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Achievements of Modified Atmospheres and Fumigation in Israel

S. Navarro

Abstract: Biogenerated modified atmospheres (MAs) successfully replaced fumigants for insect control and for quality preservation of stored products in Israel. $\rm CO_2$ based MA was used in specially constructed rigid structures for the preservation of organic wheat. The rigid metal structure was equipped with pressure relief valve and gas purge system. Plastic structures suitable for long-term storage systems, as well as intermediate storage of grain in bags or in bulk have been developed and applied in Israel. These storage systems based on the hermetic principle are:1) Bunker storage for conservation of large bulks of 10 000 to 15 000 tonnes;2) Flexible silos supported by a weld-mesh frame of 50 – 1 000 tonnes capacity for storage of grain in bulk or in bags;3) Liners for enclosing stacks of 10 – 50 tonnes capacity termed storage cubes, and designed for storage at the farmer-cooperative and small trader level.

Insect control and quality preservation of stored cocoa beans was achieved as a methyl bromide alternative, by employing the use of biogenerated MAs. A method of treatment based on hermetic storage against the large narcissus fly ($Merodon\ eques$) was developed. The MA is created due to the respiration of the bulbs that deplete the O_2 , thus controlling the maggots of M. eques. This method fully replaced the methyl bromide for treatment of narcissus bulbs for quarantine applications. Nitidulid beetles were shown to be sensitive to low O_2 or high CO_2 concentrations for disinfestation of dry fruits. Special portable chambers made of flexible tarp-like sheeting provide the benefit of treatment in any location with low pressure treatments. Under vacuum, the chamber wall shrinks over the commodity indicating retention of vacuum. Uses of these flexible chambers for narcissus bulbs, dry fruits or museum artifacts are in current use. For the disinfestation of dates, ethyl formate is being successfully tested to replace methyl bromide.

Key words: postharvest systems, grain storage, dates, narcissus bulbs, methyl bromide alternatives, hermetic storage, modified atmospheres, nitidulid beetles, ethyl formate.

Introduction

objective of modified atmosphere (MA) treatment is to attain a composition of atmospheric gases rich in CO_2 and low in O_2 , or a combination of these two gases at normal or altered atmospheric pressure within the treatment enclosure, for the exposure time necessary to control the storage pests or to protect the quality of the stored product. MA offers an alternative that is safe and environmentally benign, to the use of conventional residue producing chemical fumigants for controlling insect pests attacking stored grain, oilseeds, processed commodities and packaged foods. Pioneering modern MA storage^[1,2,3,4,5] have demonstrated the broad use of safe, pesticide-free MA and hermetic storage suitable for many commodities and seeds, particularly in hot, humid climates. In this paper, are reported the development work and achievements that have resulted in

such technologies, which are currently applied in Israel.

Types of Structures Used For MAs Rigid Structures

Existing silos were modified to provide a high degree of hermetic seal for the application of MA using $\mathrm{CO_2}^{[6]}$. Others were purposely constructed for the application of MA using $\mathrm{CO_2}$ from pressurized cylinders. The gastight metal silos were used for organic grain for which conventional fumigation was not acceptable. These silos were equipped with specially designed pressure relief valves and gas expansion chambers to permit high velocity gas $\mathrm{purge}^{[6]}(\mathrm{Fig.1})$.

Flexible Structures

In Israel, the manufacture of PVC liners that conform to required specifications of resistance to adverse climatic conditions, gas-permeability, and physical properties, enabled the development of three storage systems based on the hermetic principle. These are:

Food Technology International Consultancy Ltd. ,P. O. Box 3300 , $Beit\ Yehoshua\ ,40591$, $Israel\ [snavarro@ft-ic.info]$

- Bunker storage for conservation of large bulks of 10 000 to 15 000 tonnes capacity^[7,8].
- Flexible silos supported by a weld mesh frame of 50 1~000 tonnes capacity for storage of grain in bulk or in bags^[9,10].
- Liners for enclosing stacks of 10-50 tonnes capacity Volcani cubes termed also GrainPro Cocoons $^{\text{TM}}$, and designed for storage at the farmer-cooperative and small trader level $^{[11]}$. These structures are in current use for capacities of up to 300 tonnes for bagged storage of cereals.

