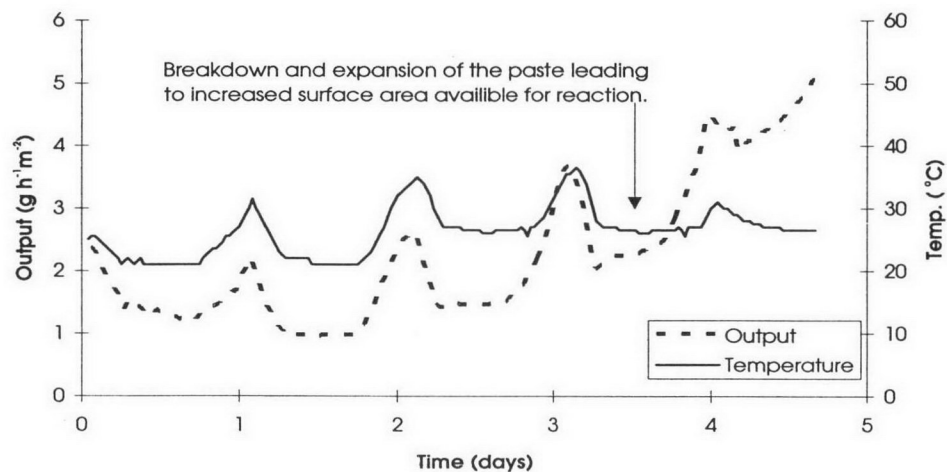


Fig. 11. Phosphine output from a tray pack of 80/20 aluminium phosphide/paraffin oil exposed to humidified air at ambient temperatures.

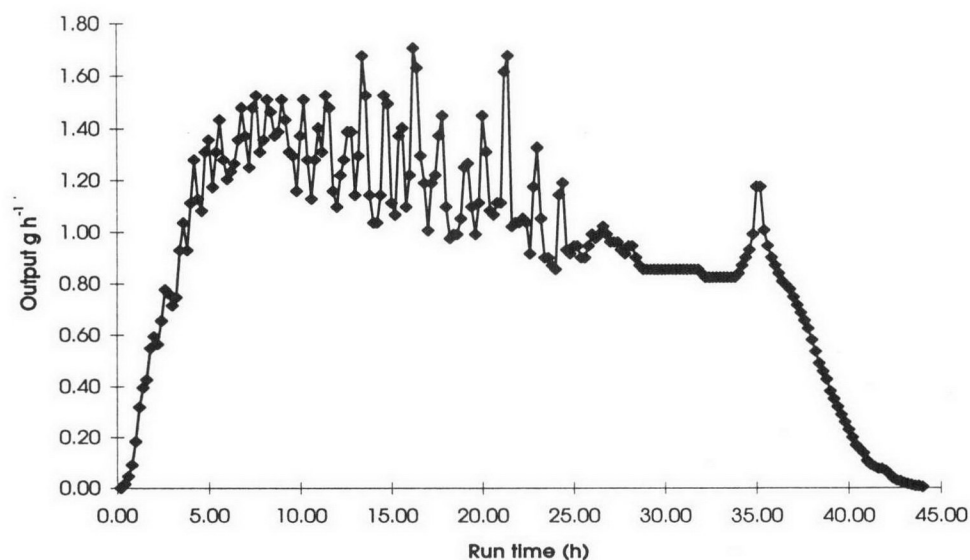


Fig. 12. Phosphine output from a generator using one block (150 g) of 73/27 aluminium phosphide/paraffin wax formulation.

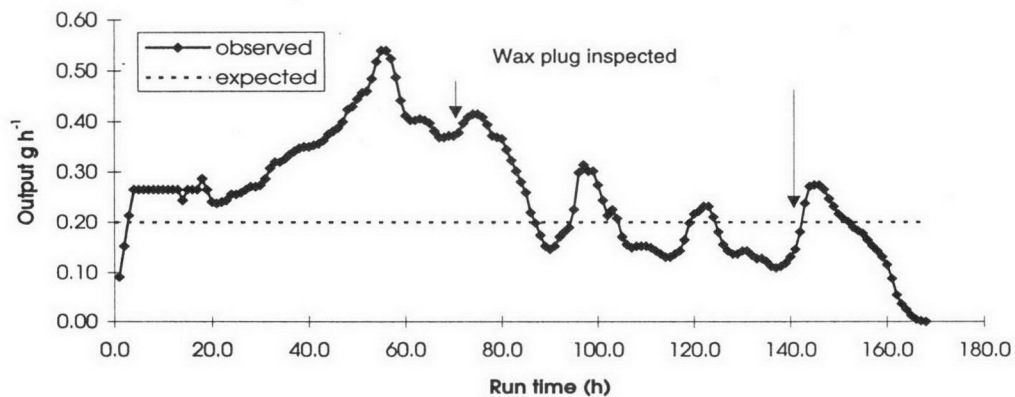


Fig. 13. Generator output from a 73/27 aluminium phosphide/paraffin wax block (140 g) held in an open glass vessel. The vessel containing the wax block was removed for inspection at the times indicated.

temperature without any additional heating. The concentration produced in the constant air flow showed a slow start and uneven reaction rates as the temperature of the water changed with ambient conditions. When the water was maintained at 32°C the plugs were reacted in less than 24 hours. When the temperature was reduced to 22°C the output became more uniform. Changes in reaction rate were presumably caused by changing viscosity of the paraffin wax with temperature. In this type of generator the production rate of phosphine can be controlled by exposed surface area of the plug and the rate of addition of plugs to the reaction vessel.

Discussion

These laboratory investigations showed that AIP can be formulated as an extrudable paste or a solid formulation. Although the formulations may not be miscible with water, reaction of the AIP with water to produce phosphine can still occur.

