# Generation and Application of Modified Atmospheres and Fumigants for the Control of Storage Insects

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## *Abstract*

Modified atmosphere (MA) and fumigation treatments are carried out to create an environment lethal to insects in stored commodities. The sole alternative to fumigation for in-storage insect control which also offers a diversity of applications and toxic-residue-free treatment is the MA method. This paper reviews what are currently the most frequently used methods for generation and application of MAs and fumigants. MAs can be generated from liquefied gas, bulk transported in road tankers, or delivered from cylinders for small-scale treatments. The alternative approach is on-site generation of MAs. This includes the use of exothermic gas generators based on combustion of hydrocarbon fuel, and the use of air compressors and molecular sieves to produce nitrogen from air. Possibilities for on-site generation of MAs from biological sources, including assisted hermetic storage by external biogeneration of MAs, as well as conventional hermetic storage, are also discussed. The effects of MAs on most common storage insects have been studied in relation to concentration and exposure time in order to establish dosage schedules. These show that carbon dioxide–air atmospheres are usually more toxic than oxygen-deficient ones. The methods of application and their gas supply requirements are reviewed in relation to the constructional limitations of the existing enclosures to be treated.

Fumigants are produced and marketed in containers convenient for application, either in liquid state in pressurised cylinders, or in solid-state formulations. Methods of generation for the most commonly used fumigants, namely methyl bromide and phosphine, and for various fumigant mixtures are discussed. Fumigant application using gravity penetration, grain stream admixture, assistance from recirculation, and vacuum and space techniques, all of which continue to be widely used, are critically reviewed.

INCREASED public concern over the adverse effects of fumigant residues in food and the environment has led to the partial substitution of fumigation by alternative control methods. Among these methods the only one that retains the special capacity of fumigation for in-situ treatment of stored commodities, as well as offering a similar diversity of application technologies, is the modified atmosphere (MA) method. Although this method has become well established for control of storage pests, its commercial use is still limited to a few countries (Banks and Ripp 1984; Fleurat Lessard and Le Torc'h 1987; Jay and d'Orazio 1984; Navarro et al. 1979; Shejbal 1980).

Assessing several possible reasons for the lack of commercial acceptance of the MA method, Annis (1987) emphasised two in particular: its high cost; and the lack of sufficient information on its reliability. However, in our opinion both these limitations are temporary. Clearly, cost comparisons between fumigation and alternative methods must be weighted against consumer acceptance. As for the reliability of the method, the considerable research that has been done on the effects of MA on insects has provided a firm basis for the technology, and the potential to largely replace conventional fumigation (Banks and Ripp 1984).

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The application of MAs and fumigants is most appropriate for bulk storage of grain either on-farm or at central storage installations, in structures that are sealed to an acceptable level of gastightness. Commodities such as dried fruits, flour, and spices requiring treatment in relatively small lots may be treated in specially designed fumigation chambers. Chambers for fumigation at atmospheric pressure have been described by Bond (1984) and these may be adapted for MA application.

Methods of generating and applying MAs and fumigants will be discussed, with emphasis on the main differences between them.

## Methods for Generating Modified Atmospheres and Fumigants

### Generation of Modified Atmospheres

The objective of MA treatment is to attain a composition of atmospheric gases rich in $CO_2$ and low in $O_2$ within the storage enclosure or treatment chamber for long enough to control the storage pests. At present, the most widely used source for production of such atmospheric gas compositions is tanker-delivered liquefied $CO_2$ or $N_2$. Availability and suitability of this means of gas supply must be questioned when the gases are transported over long distances from an industrial production area to the storage site. Therefore, potential alternative methods of generating MAs should also be considered.

*Supply of Gases from Tankers*

When the target MA gas composition is <1% $O_2$ or high $CO_2$ concentration, a commonly used method is to supply $N_2$ or $CO_2$ from pressurised tankers. The practical aspects of purging grain storages have been described by Guiffre and Segal (1984) for $CO_2$, and by Banks et al. (1980) for $N_2$ and $CO_2$. A significant portion of the cost of applying MAs generated from tankers is for transportation and on-site purging. Bulk liquid gas is transported in conventionally insulated road tankers.

For large-scale application of $N_2$ or $CO_2$, vapourisers are essential. These devices consist of a suitably designed receptacle with a heating medium (electricity, steam, diesel fuel, or propane), a hot-water-jacketed super-heated coil, and forced or natural draught. A forced-draught-type vapourizer with electrical super heating has been found to be convenient (Guiffre and Segal 1984).

*Exothermic Gas Generators*

For on-site generation of MAs by combustion of hydrocarbon fuel to produce a low $O_2$ atmosphere containing some $CO_2$, commercial installations—termed exothermic gas generators or gas burners—are available. Such equipment was originally designed for MA storage of fresh fruits. Their MA composition is designed to allow the presence of some 2–3% $O_2$ and to remove $CO_2$ through scrubbers. Therefore, their use in the grain industry requires several adaptations, such as: tuning the equipment to obtain an $O_2$ level of <1%; utilisation to full advantage of the $CO_2$ generated; and removal of excessive humidity from the atmosphere generated.

