Fumigation with phosphine under gas-proof sheets (ODNRI Bulletin No. 26)

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OVERSEAS DEVELOPMENT
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FUMIGATION WITH PHOSPHINE UNDER GAS-PROOF SHEETS

R. FRIENDSHIP

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SUMMARY

Although fumigation with phosphine is a simple technique, results, in terms of insect mortality, are often unsatisfactory. This is because complete insect control can only be achieved if an insecticidal concentration of phosphine is maintained for a sufficient length of time. Where multiple fumigations with phosphine have failed to meet these criteria insect resistance to phosphine has become established. This bulletin describes the formulations, equipment, application techniques and safety considerations required to achieve satisfactory fumigation results.

RÉSUMÉ

Bien que la fumigation à la phosphine relève d'une technique simple, ses résultats, en terme de morts d'insectes, sont souvent insatisfaisants. Ceci tient au fait qu'un contrôle total des insectes ne peut être obtenu que si la concentration insecticide de phosphine est maintenue pendant un délai suffisamment long. Là où de multiples fumigations à la phosphine ont mangué à cette exigence, les insectes ont développé une résistance à celle-ci. Le document présente les formules, le matériel, les techniques d'application et les facteurs de sécurité qui s'imposent en vue d'obtenir des résultats de fumigation satisfaisants.

RESUMEN

Si bien la fumigación con fosfina es una técnica sencilla, con frecuencia, los resultados obtenidos son poco satisfactorios, en términos de mortalidad de insectos. Ello se debe a que solamente puede lograrse un control completo de los insectos, mediante el mantenimiento de una concentración insecticida de fosfina por un período de tiempo suficientemente prolongado. En aquellos casos en que la aplicación de fumigaciones múltiples con fosfina no se han adecuado a los criterios indicados, se ha producido el arraigo de la resistencia de los insectos a la fosfina. En el presente artículo, se describen las formulaciones, equipo, técnicas de aplicación y consideraciones de seguridad requeridos para conseguir resultados satisfactorios con la fumigación.

Fumigation with phosphine under gas-proof sheets

INTRODUCTION

Background

The insecticidal properties of phosphine were first demonstrated by Freyburg in 1935 using aluminium phosphide powder in packets, but it was not until the mid-1950s, and after considerable research, that this simple and convenient method of fumigation gained world-wide popularity. In 1973 Heseltine published 'A guide to phosphine fumigation in the tropics' (Heseltine, 1973), but more recently there has been an increase in the incidence of stored product insect populations exhibiting resistance to phosphine. This gives cause for serious concern because the only alternative fumigant currently in general use is methyl bromide, and fumigations carried out with this material require more equipment and skill than those needed for phosphine if it is to be used successfully.

A particular requirement in phosphine fumigations which has often proved difficult to meet is that of maintaining lethal concentrations for the 5 days or more needed to kill all insects present. This requirement is a consequence of the mechanism by which phosphine is taken up by insects and its subsequent mode of action.

The classical way in which resistance develops is when successive generations of insects are subjected to sub-lethal doses of an insecticide. This will eliminate susceptible insects to the extent that the surviving population becomes progressively more resistant until such time as the efficacy of the insecticide being used is minimal. This has occurred in the field, where lethal concentrations of phosphine have not been maintained for a sufficient length of time to kill all insects exposed to the fumigant. The situation is further exacerbated because the minimal lethal concentration level increases as more resistant strains predominate in the insect population. Because of the grave commercial implications of large-scale development of phosphine-resistant insects there is a need to re-examine the use of phosphine. The following section is intended to serve as a check-list of the sequence of activities involved in fumigating a bag-stack with phosphine.

Practical procedures for fumigation of stacks of bagged produce

The fumigation of stacks of bagged produce under gas-proof sheets is the commonest form of fumigation carried out with phosphine in developing countries and, ideally, operators should follow the procedure described below when carrying it out:

Preparation

(a) Inspect the stack:

- is it liable to collapse?

- is it 1 metre clear of all obstructions?
- is the floor gas-proof?

(b) Dimensions of the stack:
- calculate the surface area to determine sheet requirements;
- calculate the volume or tonnage to determine dosage of fumigant required.

(c) Inform the relevant store authority when possession of the store will be required for the fumigation to take place.

(d) Spray the stack (and the fabric of the store) with a suitable residual insecticide.

Fumigation

(a) Instruct the pest control team as to how the fumigation is to be undertaken.
(b) Make sure that sufficient suitable gas-masks and canisters are available.
(c) Make sure that the building is unoccupied except for the pest control team.
(d) Cover stack(s) with fumigation sheet(s).
(e) Distribute sand-snakes around the foot of the stack.
(f) Determine where the phosphine preparation is to be placed and distribute unopened packs as evenly as possible round the stack.
(g) Place the exposed fumigant preparation and seal the sheet to the floor.
(h) Place warning notices and secure the store.

Termination of the fumigation

(a) Wearing gas-masks, enter the store and open all windows and ventilators.
(b) If live insects are present in the store, apply a suitable residual insecticide.
(c) Lift one corner of the sheet and vacate the store.
(d) After a suitable interval, check that the phosphine concentration is at a level safe enough for entry into the store without wearing gas-masks and then go in and remove the sheets completely.
(e) Safely dispose of the spent residues of the formulation used to generate phosphine.
(f) Remove warning notices.
(g) Issue a 'clear of fumigant' certificate to the person in charge of the store.
(h) Inspect the stack to find out if the insects are dead; if not, why not – what went wrong? Find out and then repeat the fumigation doing it properly.

The following sections provide background detail to these operations and discuss the reasons why it is important that each be carried out conscientiously if good results are to be obtained and if problems of resistance are to be avoided.

GENERATION OF PHOSPHINE

Phosphine is generated from solid formulations containing aluminium or magnesium phosphide. Aluminium and magnesium phosphide react with atmospheric moisture to produce phosphine (hydrogen phosphide) gas and metallic hydroxides:

$$AlP + 3H_2O \rightarrow PH_3\uparrow + Al\,(OH)_3$$

and $Mg_3P_2 + 6H_2O \rightarrow 2PH_3\uparrow + 3Mg\,(OH)_3$

At temperatures below 15°C this reaction takes place too slowly to be completed within the recommended minimum 5-day fumigation exposure period, so this is regarded as the lowest ambient temperature at which phosphine fumigations should be attempted. Increases in temperature over 15°C accelerate phosphine generation. The chemical reaction is also influenced by the relative humidity of the air within the structure under fumigation and in contact with the phosphine formulation. At relative humidities below 40%

the exposure period may have to be extended to achieve full decomposition of the phosphine formulation. Conversely a commodity with a high moisture content (say of more than 14%) may be damaged if it is covered with sheets for 5 days or more, owing to possible moisture migration leading to mould growth and heating. Complete decomposition is never achieved, with some 5% of aluminium phosphide, and smaller amounts of magnesium phosphide preparations remaining as unreacted residue. Magnesium phosphide, under similar conditions, generates phosphine more quickly than aluminium phosphide. Because phosphine is highly flammable, manufacturers include flame retardants such as ammonium carbamate, paraffin wax and urea in their formulations – the lowest concentration of phosphine at which explosions spontaneously occur is 1.79% by volume in air or 27 g of phosphine/m^3. The molecular weight of phosphine is 34.04 and approximates to that of air (1:1.2) compared to methyl bromide with a molecular weight of 94.95 (1:3.75). Phosphine diffuses through the commodity under fumigation much more rapidly and evenly than methyl bromide and is adsorbed less onto the commodity, packaging material and inner surfaces of the fumigation structure. The rate of release of different aluminium phosphide formulations is given in Table 1.