The paste which was less viscous showed a tendency to settle out or separate with time. The more viscous preparations did not suffer from this problem but were more difficult to extrude from a dispenser. Extrusion pressure depends on the viscosity of the preparation and the size of the outlet orifice. Selection of a suitable extrudable paste formulation will therefore depend, in part, on the design of the dispensing mechanism.

The solid formulation based on paraffin wax was more stable and easier to handle, and the phosphine output was generally more controllable.

Based on inherent reaction rates, the formulations incorporating a paraffin as carrier were found to be less hazardous than phosphide tablets, pellets, or blankets when exposed to air. Reaction with water (liquid or vapour) takes place only at the exposed surface of the formulation and the reaction is slow with no increase in temperature or danger of spontaneous combustion. Deliberate attempts to promote ignition or violent reaction were unsuccessful. For this reason it is anticipated, that these formulations will present less hazard during transport and storage than the currently available commercial preparations of AIP when accidentally exposed to air. It was observed that reaction in air was less likely to proceed to completion with the less viscous pastes. For pastes containing a higher content of paraffin oil the reaction essentially ceased once the surface layer had reacted. Conversely, for a paste containing only 20% paraffin oil and formulations where solid wax was the carrier, reaction in air continued slowly to completion.

Reactivity of the phosphide formulations in water was generally found to be low without agitation. For many preparations, less than 4% of the total potential phosphine was released after being in water at 23°C for 30 minutes. By comparison, under the same conditions, >50% of unformulated AIP powder reacted. Stirring the water and heating increased the reaction rate. Unexpectedly, most attempts to accelerate the reaction rate by addition of solvents or detergents were unsuccessful. Some of the additives inhibited the reaction. A notable exception was the detergent, Teepol®, which promoted rapid reaction even when unstirred.

The reactivity of AIP in paraffin wax was also unexpected. Tablets or plugs of this formulation were found to react in water steadily at the surface of the preparation. This behaviour, which produced a relatively constant reaction rate, indicated that such a formulation would be suitable for use in a phosphine generator.

It was anticipated that tests on reactivity in air would provide information relevant to safety and product packaging considerations. This aim was achieved and the investigation

led to another useful discovery. It was found that phosphine production from a fixed surface area of formulation, exposed in an air-flow of constant relative humidity, remained the same for many days. The surface area required to produce say 1 g/hour indicated that a generator using the formulation as a thin layer in a tray was feasible. This discovery has been incorporated in a patent application (Waterford et al. 1993).

Selected paste formulations tested in a prototype generator fitted with a motor driven piston for extruding paste formulation from a canister provided a supply of phosphine up to the required 1.5 g/hour. The design of the prototype generator had provision for an inert gas to sweep phosphine from the generator. In practice, this facility was unnecessary and air was used. Phosphine was constantly in excess of the flammability limit in the reaction vessel before being diluted into the inlet airstream of the silo. Even when positive steps were taken to promote ignition, spontaneous combustion or polymerisation of the phosphine, none of these phenomena occurred.

The expended paste formulations appear to pose no disposal hazard as the reaction proceeds to completion within the generators. After exposure to air, exhausted AIP pellets contain up to 5% of unreacted phosphide occluded in the residue of aluminium hydroxide (Banks 1987). This was not the case for paste formulations reacted with water where the residues were found to contain little (ppm level), if any, unreacted phosphide.

Tray-packs of phosphide paste are a novel possibility for use in a phosphine generator and have the advantage of simplicity. The results obtained with tray-packs are sufficient to demonstrate the potential of this technique. However, further work is needed to determine the best formulation for this application. Initial results indicated, that the formulation used in traypacks may require less carrier than that required for pastes designed for extrusion from a canister. This is a matter for further investigation.

The most promising results were obtained from the solid formulation made from AIP and paraffin wax as plugs or tablets. This performed very reliably in a phosphine generator and appears to be the preferred option for further development.

Conclusion

It is entirely feasible to safely produce sufficient phosphine for the purpose of fumigating large bulks of stored products by controlling the way water and AIP interact, including the addition of formulations of AIP to an excess of water. These discoveries have led to the development of a number of novel methods for generating phosphine as well as those detailed in this paper. As previously indicated the novel aspects arising from these and other studies are covered by patent applications (Banks and Waterford 1991; Waterford et al. 1993). These aspects include:

- phosphine generation by addition of phosphide formulation to an excess of water
- pellet dispensers for use in a phosphine generator
- the use of permeable membranes for controlling flow of water to phosphide
- paste and wax formulations of phosphide and reaction of these materials in water and in air.

Acknowledgment

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References

- Banks, H.J. 1987. A continuous, cumulative procedure for analysis of phosphine. *Journal of Stored Products Research*, 23, 213–221.
- Banks, H.J. and Waterford, C.J. 1991. Method and apparatus for generating phosphine, and safety system for phosphine generators. Patent Application No. PCT/AU91/00264.
- Bruce, R.B., Robbins, A.J. and Tuft, T. O. 1962. Phosphine residues from Phostoxin-treated grain. *Agriculture and Food Chemistry*, 10, 18–21.
- Vardel, H.H., Cagle, A., and Cooper, E. 1973. Phosphine residues on soybeans fumigated with aluminium phosphide. *Journal of Economic Entomology*, 66, 800–801.
- Waterford, C.J., Whittle, C.P. and Winks, R.G. 1993. Formulations, method and apparatus for the controlled generation of phosphine. Patent Application No. PCT/AU93/00270.
- Winks, R.G. 1988. SIROFLO®, a new grain protection method. *Stored Grain Australia*, 1, 4–5.