

A new phosphine releasing product

C. Reichmuth*

Abstract

Phosphine (PH₃) for pest control can now be produced from new sachets containing aluminium phosphide. Additional ingredients delay the early generation of the gas for about 30 minutes. This delay allows time for distribution without the risk of inhalation by workers before leaving the treated area.

The new formulation ensures that the product can be safely transported and stored in cans or packages without free PH₃ in the enclosed airspace. Heavy metal containing mixtures to absorb free PH₃ are no longer necessary. The initially sorbed PH₃ is totally evolved later on, when moisture activates the distributed phosphide product and the usual generating reaction begins.

Mixtures of zeolites with magnesium phosphide products may combine the advantage of slow initial release with later accelerated and complete phosphine generation.

The principle chemistry of the new mixture is described and results presented on the differences between phosphine release from various formulations including the new product.

Introduction

Phosphine has been used since the early thirties in various fields of pest control, and particularly for disinfection of grain in bags or bulk. Millions of tons of grain undergo a treatment each year. Pure phosphine has never been used for large-scale commercial use due to its flammability and the high risk of explosion. Freyberg in Germany 'tamed' this very active gaseous substance by formulating solid compounds containing phosphides and additional compounds from which phosphine is generated very slowly (Anon. 1934). One of the common methods to synthesise phosphine for insect and rodent pest control on sites is by hydrolysis of phosphides like AlP, Mg₃P₂ or Ca₃P₂:

Metal phosphide + Water → Phosphine + Metal hydroxide (1)

The exothermic reaction (1) may be more or less spontaneous and rapid, depending on the metal in the selected phosphide. Without any modifying agent, the development of phosphine occurs so quickly that within seconds the gas concentration in air locally around the phosphide exceeds the self ignition point of > 2% v/v. In addition to that, the rate of phosphine production is proportional to temperature and the amount of water which has access to the phosphide. These basic rules were known for a long time (Freyberg and Friemel 1965). The keys to the new formulation by Freyberg were the addition of a chemical ('protective compound') to the phosphide and a way of preparing the formulation under pressure to reduce the speed of the reaction and generation of

phosphine so that it was lower than the diffusion of phosphine from the formulation:

[Metal phosphide (57%) + protective compound (43%)] + Water → Phosphine + Metal hydroxide (2)

The protective compound, which amounts to 43 % by weight in most of the commercial formulations as indicated with formula (2), consists for instance of a mixture of paraffin and ammonium carbamate. This improves the properties of phosphide during manufacture to press powder, tablets or pellets and also develops CO₂ and NH₃ as inerting and warning gases. In 'strips' and 'plates' of Phostoxin¹ other chemicals are included together with magnesium phosphide to reduce the speed of reaction and release of phosphine (2).

Many authors have described dependence of the kinetics of reaction (2) on water, temperature, and the type of formulation (e.g. Banks 1991, Feuersenger 1955, Meuser et al. 1977 a, b, Mori and Kawamoto 1974, Rosebrook 1972).

All commercially available phosphide products have to pass safety examinations for inflammability and speed of reaction. One of the disadvantages of all products still is the phosphine gas content of the cans and canisters containing the formulation. This is set free immediately on opening the packing prior to use. Residual moisture present when the freshly produced formulations are packed into the cans or canisters in the factory is sufficient for production of this phosphine. Additionally, when applying and distributing the products after opening the pack, workers are in danger of inhaling the small amounts of phosphine which are produced at a low rate immediately moist air has access to the formulations.

A recent new approach is the development of formulations which prevent this type of early production of phosphine. This paper describes the advantage of the new Gas Ex-B bag¹ (Kapp and Moog 1991, 1992) in comparison with other normally used bags and pellets.

Materials and Methods

Description of the essential features of the new formulation

Phosphine generation can be prevented by addition of chemicals which tend to react with water before it diffuses into the phosphide. After long search, zeolites have been determined to be sufficiently hygroscopic to trap moisture (3) and prevent the reaction of phosphides to phosphine. Moreover, they are sorptive enough to trap traces of developing phosphine in the packing during the early stage of reaction (4) and (5), until they are saturated with the gas:

[(Metal phosphide + protective compound) + dry Zeolite] + Water → [(Metal phosphide + protective compound) + wet Zeolite] (3)

Instead of reaction (3), another step seems possible and likely to avoid the diffusion of phosphine from the product:

* Federal Biological Research Centre for Agriculture and Forestry, Institute for Stored Product Protection Königin-Luise-Straße 19, 14195 Berlin, Germany.