Combustion of propane yields about13% $CO_2$, and of butane about15%. The MA generated is more toxic than a $N_2$ atmosphere deficient in $O_2$. This is due to the presence of $CO_2$ in the MA causing hypercarbia which synergises hypoxia leading to enhanced insect mortality (Bell 1984; Calderon and Navarro 1979, 1980; Navarro and Jay 1987). Equipment has been designed to operate with open-flame burners, catalytic burners, and as internal combustion systems. Full-scale field trials using open flame burners (exothermic MA generators) (Storey 1973; Fleurat Lessard and Le Torc'h 1987), and catalytic burners (Navarro et al. 1979) to provide a low $O_2$ gas mixture, have proved successful. Open-flame burners are capable of producing high gas flow rates at low $O_2$ tension. Consequently, the generated MA can be applied directly to purge the treated enclosure. On the other hand, catalytic systems reduce the $O_2$ concentration in the atmosphere by a fixed fraction during passage through the catalyst, and therefore should preferably be used in a recirculation system. The development of a modified internal combustion engine for MA generation has been reported (Banks 1984a). In spite of its advantages over the open- flame and catalytic burners as an easily operated, transportable, and independent system, information on field application of such combustion systems is lacking.

*On-site $N_2$ Generators*

Commercial equipment which uses the

process of $O_2$ adsorption from compressed air passed through a molecular sieve bed—sometimes called 'pressure-swing adsorption' systems—is available (Zanon 1980). For continuous operation a set of two adsorbers is provided, which operate sequentially for $O_2$ adsorption and regeneration. $N_2$ at a purity of 99.9% can be obtained through regulation of inlet airflow. This method of $N_2$ generation is a relatively new approach in MA generation technology. Equipment is now being manufactured that is rated to supply an outlet flow rate of 120 $m^3$/hour at an outlet purity of 98% $N_2$. However, in view of the high capital cost involved, it would seem wise to undertake a long-term cost–benefit analysis to explore the financial viability of such installations.

### *Biogeneration of MAs*

Two principal forms of biogeneration of MAs are considered, namely, 'Hermetic storage' and 'Assisted hermetic storage'.

Hermetic storage:

A high level of gastightness is required for a structure to be suitable for hermetic storage of dry grain. The effect of restricted air supply on storage insects was studied by Oxley and Wickenden (1963) who suggested that in leaky structures it is necessary to increase the rate of $O_2$ consumption to a level at which insect infestation cannot persist. Burrell (1980) concluded that sealing infested grain using hermetic storage to kill the insects can be satisfactory for a heavy infestation in warm grain. However, because of the long storage period required before complete kill is obtained, it is likely to prove uneconomical for light infestations or when grain is cool.

To obtain complete control of all insects and so eliminate the danger of renewed infestation of grain removed from the hermetic container, Banks (1984a) proposed a possible solution of increasing consumption of $O_2$ by artificially infesting the grain with insects. Similarly, Burrell (1980) intentionally wetted a small region of the stored commodity. Because part of the commodity is sacrificed for the generation of the MA, Banks (1984a) has termed this type of storage 'hermetic storage with sacrificial areas'. Nevertheless, the authors' experience suggests that hermetic storage of grain in flexible plastic storage systems, under subtropical climatic conditions, is an excellent approach, provided there is a certain degree of tolerance to the presence of insects at critical areas in the storage structure (e.g. at the grain surface, where moisture condensation is likely to occur). At the end of long-term hermetic storage, when unloaded grain was destined for immediate consumption, the risk of spreading insect infestation was found to be negligible. Insect control success due to the hermetic storage treatments was comparable to conventional fumigants (over 99.9% kill), and losses due to insect activity were minimal (0.15% loss in weight for a storage period of 15 months) (Navarro et al. 1984).

Assisted hermetic storage:

The term 'assisted hermetic storage' was introduced by Banks (1984a) in order to define a process in which MA generation is assisted by a biogenerator source without sacrificing the commodity. Using a similar approach, Calderon et al. (1981) examined the possibility of generating a MA by inoculating wet rice bran. The best known working example of assisted hermetic storage is that in use in China (Lu 1984). With this method, removal of $O_2$ is achieved by recirculating storage gases through a closed system containing racks of moist grain and bran infected with a particular mould culture. This MA generation system merits further attention to explore the potential for its use at locations where a regular supply of industrial gases is nonexistent or cannot be economically justified.

### *Potential Systems for the Generation of MA*

Newer methods for the generation of MAs have been discussed by Banks (1984a). They include extraction of $N_2$ from the low $O_2$ exhaust stream produced by the combustion of hydrocarbons in air (Zanon 1980), catalytic oxidation of ammonia, hydrogen combustion, direct electrolytic or catalytic removal of $O_2$, removal of $O_2$ by chemical reaction, producer gas combustion systems to generate $CO_2$, combustion of methane derived from fermentation, burning carbon-containing materials in air, burning coal or charcoal in $O_2$, and production of $CO_2$ from fermentation.

