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ADVANCES IN HERMETIC STORAGE AS A METHYL BROMIDE REPLACEMENT

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ABSTRACT

Portable flexible hermetic enclosures known as CocoonsTM or Volcani CubesTM, were introduced in the 1990's. These patented, pesticide and fumigant-free devices are now used in some 20 countries for large volume applications of rice and corn under hermetic storage, as well as for preserving seed germination, without requiring cold storage. They are used for rapid treatments of coffee, cocoa or dried fruits, and these structures were developed to provide safe storage of oxygen-sensitive commodities such as rice bran and brown rice. Today, for specific applications, hermetic storage includes the patented V-HF process (Vacuum-Hermetic Fumigation) or for crushable commodities, the G-HF process (Gas Hermetic Fumigation). Process Characterization Charts for hermetic storage are included. Giant Cocoons are capable of storing up to 300 tonnes of corn or rice for periods up to a year. This allows creation of decentralized grain banks where farmers can bring their grain and have it stored until better prices are available. In Sri Lanka, a decentralized program, currently involving some 90 villages, allows local storage of paddy and for the first time it allows multi-month storage of processed, milled rice, without significant deterioration. In Turkey, the use of Gas-Hermetic Fumigation (G-HF) is used for pesticide-free storage of figs, while in Israel, these hermetic enclosures are used for disinfestation of Narcissus bulbs.

WHAT IS ORGANIC HERMETIC STORAGE?

Organic-Hermetic storage, or "hermetic storage", consists of a sealed storage system containing a modified atmosphere. This means that, as a result of respiration effects, there generally develops very low oxygen (O_2) , high carbon dioxide (CO_2)

atmosphere. The low permeability envelope maintains a constant moisture environment. Pioneering modern hermetic storage (Calderon and Navarro 1980; Navarro and Calderon, 1980; Navarro et al., 1989; 1994) has resulted in the broad use of safe, pesticide-free hermetic storage suitable for many commodities and seeds, particularly in hot, humid climates. These hermetic storage systems are used primarily in Africa, Asia, South and Central America for a growing variety of both high and medium value commodities. Hermetic storage takes three distinct forms: a) "Organic-Hermetic Storage", relies on the metabolic activity and respiration of insects, microflora and the commodity itself to generate a modified, non-life sustaining low oxygen atmosphere; b) "Vacuum-Hermetic Fumigation" (V-HF) uses a vacuum pump to rapidly create a very low pressure atmosphere for accelerated disinfestation (Mbata et al., 2004) of non-crushable commodities through asphyxiation; and c) Gas-Hermetic Fumigation (G-HF) uses an external gas source (usually CO₂) for crushable commodities, such as dried fruit, prior to shipment (Fig. 1). These methods create a low oxygen modified atmosphere that normally results in 100% insect mortality of all life stages in a few days to two weeks as well as preventing mold development, protecting quality and preventing losses in the commodity. These methods also prevent development of cancer caused by mycotoxins such as aflatoxins and ochratoxin A (OTA). The low permeability of the hermetic structure also maintains safe constant moisture levels in previously dried commodities regardless of ambient exterior humidity.

In some applications, such as for rice bran, brown rice, peanuts, and cocoa beans the quality loss due to increase of Free Fatty Acids (FFAs) are prevented through a low oxygen environment (Finkelman *et al.*, 2003; Montemayor 2004). This low FFA is often a key quality consideration. Another benefit is that these methods forego the need for chemical pesticides in post-harvest storage.

As seen further (Figs. 5 and 8), hermetic storage for grain reserves frequently uses large, flexible, plastic enclosures called CocoonsTM (also formerly called "Cubes" and "Volcani Cubes") with a capacity to 300 tons for either indoor or outdoor storage in such places as Philippines, Ghana, Sri Lanka, and Rwanda (Villers, 2003). The method is also suitable for long-term storage of rice bran, Basmati rice, and such high-value commodities as coffee, cocoa, peanuts and spices in India, Indonesia, Costa Rica and Peru, in addition to permitting long-term seed preservation without refrigeration. (Rickman and Aquino, 2004; Villers, 2003).