¹ Commercial products of Detia Degesch, Laudenbach, Germany.

Results

[(Metal phosphide + protective compound) + dry Zeolite] + Water → [(Metal phosphide + protective compound) + (dry Zeolite + phosphine) + Metal hydroxide] (4)

After the saturation of the zeolite with water, the generation of phosphine from the product begins:

[(Metal phosphide + protective compound) + wet Zeolite] + Water → Phosphine ↑ + [Metal hydroxide + wet Zeolite] (5)

The amount of zeolite together with the phosphide formulation in reaction (3), (4), and (5) determines the sorptive capacity for water. Some tiny amounts of phosphine which may develop are immediately sorbed by the zeolite (4). Later on in the process of the reaction, when the zeolite is saturated with water, further moisture diffuses to the phosphide and supports the generation of phosphine as described by reaction (5). When most of the phosphide has been transformed into phosphine and this gas has diffused away, any sorbed phosphine efficiently desorbs again from the zeolite. The new bags are made of Tyvek®, a material which has similar properties like Gore-Tex®, which reduces the speed of water transport to the phosphide formulation compared to the paper bags of the Detia Gas Ex-B product.

Comparison of different formulations

The release rate of different formulations was determined by Reichmuth (1981) by observing the build up of phosphine concentrations in a fumigation chamber. The first 30 minutes after opening the packs were especially investigated. The chamber was kept at constant temperature of 22°C and relative humidity of approximately 62%. Formulation, either in a new bag or an old conventional bag (each with 34 g product) or 56 pellets of Detia Gas Ex-P were exposed in a volume of 2.8 m³. A number of replicate exposures were carried out.

A Miran infrared analyser operating continuously at a wave length of 9.5 μm was used to record the gas concentration. The analytical parameters were: about 3.5 volume of the cell, an optical path length of 21.75 m, slit 1 mm, response time 40 seconds, with high gain. Gas chromatography (AFID, Noack et al. 1978) was used to determine phosphine concentration for calibrating the Miran.

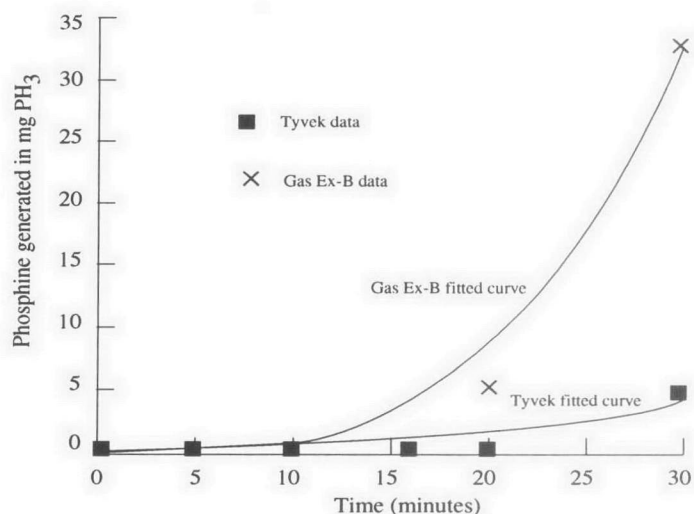


Fig. 1. Comparison of the phosphine release in mg at 20°C and 63% r.h. in a gas tight fumigation chamber between old conventional and new Detia Gas Ex-B bags for the first 30 minutes after opening the canister

Figure 1 shows data and fitted curves for release of phosphine from old conventional and new bags of Detia Gas Ex-B. The old bags started much earlier to develop gas though initially at a low rate. After about 15 minutes the rate increased significantly. During the experiments with the new Tyvek-bag, phosphine could be detected for the first time only after 30 minutes (detection limit of about 0.15 mg/m³). For the regression of the concentration data. A function to describe the increase in concentration with time was fitted to the full set of data (Figure 2). Except for the first few minutes after opening the packings, a log-normal function of the form

$$y = a + b * \exp\{-0.5 * [\ln(x/c) / d]^2\}$$

described the different concentration characteristics very closely ($r^2 = 0.996$ or better).