## Generation of Fumigants

Contrary to the MAs, the list of chemicals that fall within the definition of fumigants is long.

However, due to diverse unfavourable properties, including the fact that many can produce long-term hazardous effects, the number of fumigants approved for use has declined, and at present only a few remain in service. In the light of environmental protection awareness and a general trend in agriculture towards integrated pest management, there has been a tendency in developed countries to reduce dependence on fumigation for insect control. However, since fumigation is one of the most efficient means of insect control, it continues to play an important role in the protection of stored commodities. This is especially so in less-developed countries, mainly because of the difficulties involved in application of integrated techniques, where developments to date have been directed mainly to bulk storage, either on-farm or at central storage level. In a GASGA seminar on Fumigation Technology in Developing Countries (Anon. 1986), it was emphasised that the use of phosphine has greatly simplified application procedures for fumigation. At the same seminar the danger of relying on only two widely used fumigants, namely phosphine ($PH_3$) and methyl bromide (MB), was also recognised. In this section, we address methods of generation of fumigants, with major emphasis on $PH_3$ and MB.

### *Generation of Fumigants Applied in the Gaseous State*

The most commonly used fumigant gases are hydrogen cyanide (HCN) and MB. HCN boils at 26°C. It is generated by the action of an acid on sodium or potassium cyanide, from the reaction of calcium cyanide with moisture in the air, by volatilising liquid HCN from cylinders, or from HCN absorbed in inert materials formulated on highly porous cardboard discs. HCN was once used extensively for fumigation of stored products but because of several unfavourable properties it has been almost completely superseded by MB and $PH_3$.

MB continues to be one of the most commonly used fumigants for stored-product treatment. Its boiling point is 3.6°C. It is marketed as liquid under pressure and is generated from steel cylinders (with capacities of 2.25 to 816 kg), from cans containing 0.45 or 0.68 kg, or from glass ampoules usually containing 20 mL MB. The cylinders are equipped with siphons and in warm climates MB vapour pressure above the liquid is sufficient to produce self-discharge. To assist discharge from cylinders, some manufacturers inject $N_2$ into the space above the liquid MB. At temperatures below 15°C, or for large-scale applications where latent heat of evaporation cools the remaining MB below its boiling point, a vapouriser consisting of a coil of copper tubing immersed in a water bath heated to 65°C is advisable (Bond 1984).

### *Generation of Fumigants Applied in the Liquid State*

Well known liquid fumigants are ethylene dibromide, ethylene dichloride, carbon tetrachloride, and carbon disulphide. They have been used for fumigation of small quantities of grain, spot fumigation in large bulks, and the localised fumigation of milling equipment. Ethylene dibromide, ethylene dichloride, and carbon tetrachloride are suspected as being carcinogenic in addition to possessing other toxic effects, while the flammability of carbon disulphide presents a hazard (Navarro 1986). Although they continue to offer practical solutions for the fumigation of small quantities of commodities in less-developed countries, their application in general has not been encouraged, and legislation in some countries has banned the use of several liquid fumigants. This group of fumigants, with boiling points above room or moderate outdoor temperatures (20–25°C), are usually described as liquid fumigants. When used in a fumigation chamber, it may be necessary to volatilise the liquid by heating. During gas evaporation, even distribution should be ensured by circulation with fans or blowers.

### *Generation of Fumigants Applied in the Solid State*

Phosphine ($PH_3$) is a low boiling point fumigant (–87.4°C). To regulate its release and suppress its flammability, it is formulated as 3.0 g aluminium or magnesium phosphide tablets or 0.6 g pellets, which yield approximately 1 g and 0.2 g of $PH_3$, respectively. In addition, aluminium or magnesium phosphide powder is marketed in permeable paper bags (sachets), or in blankets, and magnesium phosphide is also marketed in the form of flat plates (206 g in weight). These plates are individually sealed in gastight foil pouches. Upon exposure of the aluminium or magnesium phosphide to atmospheric moisture, phosphine starts to evolve. In general, magnesium phosphide formulations release the phosphine more rapidly than aluminium phosphide products (Bond 1984).

## Methods for Applying Modified Atmospheres and Fumigants

### Application of Modified Atmospheres

The prerequisites for application of MA are described below:

*Choice of Atmospheric Gas Composition*

A simple and descriptive graphical presentation to illustrate the relationship between exposure period, $O_2$, and $CO_2$ concentration, and mortality of different insects' life stages, was compiled from the literature by Annis (1987). In his review, he proposed provisional dosage regimes at grain temperatures of 20–29°C.

A summary of these dosage regimes is given in Table 1, which shows that the use of an atmosphere with less than 1% $O_2$ requires considerably longer exposure times than 80% $CO_2$ atmospheres to kill insect populations other than *Trogoderma granarium*. The basis for preparing these regimes was the time response of the most tolerant developmental stage of the most tolerant insect species. In the absence of *T. granarium*, a low $O_2$ regime should be based on the response of *S. oryzae* pupae, while the $CO_2$ regimes should be based on *Tribolium castaneum* adults and larvae (Annis 1987; Navarro and Jay 1987).