Table 1

Rate of release of different aluminium phosphide formulations showing time in hours (to nearest 5 hours) to attain various concentrations

Preparation	Concentration of phosphine achieved	15°C 53% r.h.	15°C 75% r.h.	25°C 53% r.h.	25°C 75% r.h.
Phostoxin tablets	50% of maximum	40	30	20	20
	75% of maximum	60	40	30	30
	Maximum	95	75	60	45
Phostoxin pellets	50% of maximum	40	30	20	15
	75% of maximum	60	45	30	20
	Maximum	100	80	60	45
Detia packets	50% of maximum	40	40	30	20
	75% of maximum	75	75	50	30
	Maximum	145	150	120	65

Source: Heseltine (1973)

World-wide there are some 18 manufacturers of phosphine formulations, major manufacturers being: Detia GmbH and Degesch, Federal Republic of Germany; Delicia, German Democratic Republic and Excel Industries, India. Formulations and packs are summarized in Table 2.

Table 2

Summary of phosphine formulations and packs

Active ingredient	Product form	Weight (gross) g	Weight of phosphine produced g	Unit pack
Aluminium phosphide	Tablets	3	1	Tubes containing 20 or 30 tablets
Aluminium or magnesium phosphide	Pellets	0.6	0.2	166 or 1,660 per re-sealable flask
Aluminium phosphide	Bags	34	11	10 or 20 bags per tin
Magnesium phosphide	Plates	206	33	32 plates per tin
Magnesium phosphide	Strips	3,200	528	2 strips per tin
Aluminium phosphide	'Round' tablets	3	1	100 or 500 per resealable flask

In addition to the above, some manufacturers market small packs such as the Degesch tiny tins containing 30 tablets in a resealable flask for small-scale fumigations, and large packs such as the Detia blanket comprising 100 standard bags each producing 11 g of phosphine. All tins and flasks are packed in wooden cases which contain a packing slip bearing the date of manufacture. Flasks are resealable, but the contents of tubes which are fitted with plastic stoppers should all be used up once opened.

DOSAGE RATES AND EXPOSURE PERIODS

Fumigant dosages are calculated on the volume of the sheeted stack or the tonnage of commodity to be fumigated. The former is preferred because the total volume has to be treated, and this may be more than that occupied by the commodity, for example, in a part-filled silo. However, if the stack is irregular in shape it may be more convenient to calculate the dosage on tonnage. Various recommendations are given for dosage rates and exposure periods; for example, one manufacturer recommends:

1-1.5 tablets (g) per m^3 for 120-168 hours at 10-15°C
120 hours at 20°C
72-96 hours above 20°C.

Heseltine (1973) suggested 2-5 g fumigant per tonne depending upon the insect pest species prresent and the length of exposure period employed. In Australia the recommendation to farmers is a concentration in the free space of at least 100 p.p.m. (0.14 g/m^3) over an exposure period of 100 hours. The French Standard V30-107 (1988) states that all concentrations above 0.07 g/m^3 (50 p.p.m.) are active. Appropriate recommendations vary according to the prevailing circumstances, but the ODNRI general recommendation for temperatures of above 20°C is 1.5 g/m^3 for a minimum exposure period of 120 hours during which the concentration of phosphine should not fall below 0.2 g/m^3. High concentrations for short exposure periods are not recommended because the immature egg and pupal stages of the insect pest are generally more tolerant to phosphine than the larvae and adults, and it may be necessary for a susceptible stage to develop before complete control is achieved. Furthermore, under certain conditions a high concentration can induce narcosis in insects which reduces their susceptibility to phosphine poisoning. Frequently the time available for a fumigation operation to be carried out is insufficient to meet the minimum exposure requirement; in such instances methyl bromide should be used rather than phosphine, as the former requires an exposure period of only 24 - 48 hours.

Under a sheeted stack the available airspace is approximately 50% of the total volume, the remainder being occupied by the commodity and its packaging. In theory this would double the phosphine concentration, but in practice this does not occur because some of the phosphine is lost owing to:

- leakage through damaged sheets and floors and inadequate sealing of sheets to floors;
- the permeability of sheets and floors to phosphine;
- adsorption on to sheets, commodities and packaging; and
- chemical breakdown of phosphine.

The most serious losses are attributable to leakage, and a successful fumigation with a single application of fumigant requires still air conditions; the proportion of fumigant lost will increase with extended exposure periods.

On occasion it is necessary to monitor phosphine concentrations during fumigations – for example where an application technique is not giving satisfactory results, and for field research purposes. Gas-detector tubes have been commonly used for this purpose, but they are expensive and relatively inaccurate up to ±15%. Webley (1981) described the successful use of a portable infra-red gas analyser in Mali, but this apparatus costs some £16,000. A less expensive field meter known as the 'bubbler' was developed by Taylor

(1982). This instrument indicates the phosphine concentration by comparing colour changes with a Lovibond Disc Comparator, and is accurate to within 10%, but cannot be used to measure concentrations below 0.2 g/m^3. A conductimetric method was developed at ODNRI by Harris (1986) using a cell connected to a meter which gives a digital read-out in p.p.m. This equipment has been field-tested in several countries, is accurate to $\pm 5\%$ and costs less than £1,000. It is now marketed on a commercial basis and is recommended for general use where it is necessary to measure phosphine concentrations. Typical curves plotted from phosphine concentrations over time are illustrated in Figure 1. In converting p.p.m. to mg/l or g/m^3 corrections are made for temperature and barometric pressure according to the following formula:

$$\text{mg of phosphine} = \frac{\text{p.p.m.} \times P}{1832 \times (273 + T)}$$

where P = barometric pressure in mm of mercury
T = temperature in °C of the conductivity cell.

From Figure 1 it can be seen that phosphine concentrations increase at a steady rate as the preparation continues to generate phosphine, levelling off and then starting to decline as generation nears completion. Concentrations then decline at a more acute angle as phosphine is lost from the air space. Towards the end of the exposure periods, as low concentrations are approached, the curves typically level off. In both fumigations while phosphine is being actively generated it more than compensates for any losses which occur, but the rate of loss is greater in the 'failed' fumigation which peaked at a lower level than the 'successful' one. Losses were approximately 50% in the former and 35% in the latter. It will be appreciated that in both fumigations, in terms of air movement, virtually still air conditions prevailed. Champ and Dyte (1976) postulated that phosphine resistance is developed in association with the use of phosphine under conditions that conflict with the accepted principles of fumigation and the known properties of phosphine. More recently this has proved to be true where fumigations have taken place under conditions of less than adequate gas-tightness, resulting in the establishment of insect populations resistant to phosphine.

When placing tablets it is important that they are evenly spread out because high concentrations can result in spontaneous combustion; even when they are evenly exposed during active phosphine generation, gas concentrations in proximity to the preparation will be double that in the remainder of the space. However, once generated, phosphine does diffuse very quickly through the air space. Conversely it has been observed that when a heap of tablets was exposed to the air, residues from exposed tablets on the surface of the heap prevented moisture coming into contact with the remainder, so that after 5 days' exposure only partial decomposition had taken place.