A more recent but increasingly popular transportable form of hermetic storage, called SuperGrainbagsTM, as shown in Fig. 2 from the International Rice Research Institute (IRRI) in the Philippines, utilizes a thin, transparent, extremely low permeability co-extruded multi layer plastic as a liner to either a conventional jute or a polypropylene bag. SuperGrainbag capacities can range from 10 to 1,000 kg, with

50 to 60 kg capacity being the most common. At the individual small farm level SuperGrainbags can be protected from rodents by storage in empty 55-gallon drums.



Figure 1. Exposure times vs. CO_2 levels producing 95% mortality for Tribolium castaneum at 57% r.h. (Calderon and Navarro, 1980).

MICROFLORA AND CRITICAL MOISTURE CONTENT

Molds, yeasts, and bacteria make up what we call the "microflora" population. At an elevated humidity they contribute significantly to the respiration processes within the stored commodities. Most mold populations are "aerobic", i.e., they need oxygen for their development. Humidity requirements for rapid mold growth of aerobic microflora are within the range of 65% to 85% r.h. (Fig. 3).

Another term of importance is the "critical moisture content", which is the level that a commodity's moisture content will reach, at a given temperature in equilibrium with 65% r.h. (Fig. 3). At higher levels of moisture content significant mold growth will take place except, importantly, when stored in a controlled atmosphere with low O_2 and high CO_2 levels. As also seen in Fig. 3 yeasts and bacteria require a higher humidity level to flourish.



Figure 2. SuperGrainbag as a liner

WHY DIFFERENT TYPES OF HERMETIC STORAGE?

The existence of three different types and several different forms of hermetic storage has to do with meeting different post-harvest storage and transportation needs. The most widely used form of hermetic storage is Organic-Hermetic storage. These systems are used for medium- to long-term storage of conventional grain bags and are commercially available in 5 ton to 300 ton capacity. They do not require external intervention to create a modified atmosphere, relying entirely on respiration and oxidation processes. They are used for farm, village, district level, or commercial storage of bagged grains or seeds of many different types for periods ranging from a month to, in some cases, several years. The commodities range widely in value from such high volume grains as sorghum, wheat, pulses, corn and rice, to expensive commodities such as spices, cocoa, coffee and various hybrid seeds.

A further distinction in hermetic storage types has to do with transportability. Most hermetic storage systems made from flexible food grade PVC such as those in Figs. 5 and 8 are light-weight and portable when empty, but not portable when full. With the introduction in 2001 of SuperGrainbags as seen in Fig. 4, hermetic storage became possible during transport and subsequent distribution. Major applications at present are for a variety of seeds, coffee and cocoa beans.



Figure 3. Critical moisture content vs. r.h. – various commodities (Navarro and Donahaye, 2005)

WHY HERMETIC STORAGE FOR SEEDS?

In the case of seeds, maintaining seed germination percentage and vigor is the dominant consideration (Finkelman et al., 2003; Navarro et al., 2002). Another reason for using hermetic storage is to prevent further insect development by creating a low oxygen, high CO_2 atmosphere lethal to insects already present inside the container. In addition, hermetic storage can prevent rodent penetration during storage, and inhibits the growth of molds as well as deterioration of the commodity by protecting it from the high outside relative humidity levels that prevail in hot humid climates.



Figure 4. SuperGrainbags

APPLICATION OF HERMETIC STORAGE FOR SEEDS

Starting in the 1990s work on the application of hermetic storage of seeds, focusing especially on rice seeds, was carried out by the International Rice Research Institute (IRRI) in the Philippines (Rickman and Aquino, 2003; Rickman and Aquino, 2007). This led to the increasingly widespread use for seed storage, not only with the large flexible hermetic storage known as "CocoonsTM", shown storing maize seeds in Thailand, (Fig. 5) but more recently to storing seed in portable hermetic storage called SuperGrainbagsTM used as liners to conventional bags often in the 50-60 kg range, such as seen in Figs. 2 and 4. In turn, this latter form has the benefit of allowing hermetic storage during the transportation and distribution phase where otherwise previously safely stored seed might degrade. The hermetic technique for maintaining seeds, (Table 1), has results equivalent to more expensive refrigeration processes in maintaining a high level of germination and vigor. As seen in Table 2, results for hermetic storage of seeds show large differences over conventional unrefrigerated bagged storage in retention of germination and vigor when stored in hot humid climates (De Bruin, 2007).