The problem of applying present-day technology to provide hermetic storage for subsistence farmers lies in the need to provide an easily sealable low-cost container of 50 - 100 kg capacity. The most recent attempt to address this problem has been through the construction of a small granary for use by small scale farmers, suitable to store up to 1 000 kg, termed GrainSafe^{TM[12]}. This granary was equipped with an upper collapsible sleeve for loading and a lower collapsible sleeve for unloading. The hermetic flexible bag was inserted into a rigid sheath surrounding the vertical sides of the hermetic bag (Fig. 2). An additional development has been the use of hermetic storage bags called SuperGrainBagsTM, designed to hold 50 kg of paddy or corn. These gastight liners are now available with capacities of 1 000 kg. SuperGrainbags TM serve as gastight liners for outer bags made of either polypropylene or jute.

Experience Gained Using Flexible Liners

Our accumulated experience of hermetic storage using several types of flexible liners for above – ground storage, in – the – open, under tropical and subtropical conditions [7,8,9,10,11,13,14], is summarized in the following observations:

Structural Durability

The use of PVC-based sheeting without mesh reinforcement produces a material of suitable strength and elasticity for storing grain. This material was formulated to have a high resistance to solar UV irradiation. Rodents find it difficult to gain a tooth-hold on the smooth surface. This has been corroborated by laboratory studies using wild-caught roof rats and house mice. Liners have been used continuously for over 10 years, and though they have lost some plasticity, permeability to gases decreases as the plasticizers evaporate. This characteristic renders the liners more effective with time in retaining gas concentrations.

Moisture Migration

Diurnal temperature fluctuations, accentuated by solar radiation on liners, followed by rapid cooling at night, cause successive moistening and drying cycles at the upper grain surface. This may result in gradual moisture accumulation, particularly during the transient seasons between summer and winter when temperature fluctuations are greatest. The result is that initially dry grain may rise to above critical moisture levels enabling limited microfloral spoilage to occur. For bunkers of 12 000 to 15 000 tonnes capacity, the condensation phenomenon has been eliminated by leveling the peaked apex (with a ridge of less than 2 m) to a slightly convex, wide apex of bunker cross-section (with a ridge of more than 6 m) which is sufficient to permit rain-water run-off^[5,15]. For dry grain kept in "cocoons" in subtropical climates, moisture migration is not a pronounced phenomenon. However, for storage in the tropics, moisture migration is more pronounced because the initial grain moisture is closer to its critical level. Moisture migration has been solved by placing a reflective cover over the cocoons (Fig. 3).

Generation and Application of MA

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 pressurized cylinders or tankers. For small-scale applications of up to 50 tonnes capacity containers, pressurized cylinders are sufficient (Fig. 4). For largescale application of N_2 or CO_2 , vaporizers are essential.

Exothermic Gas Generators

For on-site generation of MAs by combustion of hydrocarbon fuel to produce a low O_2 atmosphere containing CO_2 , commercial installations termed exothermic gas generators or gas burners are available. Therefore, their use in the grain industry requires several adaptations, like adjusting the equipment to obtain an O_2 level of <1%; utilization to full advantage of 13%-15% CO_2 ; and removal of excessive humidity from the generated atmosphere. Full-scale field trials using catalytic burners [16] to provide a low O_2 gas mixture have proved successful.

Biogeneration of MAs

A form of biogeneration of MA is hermetic storage. A high level of gastightness is required for a structure to be suitable for hermetic stor-

age of dry grain. Experience has shown that hermetic storage in flexible plastic storage systems, under subtropical climatic conditions, continues to offer an excellent solution, provided there is a certain degree of tolerance to the presence of insects at critical areas in the storage structure (at the grain surface, where moisture condensation is likely to occur). At the end of long-term hermetic storage, when unloaded grain is destined for immediate consumption, the risk of spreading insect infestation was found to be negligible. Insect control success due to the hermetic storage treatments is comparable to conventional fumigants (over 99.9% kill), and losses due to insect activity are minimal (0.15% loss in weight for a storage period of 15 months) $\lfloor 7 \rfloor$.