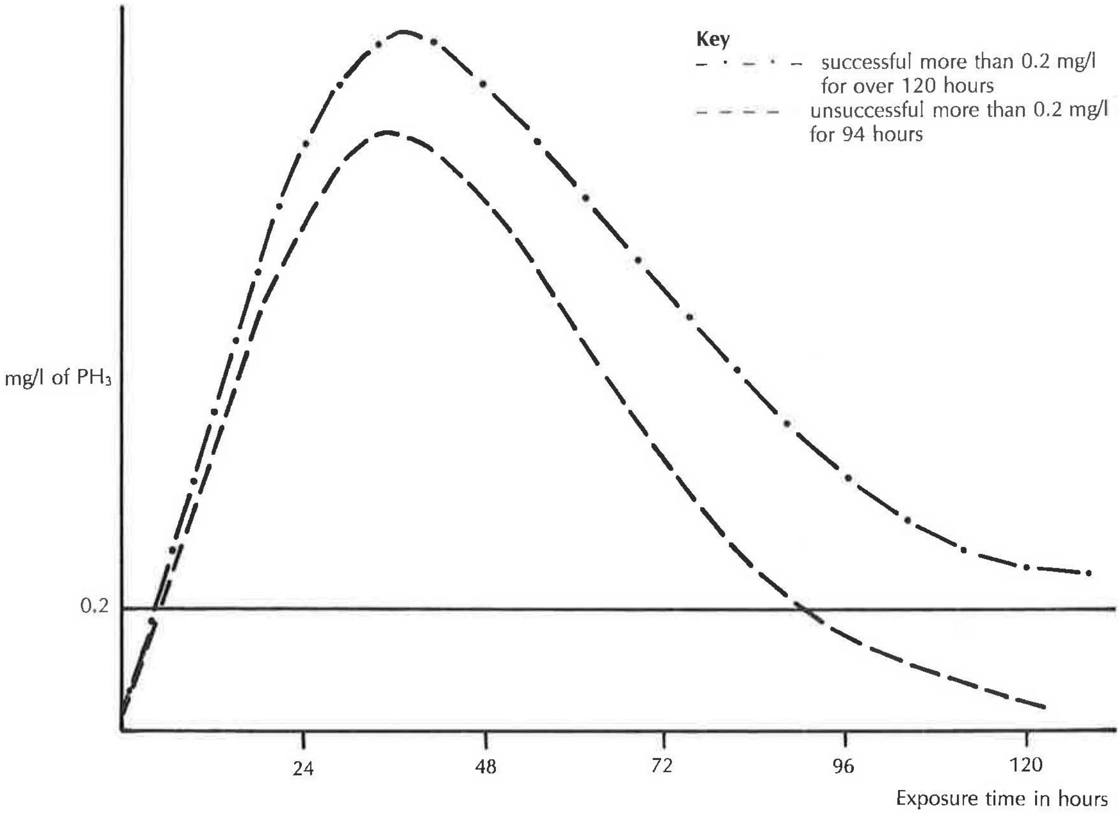
STACKS

Stacks should be constructed on a sound gas-proof floor of good quality concrete incorporating a water-vapour-proof barrier. If the floor does not meet these specifications and there is a possibility that the stack will have to be fumigated, it should be built on a gas-proof plastic ground sheet which extends one metre beyond the base of the stack, so enabling a gas-tight seal to be made between the fumigation and ground sheets.

Stacks should be well-constructed so that there is no danger of their collapsing during fumigation operations. For this purpose bags should be arranged to form a tied stack.

Rectangular stacks are to be preferred for fumigation purposes because they are more economical for covering with fumigation sheets and use of fumigant and there is a minimum of free air space under the sheet. Other stack shapes traditionally used are the stepped stack, or if built outside, stacks with tapering upper layers such as the well-documented Nigerian groundnut pyramids.

Figure 1
A comparison of successful and unsuccessful phosphine fumigations according to the ODNRI recommendation



Irregularly shaped stacks may be the result of poor construction, availbility of stock, or part issue of the stack. Although this may complicate the sheeting it has no effect on the efficacy of phosphine as a fumigant because of its excellent diffusion characteristics.

THE USE OF FUMIGATION SHEETS

The ideal fumigation sheet is light-weight, strong, flexible, impermeable to fumigant gases, heat-and UV-resistant and inexpensive. It is unlikely that any available sheet will meet all these criteria and a compromise will have to be made based on the following considerations:

- local availability of candidate sheet material;
- cost;
- intended use;
- permeability to the fumigants which are to be used;
- weight per unit (m^2) area;
- strength of the material;
- handling characteristics;
- resistance to UV light and heat (if the sheet is also to be used for methyl bromide fumigation the sheet must be resistant to damage by liquid methyl bromide).

Candidate materials for use as fumigation sheets include:

- unsupported PVC;
- woven polythene;
- PVC laminate;
- PVC on a nylon or terylene scrim;
- multi-layer thin film laminates.

The choice of sheet will also be influenced by the purpose for which it is intended to be used, for example, a new 125-mm polythene sheet is adequate for a single fumigation. Fumigation sheets which are to be used exclusively in a single storage complex do not need to be so robust as those which are to be transported to several storage sites, and unsupported 250-mm polythene or PVC would be quite satisfactory for single-site use. Several units of thickness are used; in specifying thickness of sheets these can be summarized as follows:

1000 gauge = 0.01 in = 0.254 mm = 254 mm.

Sheets can be fabricated to any given size by joining panels with high frequency welding. Where a standard stack size is used it is convenient to have sheets made to fit such stacks, or in special instances shaped covers can be made. Maximum sheet sizes are dictated by the weight which the pest control team can conveniently handle – 18 × 12 m is the convenient standard size.

The permeability of a sheet to a fumigant is an important consideration as this may cause an unacceptable loss during the exposure period. Permeability is measured according to the following formula:

$$K = \frac{2.203 \times V(\log C_o - \log C_t)}{At}$$

where K = the permeability constant and is the rate of loss in mg of fumigant per hour per cm^2 per unit concentration of one mg per litre
A = the area of exposed sheet material in cm^2
V = the volume of the fumigation chamber
C_o = the initial concentration in mg per litre
C_t = the final concentration in mg per litre after time (t) in hours.

A satisfactory sheet for methyl bromide fumigations is where the value of K = 3 or less. There is no figure quoted for phosphine, but an acceptable 18% loss of phosphine over a 5-day exposure period would give a K value of 1.12.

The area of sheet required to cover a stack can be calculated as follows: 1 + height + breadth + height + 1 = width in m. 1 + height + length + height + 1 = length of sheet in m. If the area of stack surface to be covered is greater than that which can be covered with a single sheet, two or more sheets may be joined together as shown in Figure 2, although it is more convenient if a single sheet can cover the breadth of the stack. Sheets are joined by folding the first sheet back on itself to a distance of 1 m, covering this fold with the second sheet, then rolling the two together and securing with suitable 'G' or spring clamps.

For ease of handling, fumigation sheets should be folded as illustrated in Figure 3 and described below:

(a) spread the sheet out flat on a smooth surface. At this stage the sheet can be inspected and any hole or tears repaired;
(b) mark the centre line (i);
(c) fold one side of the sheet in metre laps until the mid point is reached (ii);
(d) fold the other half in a similar manner (iii) then fold one half on top of the other (iv);
(e) fold one end of the roll until it nearly reaches the other end (iv) then fold or roll it up (vi).

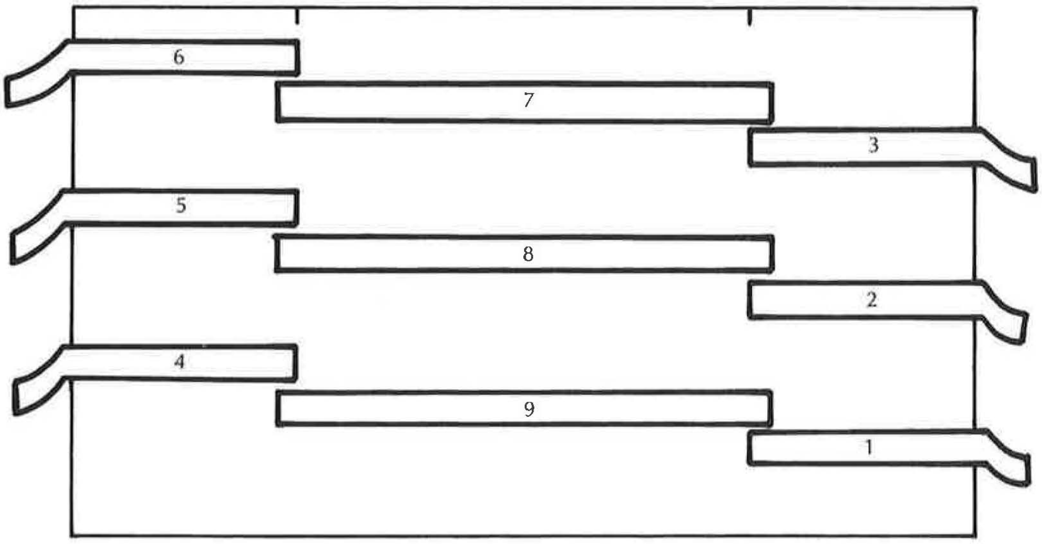
A well-folded sheet can be correctly orientated on top of the stack and then opened out to cover it with the minimum of manual effort. Sheets should always be carried and never dragged across the floor as this will cause damage and reduce the sheets' gas-proof properties. (*see* Figure 4)