Dosage regimes presented in Table 1 should be viewed as very generalised recommendations. More recently published information (Navarro and Jay 1987; Reichmuth 1987) indicates that further work is needed to enable precise dosage recommendations to be established for the application of MAs for the major stored-product insects under the wide range of intrinsic and extrinsic factors involved. Thus, recommended dosage regimes should be based on temperature ranges appropriate to specific climatic conditions and also to the dominant insect species found in the commodities involved. Aspects of commodity moisture content (Bell 1987; Navarro 1978), socioeconomically acceptable control levels, the time-frame within which control must be accomplished, and the expected leak-rate standard in which the MA treatment will be performed will probably all play an important role in future recommendations.

*Rate of Supply*

Due to the relatively long exposure time involved, one basic concept with MA application methods is the combination of two separate phases: an initial 'purge' for the establishment of the desired atmospheric gas composition, and a subsequent 'maintenance' phase in which the desired gas composition is maintained during the exposure period (Banks and Annis 1977). This concept differs from the 'single-shot' treatment suggested by Banks et al.

**Table 1** Suggested provisional dosage regimes for control of all stages of the 12 most common insect species of stored grain, using modified atmospheres at temperatures between 20 and 29°C*.

| Atmospheric gas concentration (%) | Controls most common grain insects including *Trogoderma granarium* (yes/no) | Exposure period (days) |
|---|---|---|
| <1 $O_2$ (in nitrogen) | yes | 20 |
| Constant $CO_2$ in air | | |
| 40 | no | 17 |
| 60 | no | 11 |
| 80 | no | 8.5 |
| 80 | yes | 16 |
| $CO_2$ decay in air from >70 to 35 | no | 15 |

*Compiled from Annis (1987).

(1980). This latter-type treatment is suitable basically for $CO_2$, when an initial concentration of higher than 70% is established and the gastightness of the structure is sufficient to allow maintenance of a concentration at above 35% for at least 10 days.

With MA treatment a large volume of the intergranular free space plus the headspace of the silo needs to be displaced. The rate of gas supply is purely an economic aspect of the application of MAs, since a substantial portion of the expense involved consists of the cost of transporting the liquid $CO_2$ or $N_2$ and of the on-site purging, which is a time-consuming process (Guiffre and Segal 1984). If on-site bulk gas tanks are not installed, truck demurrage charges must be added. With gas burners the aspect of transportation is less critical, since the quantities of hydrocarbon gas used are considerably less.

The gas supply rates required for the application of selected MAs are listed in Table 2. The proposed supply time at 'purge' phase for a MA of <1% $O_2$ is considerably shorter than for the other MAs. This shorter 'purge' time derives from the physical characteristics of $N_2$ (Banks and Annis 1977). A method (not included in Table 2) that has been used by the present authors in small bins of 50-tonne capacity consists of direct gas supply to the bin in a liquid state, thereby reducing the supply time considerably. This method is discussed in the section on gas supply in a liquid state.

### *Structural Requirements*

Storage structures designed specifically for the application of MAs are practically non-existent, apart from those in Australia (Ripp et al. 1984). According to Banks and Ripp (1984) there is in Australia an increasing trend toward the use of sealed storage for dry grain, accompanied by the conversion of existing structures to sealed storage rather than construction of new installations. Large-scale operations of this type have not yet been reported from other parts of the world. Therefore, before deciding on the method of MA application, careful examination should be made of sealing requirements to obtain a standard acceptable for maintaining the gas composition over the designed exposure period (Banks 1984b).

### *Application of MA in a Gaseous State*

For application of $N_2$ or $CO_2$ into upright storages, simple inlet systems fitted into the bin wall can be used for gas introduction. The design of the system should be such as to prevent excessive pressure buildup over weak areas of the silo bin wall, especially around the inlet pipe. For purge rates of 6 $m^3$/min, an inlet pipe of 8 cm diameter has proven convenient (Banks and Annis 1980). However, in bins equipped with a grain aeration system, it is advantageous to use the inlet duct system as the gas introduction point in order to obtain improved purging efficiency.

**Table 2**. Rates of gas supply requirements for modified atmosphere application.

| Selected atmospheric gas concentration | Application phase | Amount of gas per tonne commodity | Supply time (h) |
|---|---|---|---|
| <1% $O_2$ in $N_2$ | Purge<br>Maintenance | 1–2 $m^3$ $N_2$<br>0.01–0.06 $m^3$ $N_2$ | <12<br>** |
| >70% $CO_2$ in air | Purge<br>Maintenance | 0.5–1.0 $m^3$ $CO_2$<br>0.02–0.04 $m^3$ $CO_2$ | <48<br>** |
| Gas burner <1% $O_2$ with >14% $CO_2$ | Purge<br>Maintenance | 47–66 g $C_3H_8$<br>0.6–1.2 g $C_3H_8$ | <48<br>** |
| >70% $CO_2$ in air | Single-shot | 0.5–1.0 $m^3$ $CO_2$ | <48 |

* Compiled from Banks (1984a). Only gas composition supported by field experience are presented in this table. Basic assumptions for above requirements are; that storage is filled with grain (minimum headspace) and pressure decay time is <5 mins for decay from 500 to 250 Pa.