Low Pressures (Vacuum treatment)

The introduction of flexible transportable sealed chambers made of welded PVC liners has opened new opportunities to implement low pressures (vacuum) as a competitive and affordable treatment to control storage insect pests [17]. Under vacuum, these chambers shrink tightly over the periphery of the commodity. The system is sealed by an airtight zipper and is able to retain vacuum. At the base of the chamber there exists an inlet hose which enables connection to a vacuum pump to create the prerequisite low pressure. Our studies showed that it is not a practical approach to attempt to hold a pressure below 45 mm Hg because of the energy required for prolonged operation of the pump. Conversely, pressures above 55 mm Hg prolong the time to achieve kill. In contrast to fumigations where schedules are provided by defining dosages to be applied for a predetermined time, at a set temperature range, low pressure treatment schedules must be presented as exposure times at both, a temperature range and a relative humidity that is in equilibrium with the commodity moisture content.

Achievements on Specific Target Pests and Method of Control and Preservation

Insect control and preservation of organic cereals, pulses, nuts and flours using vacuum

Ten durable commodities; corn, corn chips, garden peas, chick peas, wheat, wheat flour, rice, sun flowers seeds and semolina, were exposed to five days vacuum treatment [17]. Corn, garden peas, chick peas and sun flower seeds were stored in 1 – tonne capacity bigbags. Wheat, rice and semolina were stored in

50 kg bags and corn chips and wheat flour were stored in 25 kg bags loaded on wooden pallets. In all tested commodities the treated product was well preserved and in cases where initial infestation was detected, complete mortality of insects was observed. The advantage of this treatment is that no toxic chemicals are emploved. In comparison with phosphine, exposure times to provide kill are comparable and the exposure time of five days falls within a range suitable for quarantine treatments where no rapid treatment is essential. Where the commodity can be placed in flexible liners, and packed in a manner that can withstand the low pressure. vacuum treatment can provide an appropriate solution. The transportable system was made of flexible PVC, which has been in use commercially for hermetic storage of grain and other commodities to control insect disinfestation by naturally obtained modified atmospheres^[18]. For the disinfestation of durable commodities, these flexible storage containers can be considered for the application of vacuum as an alternative to treatments with methyl bromide and other toxic fumigants.

Disinfestation of Dates Using MA

As a potential alternative to methyl bromide fumigation, the influence of different MAs in causing emigration of *Carpophilus* spp. larvae from dates was compared with that of methyl bromide $^{[11,12]}$. A concentration of 35% CO_2 was found to cause an emigration similar to methyl bromide. This method has been used for several vears in the largest packing house in Israel. Laboratory experiments were carried out to investigate the influence of different modified atmospheres (20% CO_2 in air or 2.8% O_2 in N_2), low pressures alone or methyl bromide alone in causing nitidulid beetles to emigrate from infested dates [12]. At 4 hours exposure and at 26%, the treatments that had a marked influence in causing insects to abandon the infested dates were: a low pressure of 100 mm Hg, and 2.8% O₂ in N₂, both of which caused over 80% of the initial insect populations to emigrate from the fruit. In addition to causing emigration of nitidulid beetles from dates, CO₂ atmospheres were found effective for long term preservation of the dates^[19,20].

Control the Large Narcissus Fly Using Biogenerated Atmospheres

The large narcissus fly *Merodon eques* F. attacks narcissus bulbs and also bulbs of other geophytes. This species has not been recorded

in the USA; and is therefore included within quarantine requirements that demand total mortality prior to export to the USA^[21]. Fumigation with methyl bromide (MB) has been used to eliminate narcissus fly infestation in flower bulbs due to its rapid killing time (4 hours). However, MB is also known to cause damage to the bulbs. Therefore, our initial trials were aimed at finding alternative treatments to MB so as to prevent phytotoxicity. These trials were carried out in flexible plastic chambers that replaced the previously used rigid fumigation chambers (rooms).

In experimental procedures, due to the respiration of the newly harvested narcissus bulbs, there was an extremely rapid depletion of $\rm O_2$ within the sealed gastight enclosure where the bulbs were stored $^{[22]}$. This procedure also revealed that significant anoxia was achieved within less than 20 hours (less than 0.1% $\rm O_2$ and about 15% $\rm CO_2$) during treatment at 28°C to 30°C and the possibility arose of using this method alone as a control measure $^{[23]}$. This use of bio – generated modified atmosphere utilizing the bulb respiration alone was adopted by farmers as an alternative to methyl bromide; offering a practical solution in specially designed flexible treatment chambers (Fig. 5) $^{[24]}$.