To keep fumigant leakage to a minimum sheets must be carefully sealed to the floor. Two operators standing at adjacent corners of the stack should each place one hand to hold the sheet flat against the stack, and with the other grip the edge of the sheet and pull against each other until all the wrinkles are straightened out from that part of the sheet lying on the floor. This can then be sealed to the floor with 'sand-snakes'. Sand-snakes can be made from 12 cm diameter fire-hose or suitable lay-flat tubing cut into lengths of

Figure 2

Multiple sheeting of a large stack

(a) Place and unfold sheets on the stack in sequence from 1 to 9



(b) Make roll joints in sequence from A to H. Note that the joints are offset so that no four sheets are joined together

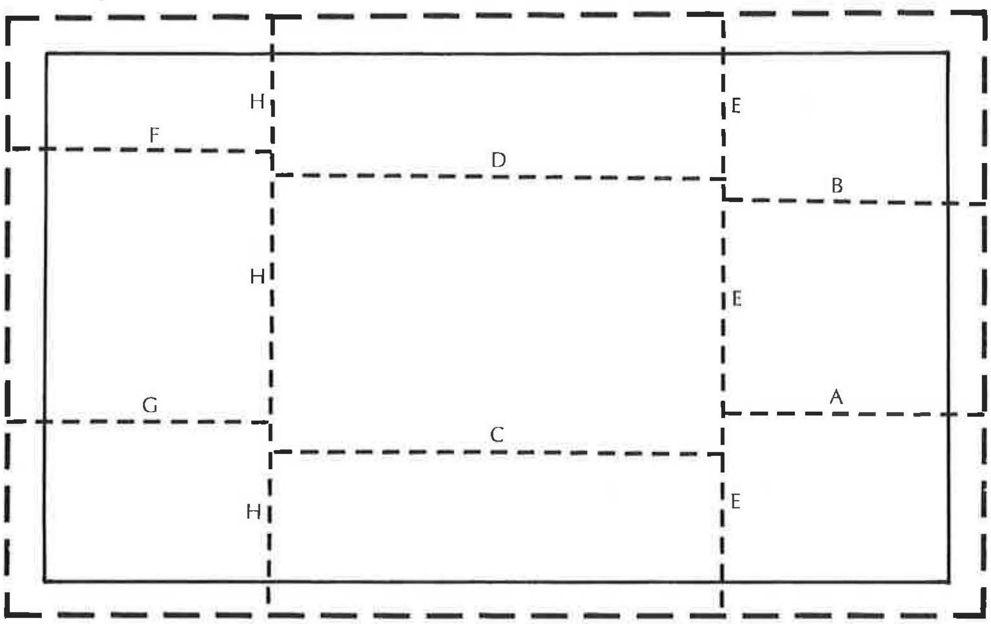
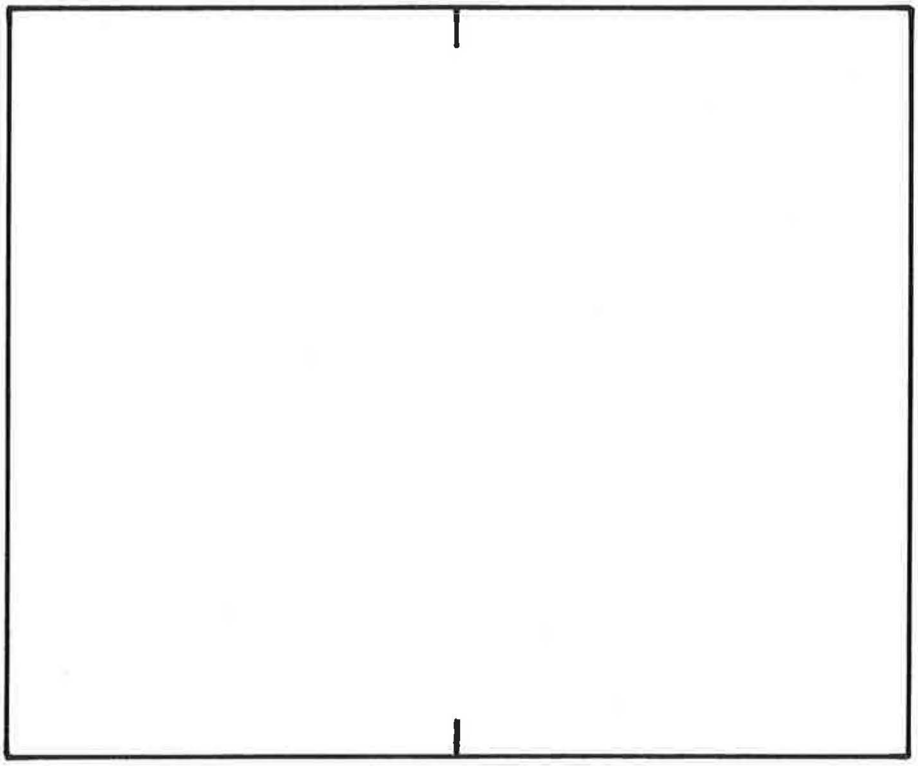