It became obvious that the zeolites reduce the release rate of phosphine during the first 30 minutes of the initial fumigation period by factor of three or more. The regression curves in Figure 2 demonstrate the pronounced differences of the speed of phosphine generation for these formulations. After several hours, the total amount of released phosphine of the pellets and Tyvek bags was similar, between pellets and Tyvek bags as shown in Figure 4. The inhibition of the initial release rate can clearly be seen. Old and new bags evolved the phosphine markedly more slowly than pellets, with Tyvek bags giving the lowest rate (Figure 4).

In the normal practice of fumigation, the actual concentration of phosphine in air is the critical factor for worker safety. From Figure 5 it can be seen that the phosphine concentration remained in the chamber below 1 ppm for more than 30 minutes, and for 12 minutes below 0.1 ppm, the TLV (Threshold Limit Value) in many countries (Anon. 1988).

Discussion

Even competitors in the market of phosphine releasing products admit that the new Detia-Degesh formulation results in packs which are nearly free of gas on opening. This has been noticed also by the author.

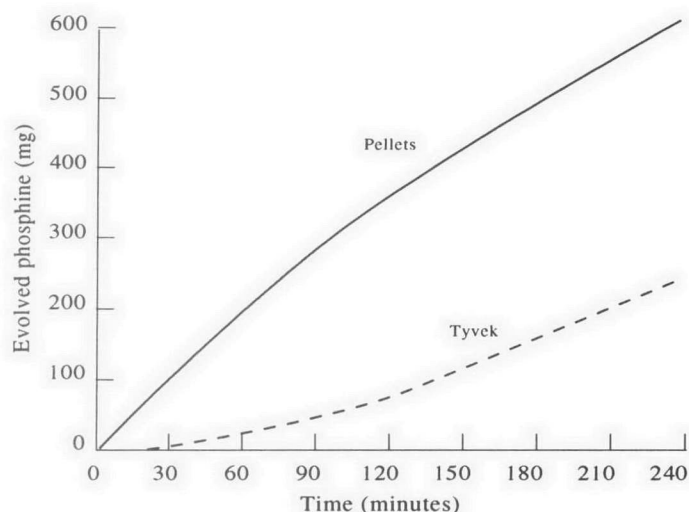


Fig. 2. Comparison of the generation of phosphine in mg at 20°C and 62.5% r.h. and 64% r.h., respectively, between new Gas Ex-B (Tyvek) bags and Gas Ex-P pellets for 4 hours

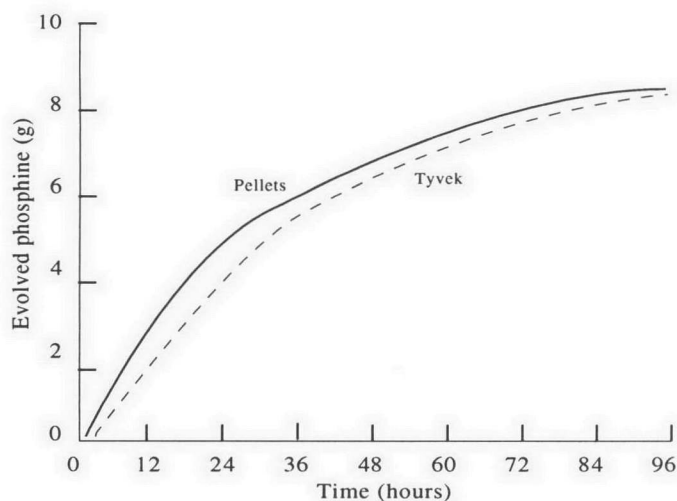


Fig. 3. Comparison of the phosphine release in mg at 20°C and 62.5% r.h. and 64% r.h., respectively, between new Gas Ex-B (Tyvek) bags and Gas Ex-P pellets for 4 days