** According to the dosage regime, see also Table 1.

When purging upwards, high $CO_2$ levels tend to remain in the lower layers of large bins and this may result in uneven and sometimes inadequate $CO_2$ concentrations for insect control, especially in the upper layers of bins (Wilson et al. 1980). To overcome this, especially in the 'single-shot' $CO_2$ application method where no maintenance phase is used, it is important to introduce an air injector into the $CO_2$ stream so as to produce a $CO_2$–air pre-mix at the designed concentration, or to recirculate the $CO_2$–air mixture until the desired $CO_2$ concentration is attained in all regions of the bin.

For the application of $CO_2$, Jay (1971, 1980) has proposed three methods. These, together with the recirculation and blending method (Navarro et al. 1979; Wilson et al. 1984) comprise the five basic application methods suitable for MAs. They are summarised in Table 3 and presented schematically in Figure 1. Recirculation gives the most uniform concentration and it can be applied by moving the gases inside the bins upwards or downwards (Navarro et al. 1986). The main gain in using downwards flow is with application by burner gas. It permits advantage to be taken of the long path of the external gas delivery pipe to cool and thereby dehumidify the hot gases after the burner.

*Application of MA in Liquid or Solid State*

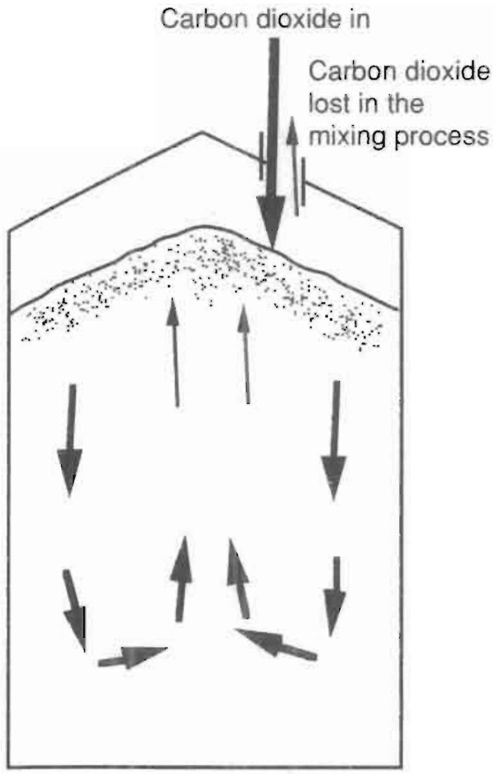
For small silos and MA treatment chambers of up to 100 $m^3$, a direct supply of $CO_2$ from cylinders equipped with a siphon was tested by the authors. By this means, $CO_2$ is released in a liquid state from the pressurised cylinder (Fig. 2).

**Table 3** Methods of application of modified atmospheres

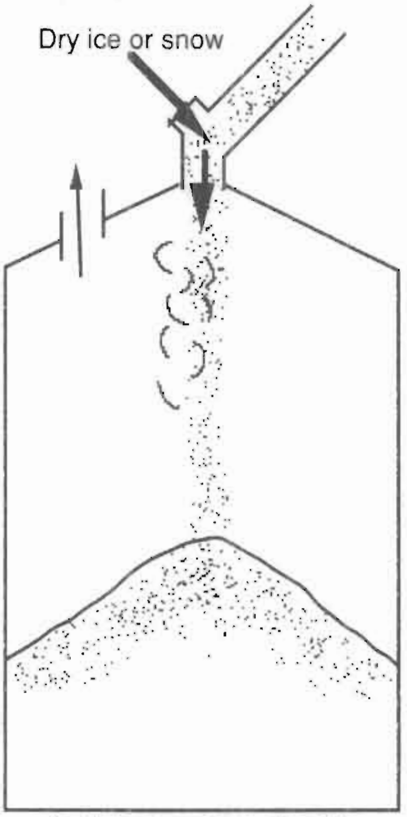
| Method of application | Applicable MA | Main advantages | Main disadvantages | Reference |
|---|---|---|---|---|
| 1. Purge a full silo from the top. | $CO_2$ | Requires only one application. Labour requirements are minimal. | Purging time is long. Some $CO_2$ is lost in outflow with air mix. | (3)<br>(4) |
| 2. Lift the atmosphere out (air displacement method). Continuous purge from bottom. | $CO_2$<br>$N_2$<br>GB* | Labour requirements are low. No loss of gas in mixing. Works best with $N_2$ | Gas purging region of silo should be leak-free. With $CO_2$ it creates high localised concentration, so blending may be necessary. | (1)<br>(2)<br>(3)<br>(6) |
| 3. Apply $CO_2$ in the grain stream (snow, dry ice). | $CO_2$ | Method is fast. No vaporisaton equipment is needed. | Danger of explosion. Constant supervision during application. | (3) |
| 4. Recirculation. | $CO_2$<br>GB | Homogenous concentration is obtained. No loss of gas in mixing. | Recirculation equipment is necessary. | (5)<br>(7) |
| 5. Blending and purging. | $CO_2$ | Homogenous concentration is obtained. No loss of gas in mixing. | Air $CO_2$ mixing equipment is necessary | (7) |

* GB, gas burner atmosphere, consisting of <1% $O_2$, 15% $CO_2$, and 84% $N_2$).