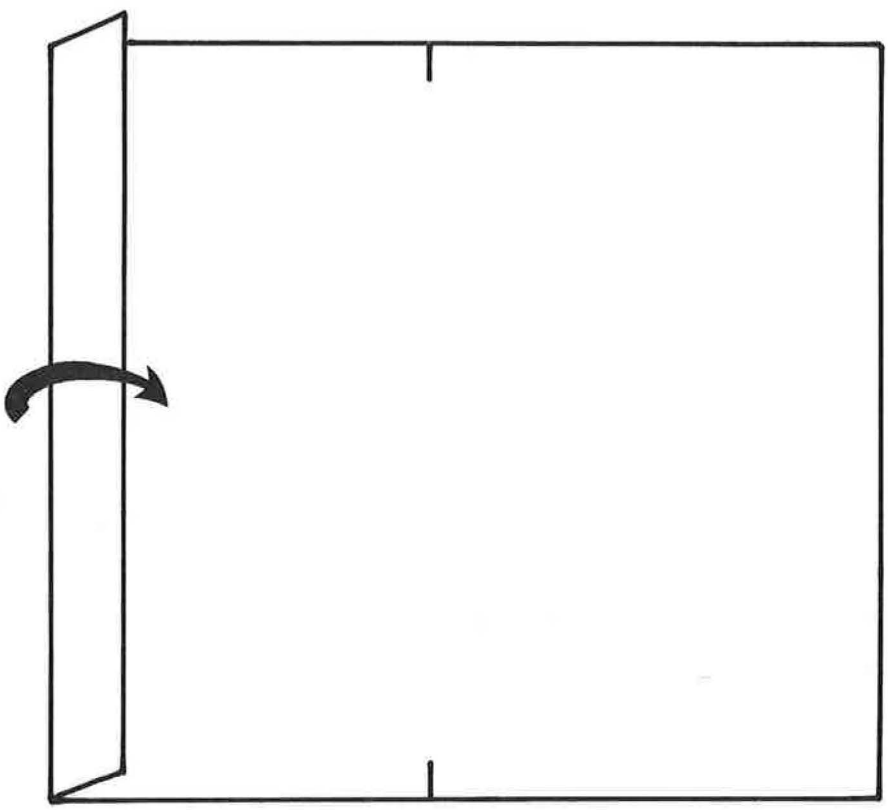
Figure 3

Folding a fumigation sheet

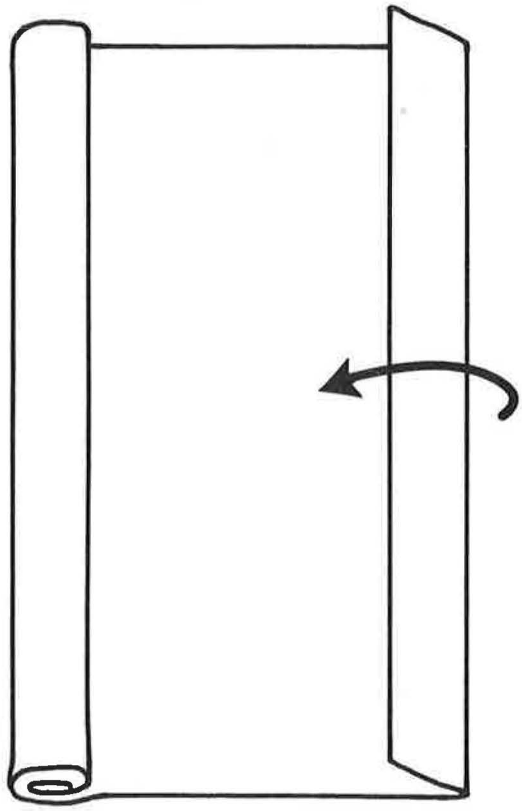
(i) Mark the centre of the sheet



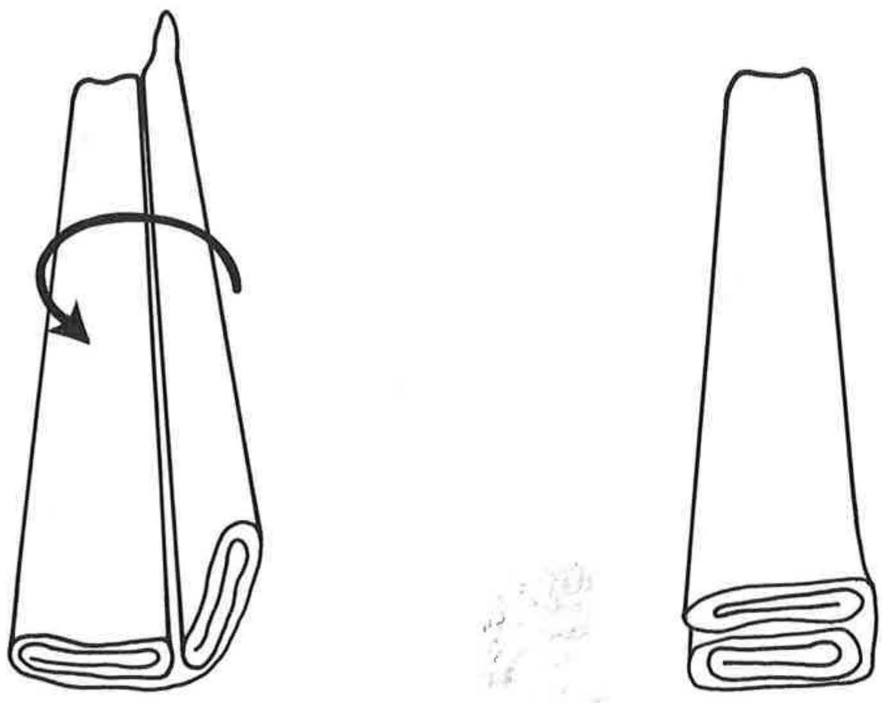
(ii) Fold one half towards the middle in 1–metre wide folds



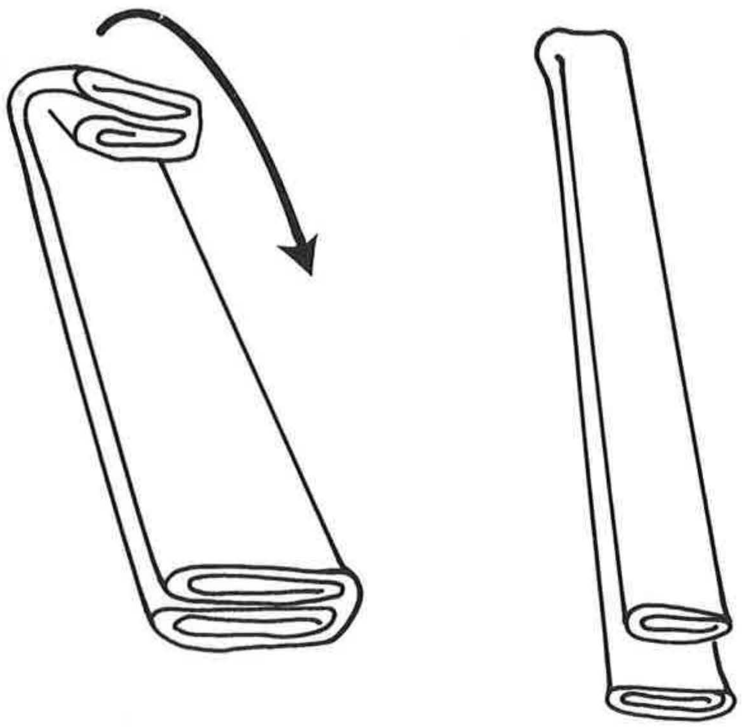
(iii) After half the sheet has been folded repeat this procedure for the remainder



(iv) Fold one half on top of the other



(v) Pull one end down over the other until the sheet is almost folded double

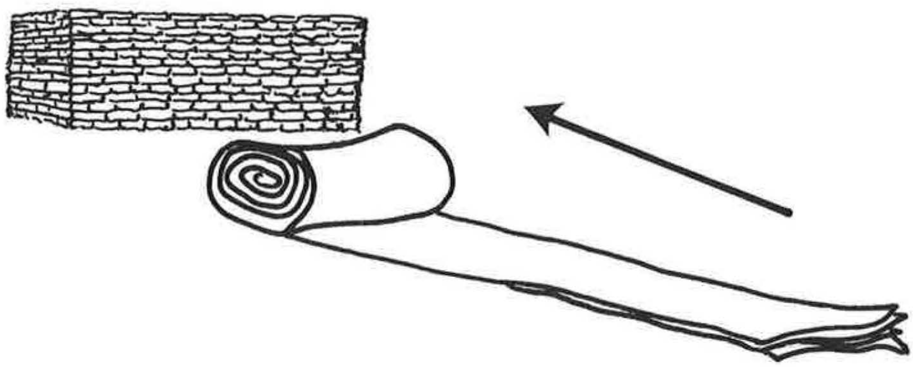


(vi) Then fold or roll in the direction of the arrow shown in (v) to achieve a well-folded sheet occupying the minimum of space