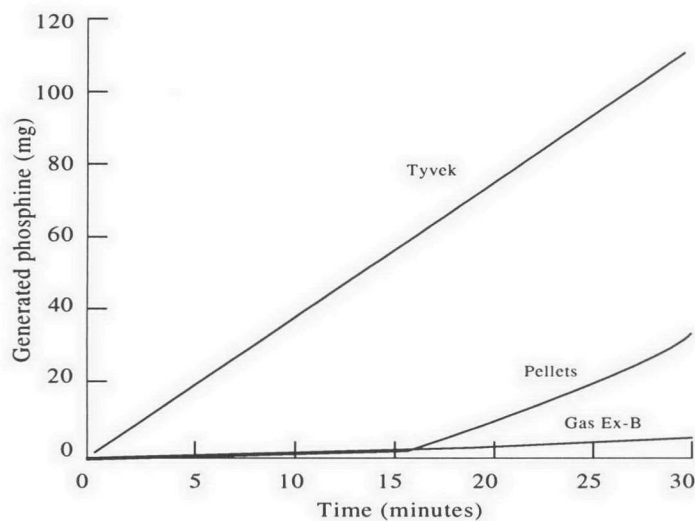


Fig. 4. Initial phosphine release in mg from new and old conventional Gas Ex-B bags and Gas Ex-P pellets within the first 30 minutes at 20°C and 62.5% r.h., and 64% r.h., respectively

The presented results were obtained at a dosage of 1 bag/ 2.8 m³ at 20°C and 60% r.h. in an empty fumigation chamber. This dosage lies above that usual in many fumigations, but still in the range of some practical applications. The transport of this type of phosphine formulation is safer than of usual products, because of the reduced risk of ignition and explosion in case of any accidental breakage. In many countries and at least in Germany, worker safety plays a predominant role in the transport and use of fumigants in pest control. This convenient new formulation can potentially be dispensed without the risk of inhalation of phosphine for more than half an hour after opening the packs.

Other approaches try to overcome the problem of release of phosphine by applying the gas as a mixture with carbon dioxide from steel cylinders (Chakrabarti et al. 1992, Winks and Ryan 1992). These heavy weights are not easy to handle in many situations. The use of cylinder gas has the advantage of being interruptable at any time but it remains restricted to applicators with a fair degree of engineering skill and needs continuous observation.

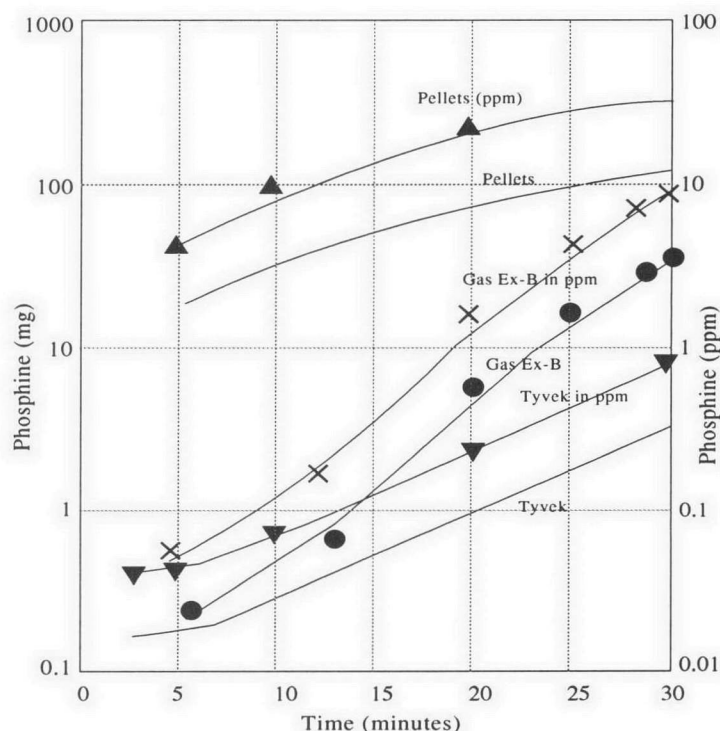


Fig. 5. Build up of phosphine concentrations in ppm from different formulations during the first 30 minutes of exposure

The new formulation tries to improve the idea of a light powder which can safely be transported, distributed and applied before the generation of the effective gas starts by hydrolysis with ambient water vapour, leaving behind harmless residues.