** [1] = Banks and Annis (1977).
[2] = Fleurat Lessard and Le Torc'h (1987).
[3] = Jay (1980).
[4] = Jay and Pearman (1973).
[5] = Navarro et al. (1979).
[6] = Storey (1973).
[7] = Wilson et al. (1984).



**Purge from the top**



**Applying carbon dioxide in the grain stream**

**Fig. 1.** Different modified atmosphere application methods.

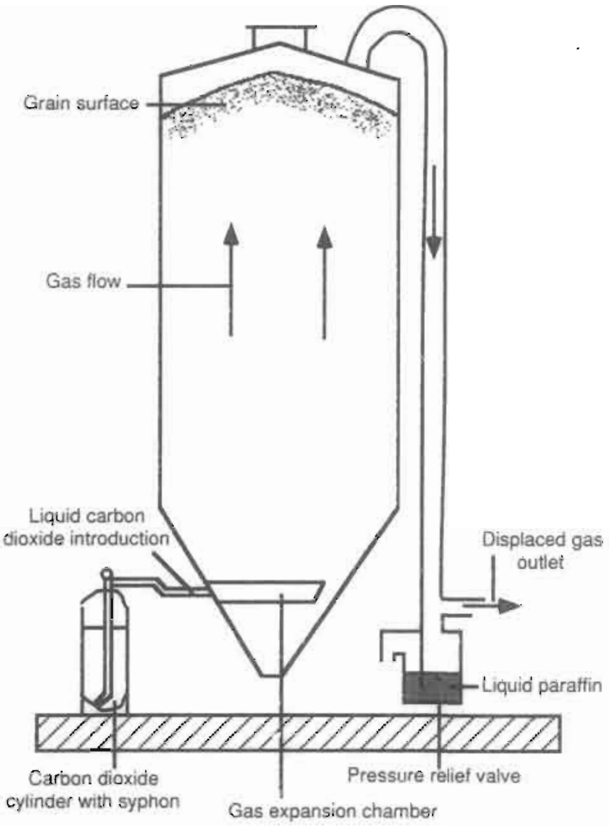


**Fig. 2.** Liquid application of $CO_2$ suitable for small silos and modified fumigation chambers.

A large volume of $CO_2$ can thus be introduced into the treated enclosure in a relatively short time, thereby causing displacement by lift-out of a substantial portion of the atmosphere from the free space of the treated structure. Great care should therefore be taken to install a large enough vent pipe and to ensure that the structure can withstand the pressure build-up at the initial purging phase. In addition, it is strongly recommended that the pressure of the treated structure be monitored. Our experience with this method of gas supply has been that at a rate of 4 $m^3$ $CO_2$/min, pressure build-up within a chamber of 110 $m^3$ was less than 60 Pa when the vent pipe's internal diameter was 75 mm.

Application of $CO_2$ in the form of dry ice to control insects infesting flour in hopper cars (Ronai and Jay 1982) and in freight containers (Sharp and Banks 1980) was investigated. The results indicate that further field trials are needed before recommending this method of application under commercial conditions.

## Application of Fumigants

*Structural Requirements:*

A fundamental requirement rarely met in

practice is that fumigable structures be gastight. The major factors which determine the level of gastightness are the porosity of the structural fabric and the structural defects which cause leakage. On the other hand, even when large structures are rendered virtually gastight, external factors—including diurnal ambient temperature fluctuations, changes in barometric pressure, and wind velocities—should be recognised as influencing gas loss after application (Winks 1979). For fumigable silo bins which meet the demand for high standards of gastightness, it is therefore also necessary to provide an adequate pressure-relief valve similar to that recommended for MA treatments. Insect control by fumigant applications is achieved by maintaining a certain concentration over a predetermined exposure period. After a fumigant has been applied, its concentration within the interstitial air space rises and then progressively declines at a rate depending on the gastightness of the structure. Several factors contribute to the formation of this typical concentration decay curve, in addition to the external factors mentioned above: diffusion through leaks; permeation through the structural fabric; and sorption of the fumigant by the commodity. Banks (1985b) and Winks (1986) have reported on current work to overcome these factors: a flow-through method which is capable of maintaining a constant concentration for the entire length of the required exposure time.

### *Dosage Schedules for the Application of Fumigants:*

In practice, fumigant concentrations exhibit a characteristic decay which differs from that of the typically constant concentrations under which their toxicity to insects has been determined in the laboratory. Very little work has been done to demonstrate the differences between the effects of constant and changing concentrations of fumigants on their toxicity to insects (Reichmuth 1986).