Figure 4

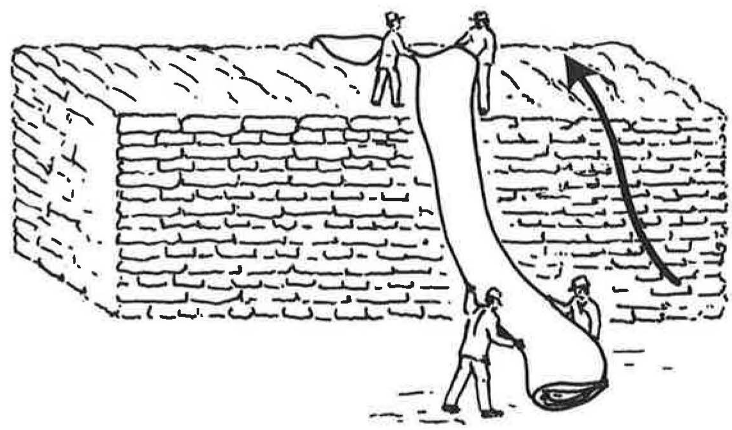
Covering a stack

(i) Unroll the sheet towards the stack

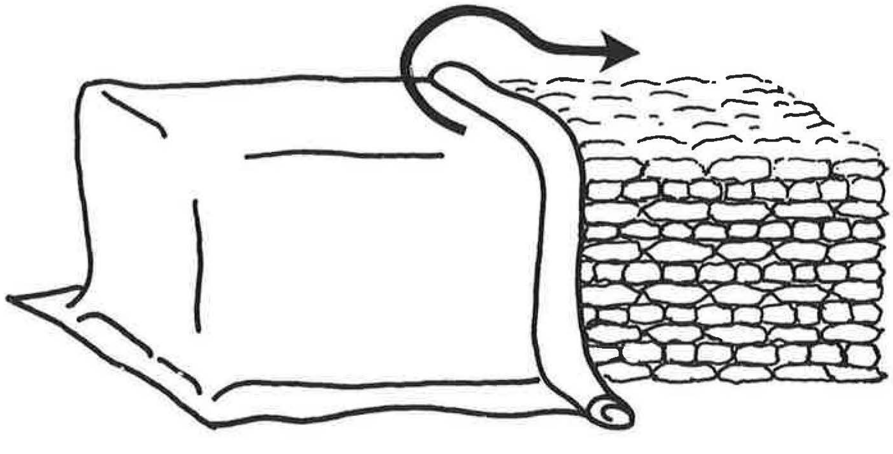


(ii) Carry, never drag, the sheet –

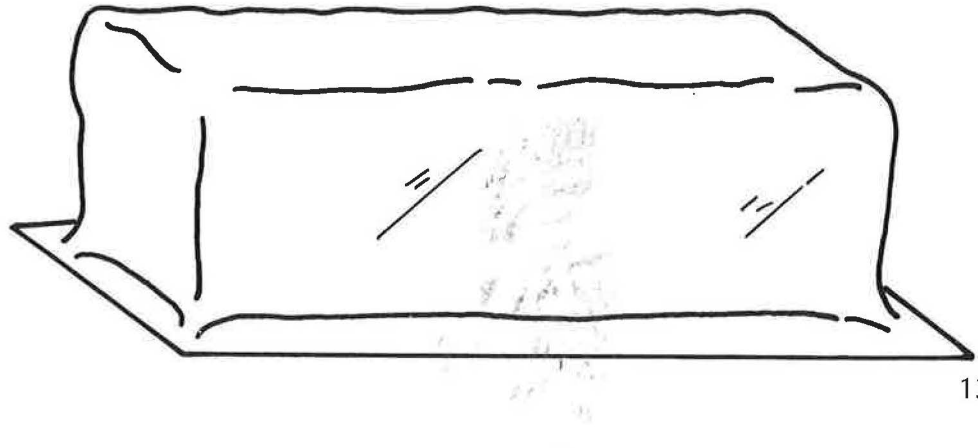
(iii) – and place it over the centre of the stack



(iv) Unroll one half dropping part of it over the sides in such a way as to place one metre flat on the floor



(v) Do the same with the remainder of the sheet



approximately 2.5 m and filled with dry sand. They must be placed on the sheet at the foot of the stack in such a manner that they overlap. This procedure must be repeated for the remaining three sides of the stack. To fold the sheet at the corners, one operator should kneel down on the sheet at a corner of the stack, place both hands on the sheet and push it round the corner so that a portion lies flat on the floor. Keeping this in place with one hand, the other should be used to work a piece of sheet from round the corner towards him until it is positioned flat on top of the sheet he is holding. This should be continued in concertina-fashion until all the sheet material forms a neat, tight fold; sand-snakes should then be placed at the remaining corners and a check made to see that the sheet is completely sealed to the floor. Where there is sheet material in excess of that required to cover the stack, the excess should be pulled up and folded on top of the stack rather than left lying on the floor, where it would make it more difficult to obtain a gas-tight seal at the corners, and would also serve as a safe harbourage for live insects. These insects could be a source of reinfestation once the fumigation is completed and the sheets removed.

As mentioned above, sheets should be inspected for any defects when laid out flat on the ground before folding. Inspection should again take place when the sheets are in position on a stack immediately before introducing the fumigant. It is sound practice to make a more thorough inspection at regular, monthly intervals. One method of doing this is to suspend the sheet from a roof truss in a store and inspect it against a light source, such as an open doorway, when holes can easily be detected by daylight showing through them. Temporary repairs can be effected using a suitable adhesive tape such as fabric-backed adhesive strip, but this will lift off in time and a more permanent repair should be made using a patch of sheet material fixed with an adhesive such as 'Bostik' which is compatible with the sheet material.

Rodents sometimes nest in folded fumigation sheets, causing considerable damage, even to the extent of making sheets unusable. Stored sheets should be protected against rodents by using a suitable rodenticide to control infestation.

PLACEMENT OF PHOSPHINE PREPARATIONS

Before opening any airtight pack containing a phosphine preparation, the fumigation sheets must be in place completely covering the stack with sufficient sand-snakes to seal the sheets to the floor distributed round the foot of the stack. Packs containing the phosphine preparation should be placed round the stack so that they will be distributed as evenly as possible. Formulations such as plates and bags can be suspended from the sides of the stack, but tablets and pellets should be placed on cardboard or plastic trays (30 × 30 cm is a convenient size) to facilitate recovery of the spent residue at the end of the fumigation and to prevent it from contaminating the bagged produce. When the stack has been constructed on dunnage, these trays can be conveniently slipped under the pallets, but if the stack has been built directly on the floor it will be necessary to place trays in previously constructed pits on top of the stack. This is to prevent disturbance of the tablets (or pellets) when replacing the fumigation sheet. Except where exposure is to be on top of the stack, a three-man team will be sufficient to place the phosphine preparation, with one man lifting the sheet, a second placing the preparation and the third sealing the sheet to the floor. This operation will take less time if it is possible to seal corners before placing the preparation.

Phosphine formulations contain substances which repel water and retard combustion, so reducing the rate at which phosphine is generated and reaches significant proportions in the atmosphere. However, magnesium phosphide generates phosphine more quickly than aluminium phosphide; pellets and tablets generate phosphine more quickly than Detia bags. As explained in the section on dosage rates and exposure periods (*see* p.5), temperature and atmospheric moisture also control the rate of phosphine evolution. Under warm, humid conditions (30°C and 80% R.H.) distribution of the fumigant, covering and sealing the stack and vacating the store must be completed within 15 minutes, while under more temperate conditions the safe period, before unacceptably high levels of phosphine occur, may extend to 1 hour or more. Usually it is not necessary to wear a gas-mask during this operation, but sufficient respirators should be available for the full pest control team present in case any delays beyond the safe period occur. The Australian CSIRO Division of Entomology and Queensland Department of Primary Industries tested several batches of phosphine tablets and observed that as soon as they were exposed to humid air gas was evolved and continued evolving at a steady almost linear rate. The delay period was never observed.

VENTILATION

It is good practice to fumigate all infestible material in a store at one and the same time to control all the insects present and so delay reinfestation. When this takes place, the store should be closed up and locked until ventilation takes place, and no persons other than the pest control personnel should enter until the pest control officer has issued a certificate to the person in charge of the store saying that it is safe to do so. Even if only part of the contents of the store are under fumigation, it is in the interests of safety to follow the same procedure, because unauthorized persons may displace fumigation sheets and leakage of fumigant may pose a hazard to people working in the building.

In a successful fumigation, even after a 7-day exposure period, the phosphine concentration under the fumigation sheet will be lethal to human beings. Only the pest control team, wearing suitable gas-masks, should enter the store. A routine for ventilating stacks (illustrated in Figure 5) is given below.

(a) All available doors and windows should be opened to create as much air movement as possible (**i**).

(b) Enough sand-snakes should be removed from one corner of the stack so that the fumigation sheet can be lifted up to expose a corner of the stack (**ii**).

(c) A ladder should be placed against the stack and two men, one with a length of rope, should climb on top (**iii**).

(d) The third man should then remove the ladder and tie the lowered end of the rope to the corner of the fumigation sheet (**iv**).