Months	Cocoons	Open Storage	Air Conditioner	Cold Room	251 plastic containers	Aluminum Sacks
0	4.4	1.6	4.2	4.2	3.7	5
3	0	117.6	0.8	0	0.7	1
6	0.2	57.2	1.5	0	0.8	1.8
9	0.2	27.2	1.7	0	0.6	0.6
12	1.1	13.6	4.5	0	0.6	0.1

TABLE 1Live insects per 500 g of grain for 12-month storage, Philippines, 2002
(From. Rickman and Aquino, 2003).

IRRI concluded in its August 2003 report that:

"Hermetic storage of rice seed and grain is a very effective means of:

- * Maintaining the grain moisture levels as at the time of storage,
- * Reducing insect damage during storage,
- * Reducing rodent and bird damage, and
- * Increasing the viable life of seed.

Hermetic storage systems can be made from any container that can be sealed from the outside environment."

GAS-HERMETIC FUMIGATION (G-HF): HERMETIC STORAGE FOR DISINFESTATION OF DRIED FRUIT

G-HF hermetic storage is used for dried fruit such as for figs in Turkey, for rapid pesticide-free "fumigation" before shipment, using bottled CO_2 , as shown in Fig. 6 (a and b). This modified atmosphere at room temperature causes complete kill of all life stages of such pests as the tropical warehouse moth (*Ephestia cautella*), a major pest of dried figs, within 5 days or less.

Seed Stored	Storage condition	Length of trial (days)	Initial germin- ation %	Germin- ation potential at end of trial (%)	Moisture Content (%) at start of trial	Moisture Content (%) at End of Trial	Insect infestation live insects/kg at start of trial	Insect nfestation Live insects/kg at end of trial
Mexico ¹								
(maize)	hermetic non- hermetic	90 90	97 97	95 97	14.5 14.5	14.3 14.2		
	hermetic non- hermetic	180 180	97 97	78 74	14.5 14.5	14.2 14.0		
	hermetic non- hermetic	90 90	96 96	76 19	16.6 16.6	17.6 16.5		
	hermetic non- hermetic	120 120	96 96	44 14	16.6 16.6	17.6 16.5		
Thailand ² Outdoor (paddy)	hermetic non- hermetic	90 90	97.21 97.21	98.2 95	12.4 12.4	12.2 11.5	2 0	0 27
Thailand Outdoor (paddy)	hermetic non- hermetic	280 280	97.21 97.21	81.21 0	12.2 12.2	13.6	0 0	0 100
Bangladesh ³ (maize)	hermetic non- hermetic	120 120		87 9	10	11	-	-
Bangladesh ⁴ (paddy)	hermetic non- hermetic	100	98 98.3	95 74 9	13.1 13.2	12.7 12.8	85 74	1 77
	hermetic non- hermetic	210	98 98.3	90 1	13.1 13.2	13 13.5	85 74	12 47
Cambodia ⁵ (paddy)	hermetic non- hermetic	223	97 95	91 66	13 13.1	13.6 14.8	13.7 32.3	0 25.8

TABLE 2 Maize (Corn) and Paddy Trials of Hermetic vs. Non-Hermetic Storage

Moreno, E., C. Benavides and J. Ramirez, "The Influence of Hermetic Storage on the Behaviour of Maize Seed Germination" (1988). Seed Science and Technology 16, 427-434.
Sukprakarni, Chuwit (1998). "Trial on Storing Corn Seed in Airtight Storage", Ministry of Agriculture, Stored Product Insect Research Group, Division of Entomology and Zoology, Bangkok, Thailand.
Data supplied by Allied Agro Industries, Dhaka, Bangladesh (Jan. 1999).
Testing of the GrainPro Cocoon for storage of Paddy in BRRI, prepared by M. Aul Quasem, SSO, FMPHT Div. and A. Abdur Rahman, SSO, FMPHT Div. Gazipur, India – 2001.
Data collected by Som Bunna, Agricultural Engineer at CARDI, Phnom Penh, dated 15 Mar 2001.

A different version called a PITS Tunnel[™], is suspended from a light frame and is especially designed for more rapid loading/unloading.