Quality Preservation of Stored Cocoa Beans Using Biogenerated Atmospheres

Intermediate moisture contents (at equilibrium air relative humidities of 65% to 75%) of stored commodities are inevitable in tropical climates due to the difficulties in maintaining safe moisture contents for long-term storage. Under hermetic conditions, stored commodities with intermediate moisture contents generate modified atmospheres due to the respiration of the microflora and the commodity itself. Data was shown for insect control and for quality preservation of stored cocoa beans by employing a novel approach through the use of biogenerated modified atmospheres as a methyl bromide alternative. The respiration rates of fermented cocoa beans at equilibrium relative humidities of 73% at 26°C in hermetically sealed containers depleted the oxygen concentration to < 1% and increased the carbon dioxide concentration to 23% within six days. Laboratory studies in Israel were implemented under field conditions in a cocoa bean storage facility. A hermetically sealed flexible structure containing 6.7 tonnes of cocoa beans at an initial moisture content of 7.3% (70% equilibrium R. H.) was monitored for oxygen concentration and quality parameters of the beans^[25] (Fig. 6). The measurements showed a decrease in oxygen concentration to 0.3% after 5.5 days. No insects survived the oxygen depleted biogenerated atmosphere. These encouraging results reveal the possibility of utilizing biogenerated atmospheres in integrated pest management (IPM) for quality preservation (by preventing the development of FFA, molds, and mycotoxins), and insect control of cocoa pests.

Preservation of High Moisture Corn Using Biogenerated Atmospheres

Under humid and warm conditions harvested grains are susceptible to molding and rapid deterioration. Therefore, they should be dried to safe moisture levels that inhibit the activity of microorganisms. Drying to these moisture levels is not economical for farmers in developing countries. Laboratory studies were carried out on the effect of various moisture contents on the quality of corn grains in self-regulated modified atmospheres during hermetic storage^[26]. Laboratory results experiments indicated that corn at the tested moisture levels can be stored satisfactorily under sealed conditions in which self-regulated atmospheres provide protection against microflora damage. Further large scale trials were carried out to evaluate the economic feasibility of storing high moisture corn. Shelled corn of 26% moisture content was stored in a Cocoon under hermetic conditions for 96 days to demonstrate the effectiveness of maintaining its quality prior to subsequent drying or processing into feeds or ethanol. The initial oxygen concentration dropped within one day and remained at an average of 0.54% throughout the storage period. No significant change in starch content was observed throughout the storage period. Corn in the control bags deteriorated after three days and temperature increased to 55° C. The high moisture corn in the CocoonTM initially had 59 ppb of aflatoxin which increased to 90 ppb after one week of storage and remained at that level for 96 days. Feeding trials indicated that the corn from hermetic storage was palatable to cows and swine. Results of the study indicate that wet corn can be safely stored for extended periods of time without significant increase in aflatoxin, and without significant changes in starch.

Disinfestation of Dates Using Ethyl Formate

Laboratory fumigation tests were carried out using the gas mixture of CO₂/Ethyl formate

(83: 17 w/w) to control nitidulid beetles larvae. Mixed populations of C. hemipterus and C. mutilatus larvae obtained from the field were tested in an incubator at $30 \pm 1^{\circ}C$. The effectiveness of CO_2 /Ethyl formate in causing emigration of Carpophilus spp. larvae from artificial feeding sites was tested. Mortality at exposure to 420 mg/L resulted in complete kill and average disinfestation value of 69.6% was recorded within 12 h exposure. Commercial scale pilot fumigation trials were carried out that yielded promising information on the disinfestation capacity of the gas mixture during short exposure times.

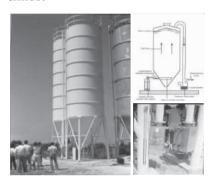




Fig. 1 Application of carbon dioxide based MA on a silo bin and the schematic presentation of the application process.

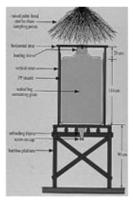


Fig. 2 Hermetic granary for use by small scale farmers, suitable to store up to 1,000 kg, termed GrainSafe.



Fig. 3 Moisture migration has been solved by placing a reflective cover over the cocoons.



Fig. 4 For small-scale applications of up to 50 tonnes capacity containers, pressurized cylinders are sufficient.



Fig. 5 Bio-generated modified atmosphere for the control of narcissus fly utilizing the bulb respiration alone in specially designed flexible treatment chambers.



Fig. 6 Bio-generated atmospheres for the control of cocoa beans insects utilizing respiration of cocoa beans in a hermetically sealed cocoon.

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