(e) The two men on top of the stack should then haul up the rope until they can reach the corner of the fumigation sheet. It should be noted that they must stand as near to the corner of the stack as possible otherwise the rope will become trapped between the bags. It is good practice to tie the rope to a convenient roof-truss to prevent the sheet from slipping back down the stack. Meanwhile the third man should replace the ladder against part of the stack which is to remain sheeted (**v**).

(f) Once a corner of the stack has been exposed, this part of the ventilation procedure has been completed. The three men should now leave the store (**vi**).

(g) The ventilation period is not yet complete and nobody should enter the store until the phosphine concentration has dropped to a safe level.

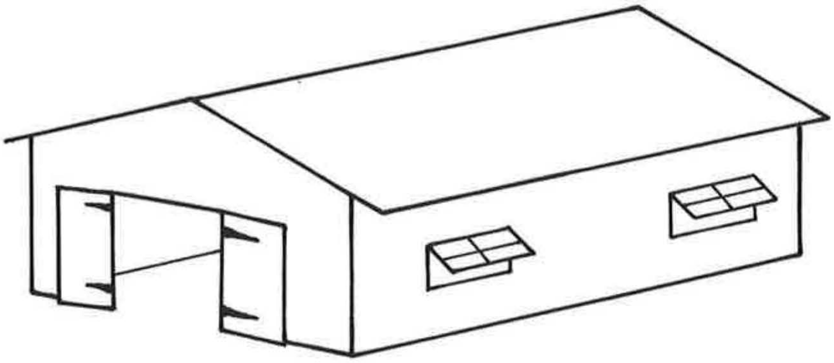
(h) Within a few hours, depending upon how well the store is ventilated, it should be safe to re-enter the store without wearing gas-masks. If in doubt, the phosphine concentration should be checked with a low range gas-detector tube. Next the remaining sand-snakes should be removed and the fumigation sheets folded up as described above. Warning notices should be removed and the store-keeper issued with a written certificate declaring the store safe (**vii**).

(i) Stacks should not be disturbed until at least 24 hours after ventilation has been completed. Scudamore and Goodship (1986) described a laboratory method for measuring phosphine residues in grain. It was found that maize absorbed more phosphine than wheat, oats or barley, but the pattern of desorption was similar – very rapidly at first when most of the phosphine

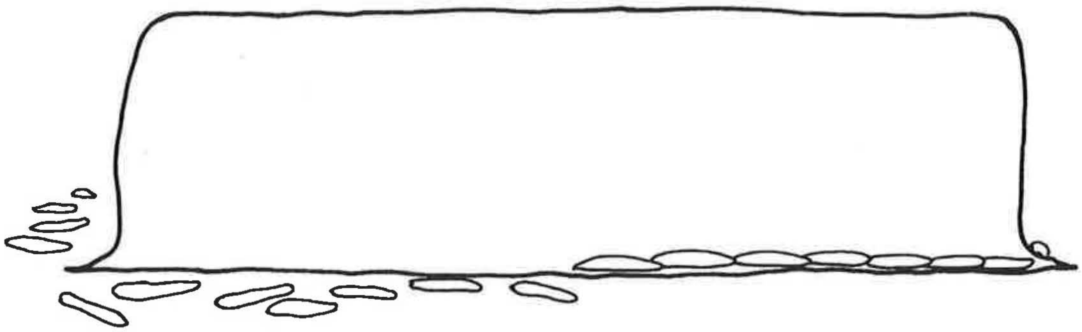
Figure 5

Ventilation of a stack

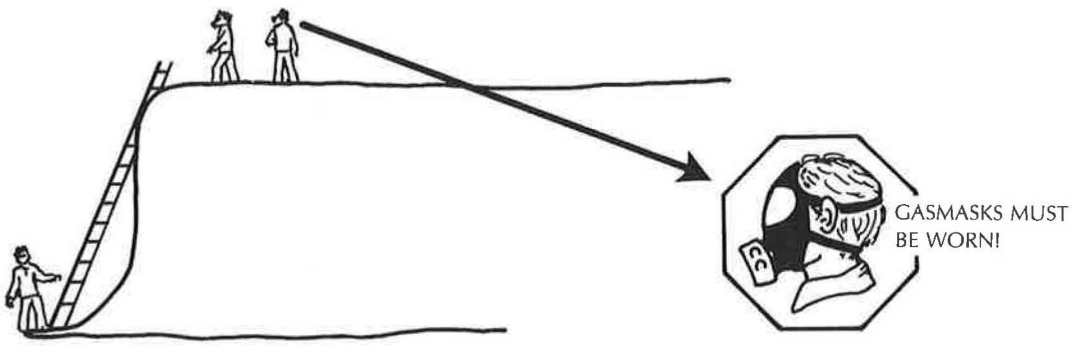
(i) Open as many doors, windows and ventilators as possible



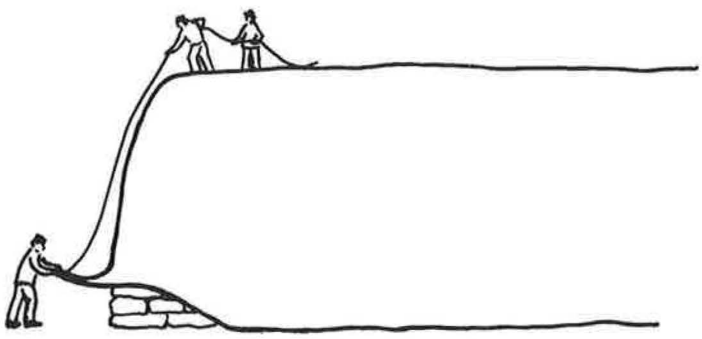
(ii) Remove sand-snakes from one corner of the stack



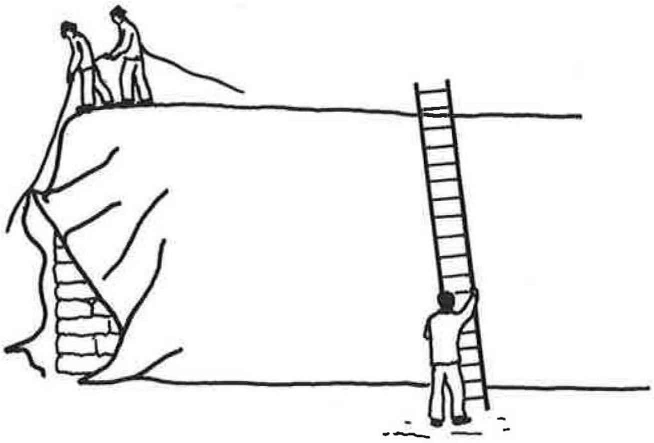
(iii) Two men climb on top of stack, the third remaining at floor level



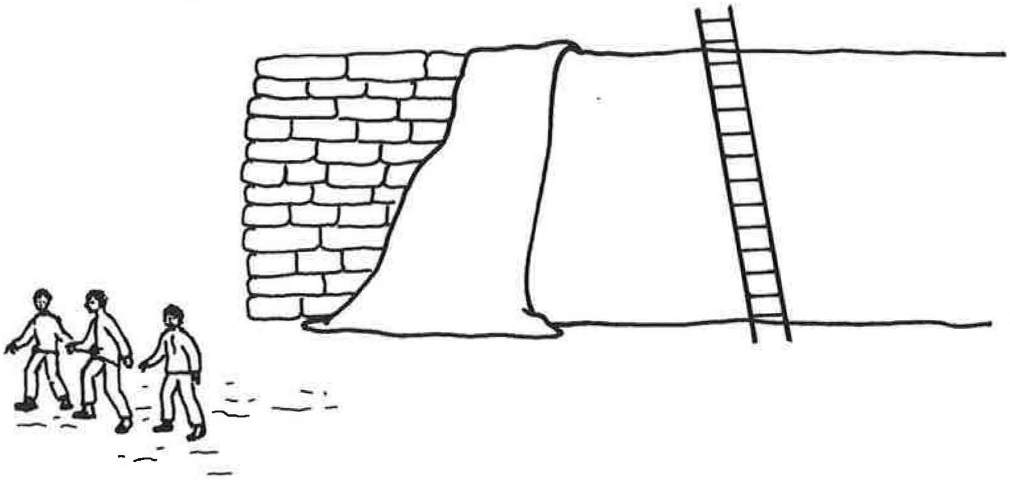
(iv) Lower one end of a rope to the man on the floor who secures it to a corner of the sheet



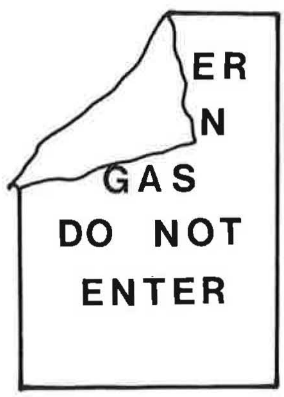
(v) The men on the stack haul up the sheet, while the other man repositions the ladder



(vi) When the sheet has been pulled back far enough to uncover the stack corner all three men vacate the store



(vii) Warning notices are removed when the ventilation period has been completed



disappeared, and then much more slowly, with trace amounts being detected after 29 days. The Codex maxium residue limit for phosphine in cereals is 0.1 mg/kg and for flour and other milled cereals it is 0.01 mg/kg.