Dosage schedules for the application of fumigants have been recommended both by professional bodies and commercial companies. Research on dosage recommendations is usually based on the response of pests to fumigants directed toward complete control, in order to avoid selection for resistance. Recent critical evaluation of the concept of concentration time product (Ct-product), especially when $PH_3$ is applied at high concentrations, has led to revision of previously established dosage and exposure recommendations.

Methyl bromide continues to provide an effective solution for fumigations of short duration and has been used effectively where exposure time poses serious limitations, as in cases where throughput of fumigation chambers requires rapid turnover, or for quarantine applications. For example, a recommended 24 hour dosage for fumigation of bulk grain in flat storages is 32.0 $g/m^3$ for MB applied under gastight sheets within a temperature range 21–25°C (Bond 1984).

Laboratory results on MB Ct-products that produce 99.9% kill of a wide range of insects (except *T. granarium* and certain species of mites) continue to serve as a basis for calculation of initial dosages and exposure times for a wide range of commodities (Anon. 1970). To calculate the desired Ct-product in practical fumigation, allowances must be made for possible losses of fumigant through leaks, and for sorption by the commodity. Information on the intensity and speed of sorption of the fumigant by the commodity is essential for determination of the effective concentration in the interstitial space. However, test results on fumigant–commodity interaction are lacking (Banks 1985a). Recommended dosages, especially for MB, therefore differ markedly from those calculated in the laboratory (Anon. 1970).

Recent information on dosages of $PH_3$ has pointed to two characteristics of this material which differ basically from those of other fumigants and which pose problems in the establishment of dosage schedules: (i) the large variation in susceptibility of different species and stages of the same species; and (ii) the relatively long initial exposure time necessary to achieve a toxic effect (Bell 1986). A summary of some recommended dosage rates and exposure periods for $PH_3$ is given in Table 4.

There has been a noticeable trend towards lowering the concentrations while extending the exposure period. This is the outcome of the fact that for short exposures at high concentrations there is a protective stupefaction effect that renders the more tolerant stages, especially eggs and young pupae, even less susceptible (Winks 1986, 1987). Conversely, prolonged exposure at low $PH_3$ concentrations allows insect development to continue, so that tolerant stages develop into susceptible ones and are thus controlled. However, for the adoption of this approach the gastightness level of the fumigated structure must be high enough to allow retention of the fumigant for a sufficient time to achieve complete kill.

Control of $PH_3$-resistant strains certainly requires further attention, and would justify revision of current recommended dosage schedules shown in Table 4. However, to avoid spread of $PH_3$ resistance (Mills 1986) at this stage, and until new methods of application are proven feasible, it would be prudent to fumigate with $PH_3$ only in structures with a high standard of gastightness (Winks 1986). The following discussion on methods of application, although adaptable to other fumigants, is directed mainly to the use of MB and $PH_3$.

*Gravity Penetration (Surface Application)*

For large-scale fumigation of bulk grain, liquid-type fumigants are best applied to the surface of the grain by means of sprayers. Although MB and $PH_3$ are both heavier than air in the gaseous phase, they have been considered inappropriate for deep penetration of the grain mass by surface application. However, for flat storage, in gastight systems where the grain pile is either longer or wider than high, then fumigation by simple surface-application relying on natural convection currents assisted by diffusion, should be sufficient to provide an even distribution.

The presence of high dockage concentrations within the grain bulk may create pockets which act as barriers to fumigant penetration (Viljoen et al. 1981). Convection currents induced by temperature gradients, depending on their direction, may also impede dispersal of the fumigant applied to the surface of the grain bulk. This aspect, usually neglected in relation

**Table 4** Recommended dosage regimes for the control by phosphine of stored product insects in grain, in well sealed storages, at different temperatures.

| Temperature range °C | Dosage ($g/m^3$) | Controls most common stored grain insects including S.o.* | T.c.* | T.g.* | Exposure period (days) | Recommending body @ | Reference*** |
|---|---|---|---|---|---|---|---|
| 10-20 | 1.0 | yes | yes | yes | 16 | P | [2] |
| | 1.0 | no | yes | no | 10 | P | [2] |
| >15 | 4 | CK** | CK | CK | 14 | C | [6] |
| | 7.5 | CK | CK | CK | 8 | C | [6] |
| | 12.5 | CK | CK | CK | 14 | C | [6] |
| | 16.5 | CK | CK | CK | 8 | C | [6] |
| | 18.5 | CK | CK | CK | 4 | C | [6] |
| | 21 | CK | CK | CK | 5 | C | [6] |
| | 1.1-2.75 | CK | CK | CK | 4 | C | [1] |
| | 2.4 | CK | CK | no | 4 | P | [4] |
| 20-30 | 1.0 | yes | yes | yes | 12 | P | [2] |
| | 1.0 | no | yes | yes | 8 | P | [2] |
| | 1.0 | no | yes | no | 5 | P | [2] |
| 15-25 | 1.5 | yes | yes | yes(?) | 10 | P | [5] |
| | 2.5 | yes | yes | yes | 7 | P | [5] |
| >25 | 0.3 | CK | CK | CK | 28 | C | [3] |
| | 0.4 | CK | CK | CK | 28 | C | [3] |
| | 1.5 | yes | yes | yes | 7 | P | [5] |
| | 2.5 | yes | yes | no | 5 | P | [5] |