Acknowledgments

The author thanks Miss B. Hennig and Mr. G. Schmidt for splendid technical support. Mr. Schmidt also helped to prepare the graphs. Detia-Degesch supplied the products and gave financial support to Miss Hennig. Dr.C. Adler commented on the manuscript.

References

- Anonymous 1934. title German Patent No. 698721 (November 7).
- Anonymous 1988. Phosphine and selected metal phosphides. Environmental Health Criteria No. 73. WHO, Geneva, 100 p.
- Banks, H.J. 1991. Influence of water and temperature on release of phosphine from aluminium phosphide-containing formulations. *Journal of Stored Products Research*, 27, 41–56.
- Chakrabarti, B., Mills, K.A., Bell, C.H., Woner-Smith, T. and Clifton, A.L. 1992. In: Fleurat-Lessard, F. and Ducom, P., ed., *Proceedings of the Fifth International Working Conference on Stored-product Protection*, Bordeaux, France, September 1990, 2, 775–784.
- Feuersenger, M. 1955. *Lebensmittelhygienische Fragen der Kornkferbekpfung mit Phosphorwasserstoff*. *Deutsche Lebensmittel Rundschau*, 51, 293–296.
- Freyberg, W. and Friemel, W. 1965. *Verfahren zur Bekpfung von Schdlingen [Procedure for pest control]*. German Patent No. 1143053, 3p.
- Kapp, W. and Moog, A. 1991. Method and means for preventing or delaying undesired phosphine levels. United States Patent, No. 5,015,475.
- Kapp, W. and Moog, A. 1992. *Verfahren zur Phosphinregulierung, Schdlingsbekpfungsmittel und dessen Verwendung [Procedure to regulate phosphine, control pest agent and its application]*. European Patent, No. 0 342 471 B, 119 p.

- Meuser, F., Rajani, C. and Reimers, H. 1977a. Bestimmung der Hydrolysegeschwindigkeit von pelletierten Metallphosphiden zur Getreidebegasung [Determination of the speed of hydrolysis of pelleted metal phosphides for grain fumigation]. *Mühle + Mischfüttertechnik*, 114, 423–426.
- Meuser, F., Rajani, C. and Reimers, H. 1977b. Rate of hydrolysis of pelleted metal phosphides in grain fumigation. *Milling Feed and Fertilizer*, 160, (10) 15–16, 18, (11) 27–28, 34.
- Mori, T. and Kawamoto, N. 1966. Studies on the properties and effect of fumigant, aluminium phosphide. *Research Bulletin Japan Plant Protection Service*, 12, 28–30.
- Reichmuth, Ch. 1981. Inbetriebnahme der Begasungsstation des Instituts für Vorratsschutz der Biologischen Bundesanstalt für Land- und Forstwirtschaft in Berlin-Dahlem [The new fumigation laboratory of the Institute for Stored Product Protection of the Federal Biological Research Centre for Agriculture and Forestry in Berlin-Dahlem]. *Nachrichtenblatt des Deutschen Pflanzenschutzdienstes*, 33, 161–165.
- Reichmuth, Ch. 1992. New techniques in fumigation research today. In: Fleurat-Lessard, F. and Ducom, P., ed., *Proceedings of the Fifth International Working Conference on Stored-product Protection*, Bordeaux, France, September 1990, 2, 709–725.
- Rosebrook, D. 1972. Evaluation of phosphine preparation Detia Gas Ex.-B. Midwest Research Institute Project No. 3502-C. 38 p.
- Tateya, A., Saeki, S. and Kawamoto, N. 1974. Effect of temperature and humidity on the decomposition of aluminium phosphides. *Research Bulletin Japan Plant Protection Service*, 12, 28–30.
- Winks, R.G. and Ryan, R. 1992. Recent developments in the fumigation of grain with phosphine. In: Fleurat-Lessard, F. and Ducom, P., ed., *Proceedings of the Fifth International Working Conference on Stored-product Protection*, Bordeaux, France, September 1990, 2, 935–943.