SAFETY

Toxicity

Phosphine is very toxic to all forms of animal life either through inhalation of the gas or by ingestion of the phosphide; cats died after 2 hours' exposure to 120 p.p.m. (0.17 mg/l) and 2.8 mg/l is lethal to human beings in a very short time. The threshold limit value (TLV) for a 40-hour working week is 0.3 p.p.m. in the United States and 0.1 p.p.m. in the Federal Republic of Germany.

As mentioned above, respirators must be available when dispensing phosphine preparations and they must be worn when ventilating a stack on completion of a fumigation. Some government authorities recommend an approved type of mask; in the United Kingdom it should conform to BS2091 and is a full face mask fitted with a type 'cc' canister. The gas-mask must fit in such a way that only filtered air is breathed in. The maximum concentration of phosphine when wearing a mask should not exceed 0.5% by volume in air (approximately 5000 p.p.m. or 7 mg/l), but for working conditions the maximum is lowered to 200 p.p.m. (0.28 mg/l). Each pest control operator should be issued with a personal mask and be made responsible for maintaining it in good order.

It is recommended that the canister be changed for a new one whenever high concentrations of phosphine have been encountered, or after 2 hours at lower concentrations. Contact with water will render the canister useless. Rubber or plastic gloves should always be worn when handling phosphine preparations and residues after exposure.

Under no circumstances should anyone eat, drink, or smoke during a fumigation – the latter is particularly important because of the highly flammable property of phosphine.

Detection of phosphine concentrations in the air

The characteristic garlic smell of phosphine is not a valid indicator of phosphine concentration because individuals differ in their response to a given concentration. To determine low concentrations, low range gas-detector tubes such as those manufactured by Draeger and Auer should be used. The Draeger Ph 0.1/a tube has a range from 0.1 to 4 p.p.m. with 10 pump motions.

Disposal of residues

As mentioned above, some untreated metallic phosphide remains in residues after exposure and is more likely to occur with aluminium phosphide preparations. For this reason, after a fumigation has been completed and residues collected the residues must not be allowed to accumulate or be stored under restricted air conditions. Residues from tablets and pellets should be slowly stirred into a bucket containing warm water and detergent. Once bubbling has ceased and the residue sinks, the contents of the buckets can be discarded.

Reaction with metals

Phosphine reacts with copper, silver and gold causing corrosion, and any equipment containing these metals or compounds such as brass must be protected from exposure to phosphine.

Symptoms of poisoning

Whenever a phosphine fumigation is undertaken written details of symptoms and treatment for poisoning should be available. Treatment must be undertaken by a qualified medical practitioner and preferably in a hospital. In many situations the nearest doctor may not be familiar with phosphine poisoning and he should be provided with the written description and possibly a supply of the antidote. The symptoms of slight poisoning are nausea, faintness, headache and vomiting – anyone suffering from the above should immediately be removed to fresh air until he has recovered. Higher concentrations cause vertigo, diarrhoea, disturbance of equilibrium and severe chest pains. In both cases medical assistance must be obtained.

THE TIME TO FUMIGATE

It is difficult to give a precise answer to the question of when to fumigate, but it is advisable to control insect infestations before unacceptable levels of damage are sustained by the stored commodity. This is when the insect population is in an early stage of development. The time when the fumigation can take place will be dictated by when the storage situation is such that there is an opportunity to do so, for example:

- fumigate carry-over stocks in stores before the new crop arrives;
- fumigate the contents of each store as soon as it is loaded with new crop.

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Appendix

UPTAKE OF PHOSPHINE BY INSECTS AND ITS MODE OF ACTION

1. Oxygen appears to be essential for the absorption of phosphine by insects as it does not occur to any appreciable extent under anoxic conditions (Bond *et al.*, 1969). Opening and closing of the spiracles had little effect on absorption, possibly because phosphine diffuses readily through the insect integumen. It was observed that after cockroaches had been exposed to phosphine, they continued to exhibit muscular spasms until exhausted. The extent of the injuries sustained appeared to be related to the concentration of phosphine to which the insects had been exposed, and this condition was irreversible.

   The rate at which phosphine is absorbed varies with different insect species, *Tribolium confusum* rapidly became saturated during a 5-hour exposure to 5 mg/l of phosphine, whereas *Sitophilus granarius* absorbed phosphine more slowly over a 24-hour period. The authors suggest that the reaction of phosphine with copper and copper compounds indicates a possible reaction with cytochrome oxidase, and that phosphine may have a direct effect on the biochemical components of the respiratory system.

   More recently the insecticidal properties of phosphine have been reviewed by Price (1985) who stated that it was the inhibition of the enzyme catalase, rather than cytochrome oxidase, which caused mortality in insects. Catalase lowers the level of energy required to reduce hydrogen peroxide to oxygen and water.

2. In addition to variations in the rate of phosphine uptake exhibited by different insect species, Bell (1975) reported that the adult and juvenile phases within a single species exhibit different tolerance levels to phosphine; in four species of stored product moths, eggs and pupae were generally more tolerant than larvae and adults. Furthermore, young eggs were less susceptible than older ones, and to a lesser extent the same applied to pupae. Variations also occurred between strains within a single insect species as to their susceptibility to phosphine. This characteristic can be induced under laboratory conditions, and it was found that a resistant strain of *Cryptolestes ferrugineus* required a C : T product 12 times greater, and over a longer exposure period than a susceptible strain to achieve 100% mortality (Price and Mills 1988).

3. Using radio-active phosphine, Price (1984) carried out experiments which indicated that a resistant strain of *Rhizopertha dominica* actively excluded phosphine absorbing less than a susceptible strain. Non-absorption was enhanced by increases in both temperature and carbon dioxide content, and metabolic detoxification did not appear to contribute to resistance. Live and dead adult insects from susceptible strains were used in the experiment and it was observed that:
   - live susceptible insects absorbed phosphine rapidly for the first two hours of exposure and then the rate declined;

- live resistant insects absorbed phosphine slowly for the first 5 hours after which there was a slight increase; and
- dead susceptible and resistant insects absorbed phosphine at approximately the same rate, but more slowly than live susceptibles. Only dead insects desorbed phosphine.

Live resistant adults absorbed phosphine at a slower rate than dead insects and exhibited negative exclusion for the first 5 hours.

4. From the above it can be seen that the precise way in which phosphine kills insects is not known. However it is clear that there is considerable variation in both the minimum lethal concentration and exposure period to obtain 100% mortality for the different insect species, strains within a single species and the adults and juveniles which may be present in any given infestation. For this reason recommendations are based on dosage rates and exposure periods to kill the most tolerant insects. In any given field situation these recommendations may have to be adjusted upwards where more tolerant insect pest complexes commonly occur. Because of variations in the rate of phosphine uptake within a mixed insect population higher dosage rates will not compensate for reduced exposure periods.

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