Figure 5. Cocoon[™], 10 tonnes

STORAGE OF RICE AND RICE PRODUCTS

Asia has become the largest user of hermetic storage principally because of its use for safe storage of rice seeds and rice products. Rice stored in hot humid climates not only has a high degree of insect infestation and problems with rodents, but also has issues with quality: milling recovery and appearance deteriorate significantly in storage – typically after about 6 months. Milled rice, which is more difficult to store, takes 20% less storage space than paddy (un-milled rice). Experiments in the Philippines at IRRI have shown that when milled rice is stored hermetically, it can be safely kept for more than one year (Rickman and Aquino, 2003; Rickman and Aquino, 2007).

In the case of rice bran and brown rice low oxygen levels occur very rapidly due to the commodity's respiration, typically to below 1% oxygen (Montemayor 2004), allowing safe storage for periods of time otherwise not possible.

BULK APPLICATIONS OF ORGANIC HERMETIC STORAGE

Today hermetic storage of maize and wheat is used on a large scale in several countries. For instance, in Rwanda a total of several hundred 50-tonnes to 225-tonnes capacity Cocoons, such as those seen in Figs. 7 and 8, are now used. Cocoons are used there for long-term storage of corn, sorghum, and beans. They estimate losses under conventional storage as 12.5-25% over 12 months. A USAID sponsored study (Navarro et al., 1995) showed that wheat could be preserved with excellent results in flexible hermetic storage systems for periods of up to five years. Figure 8 shows a 150-tonnes Cocoon together with its GrainShadeTM used outdoors in the Philippines for storing rice paddy by the National Food Authority (NFA).



Figures 6a & 6b. Dried figs in Turkey. Dried figs in boxes (left), G-HF Cocoons (right) (Ferizli and Emekci, 2000)



Figure 7. Coffee, Monte D'Oro Cooperative

STORAGE OF PREMIUM COFFEE AND OF SHELLED PEANUTS

Only in the last few years have the benefits of hermetic storage been fully appreciated in maintaining the quality, aroma and taste, of coffee as determined by cupping tests, as well as the appearance of coffee stored in hot humid climates. In Costa Rica for instance, the coffee crop is harvested from October through February. This coffee is then consumed or exported from March onward. Therefore, the need for long-term storage, which preserves the quality of premium coffee beans, is critical. The first large commercial user of hermetic storage for coffee was Café Britt in Costa Rica. According to their professional cupper, after storage of five months: "The (cup average) quality remained at 4.0 (5 point scale) for those in the Cocoon and dropped to 3.0 for unprotected coffee beans. The superiority of coffee stored in hermetic Cocoons became very noticeable."

Recently the use of hermetic storage has been extended to the storage of peanuts, for which the increase of FFA (Free Fatty Acids) and mold development may result in production of cancer-causing aflatoxins, and can cause entire shipments to be rejected. Studies done in Vietnam found, as seen in Fig. 10, that hermetic storage of unshelled peanut seeds for 8 months in SuperGrainbags maintains constant moisture and germination rates virtually identical with the costly refrigerated storage. In unprotected storage, the germination rate dropped to 3%. As seen in Table 2, similar results have been observed for rice seed.



Figure 8. 150 tonnes Cocoon with GrainShade[™], Philippines

STORAGE OF COCOA – SPECIAL CONSIDERATIONS

The deleterious effects of molds, microflora, and oxidation are particularly problematic in cocoa bean storage. Oxidation leads to the increase of FFAs, which have a negative impact on the quality of cocoa. With hermetic storage of cocoa, as seen in Fig. 11, oxygen levels typically go down to 2% or less in a week, protecting the commodity against insects, oxidations effects, and the growth of molds.



RECOMMENDED USES OF MODIFIED ATMOSPHERE STORAGE

Information on field use of hermetic storage for various commodities, the reasons for use, and the results obtained whether in $Cocoons^{TM}$ (15 tons to 300 tons) or in transportable SuperGrainbags (10 kg to 1000 kg) are given in Table 3.

Figure 9. Equilibrium moisture content (EMC) of coffee beans vs. r.h. under equilibrium conditions at 28°C.