@C = commercial
P = professional
*S.o. = *Sitophilus oryzae* or *S. granarius*
*T.c. = *Tribolium castaneum* or *T. confusum*
*T.g. = *Trogoderma granarium*
** CK = assumes complete kill
*** [1] = Anon. (1981)
[2] = Anon. (1984)
[3] = Banks (1986)
[4] = Bry et al. (1980)
[5] = Winks et al. (1980)
[6] = Wohlgemuth (1986)

to fumigant distribution in grain bulks, has recently been considered by Nguyen (1985), who proposed a mathematical model to conduct numerical experiments. Experimental work is needed to elucidate the influence of convection on retention of fumigant concentrations in certain locations of the bulk or to assist in their distribution.

Application of MB assisted by $CO_2$ in vertical grain bins (Calderon and Carmi 1973; Cohen et al. 1980; Viljoen et al. 1981), and its use as a space fumigant (Wainman et al. 1983), has been reported. With this method of application $CO_2$ apparently acts as a carrier and conveys the MB through the grain mass to the lower layers, thereby achieving adequate distribution. It is noteworthy that no detailed experimental work has yet been reported on the distribution of $PH_3$ assisted by $CO_2$.

### *Direct Mixing of Fumigant into the Grain Stream*

Only solid or liquid-type fumigants should be used for this method of application. In direct mixing, the fumigant is applied to the grain stream during loading of the bin. Granular calcium cyanide evolving HCN, and aluminium phosphide tablets or pellets evolving $PH_3$ , are the most common solid-type fumigants used (Bond 1984; Wohlgemuth 1986). The principal disadvantages of the method are: an empty silo bin is required; the movement of material from one bin to another involves expenditure of energy; the amount of broken kernels is increased; the application time is longer; and, if sachets of aluminium phosphide are applied, manual addition into the grain stream is necessary.

### *Recirculated Fumigation*

For recirculation using permanent or temporary installations, a silo structure should be sufficiently gastight to prevent the fumigant–air mixture from being forced out under the pressure exerted by the recirculation fan. This method has been recommended for MB and HCN (Bond 1984) and consideration of the results of an investigation of the flammability properties of $PH_3$ (Green et al. 1984) leads to the conclusion that phosphine could be recirculated using the systems described by Cook (1984) and Boland (1984). Recirculation ensures adequate distribution of the fumigant within a shorter time than with natural convection. A further improvement to application of $CO_2$/MB mixtures into the bases of bins was developed by Williams et al. (1984), under whose system the $CO_2$/MB mixture displaces the air in the storage evenly, thereby resulting in a shorter fumigation time and lower MB residues than those for MB alone.

### *Vacuum Fumigation*

Vacuum fumigation has been used mainly in plant quarantine work, and for fumigating commodities which are difficult to penetrate at atmospheric pressure (Bond 1984). Methyl bromide has been used as a general-purpose fumigant in vacuum fumigation. Sensitivity of two *Carpophilus* species to MB at reduced pressure was found to be greater when individuals were exposed to a MB–$CO_2$ mixture, rather than MB alone (Navarro and Donahaye 1987). Since penetration of MB into coarse granular products such as wheat is very rapid at atmospheric pressure, there seems to be no advantage in using vacuum methods for the control of stored grain pests (Burns-Brown and Heuser 1953).

### *Stack Fumigation*

Cereals and other grain products stored in bags, dried fruits stored in boxes, and tobacco, are the commodities most often fumigated under sheets. An important aspect of this method of fumigation has been the development of new plastic materials, leading to the introduction of types of sheeting satisfactory for fumigation (Bond 1984; Winks 1979). PVC sheets have been used to cover stacks of bagged grain for fumigation (Annis et al. 1984). The method consists of two PVC sheets; one to cover the floor and the other to cover the stack, both chemically bonded to provide a sealed enclosure. This improved method of fumigation of stacks has proven satisfactory for the application of $PH_3$ or $CO_2$ (Annis et al. 1984). This method of fumigation differs in principle from the general concept of fumigation under 'gas-proof sheets' (Anon, 1974), where the cover sheets are 'sealed' to the untreated floor using 'sand snakes.'

### *Fumigant Mixtures*

The application of fumigant mixtures has long been recognised as a means of overcoming the disadvantages of using a single fumigant. This practice, particularly with mixtures of $CO_2$ with $PH_3$ or MB, was reviewed by Navarro (1986). The use of some fumigants with inconvenient properties has been discontinued, leaving the field of stored products protection with two common fumigants, MB and $PH_3$ . The use of these fumigants in conjunction with $CO_2$ appears to offer a possible solution for the improvement of their application.

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