40

50

Relative Humidity %

60

70

80

90

30

20

ALTERNATIVES TO HERMETIC STORAGE

Alternatives to hermetic storage and modified atmospheres include use of fumigant gases, refrigeration, freezing, and conventional unprotected storage. Full penetration

TABLE 3

Recommended Uses of Modified Atmosphere Storage for Dry Agricultural Products when control of insect infestation is an issue; when the commodity is hygroscopic (tends to absorb moisture); when taste, color and chemical composition change during storage; and when molds (fungi) tend to cause spoilage. Each commodity listed below has been tested on laboratory or field test level. Commodities are in alphabetical order:

Name	Problem	Technical Solution	Result
Anatto (Achueta)	Insect infestation; loss of chemical properties		
Aromatic Rice (including Basmati rice)	Loss of taste, aroma; insect infestation	SuperGrainbags TM , Cocoons TM	Taste and aroma will be retained. Control of insect infestation.
Cement	Highly hygroscopic		
Cocoa Beans	Loss of color, taste, aroma; insect infestation; molds	SuperGrainbags, Cocoons	Taste, color, aroma will be retained. Insects controlled.
Coffee	Loss of color, taste, aroma; insect infestation; molds	SuperGrainbags, Cocoons	Taste, color, aroma will be retained. Insects controlled.
Corn	Insect infestation, mycotoxins, rodents, birds (aflatoxins).	Hermetic storage in Grainsafe TM , Cocoon or Bunker TM	Insects will be controlled. Fungal developments will be halted.
Corn seeds (including hybrid seeds)	Insect infestation, loss of germination	SuperGrainbag, GrainSafe [™] , Cocoon	Insects will be controlled. Works as well as conditioned storage. Germination retained.
Flour (in bags)	Insect infestation, rodents	V-HF	Vacuum kills insects at all level of development in <72 hours.
Malt (sprouted barley)	Hygroscopic, insect infestation		
Museum fumigation	Pests, wood and book worms	The Cocoon provides as safe gas-tight enclosure enabling use of toxic gases, phosphine (PH3), CO ₂ , or Nitrogen	Fumigation can be performed "at the site" without need to move museum objects out of museum compound.
Paddy	Insect infestation, yellowing, molds. Weight loss on long-term storage	Hermetic Storage in GrainSafe or Cocoon.	Insects will be controlled. Fungal developments will be halted. No weight loss.
Paddy seeds (including hybrid seeds)	Insect infestation, loss of germination	SuperGrainbag, GrainSafe, Cocoon	Insects will be controlled. Works as well as conditioned storage. Germination retained.
Rice (milled)	Insect infestation, discoloring, chemical changes due to oxidation	Cocoon	Insects will be controlled, chemical breakdown process slowed down.
Rice bran	Insect infestation, oil content turns rancid starting 12-hours from milling	Cocoon	Insects will be controlled, chemical breakdown process slowed down.
Sorghum	Insect infestation, weight loss on long-term storage	GrainSafe, Cocoon	
Wheat	Insect infestation	Hermetic storage in GrainSafe, Cocoon or bunker	Control of insect infestation

of the commodity is often a problem with fumigants, repeated applications are frequently necessary and fumigants do not prevent losses from rodents or the growth of molds. In addition, insects have developed tolerance to widely used fumigants and the most popular fumigant, Methyl Bromide is being phased out. Refrigeration, in the case of seeds, remains widely used, but consumes significant energy, and requires special facilities. Freezing, which is another expensive process, has also been used. However, most of the world still uses conventional storage, such as storage of bagged grains under large tin roofs in open warehouses. Conventional storage provides almost no protection from rodents, limited protection by spraying against insects, and no meaningful steps to prevent mold growth. In hot humid climates, total post harvest losses are frequently of 12.5% to 25%.

Hermetic storage, as compared to older storage processes, is still relatively new, and not as well known, but its use in some 20 countries and its increasing acceptance in particular niche markets where the need for better storage techniques is urgent, is causing rapid growth. Particularly noteworthy in this respect are applications for seeds, cocoa, coffee, rice (including Basmati rice, brown rice and rice bran) as well as large stores of staple grains, often maize and wheat.



Figure 10. Peanut seed storage germination vs. time.



Figure 11. Changes in modified atmosphere, cocoa beans, 73.2% ERH (Navarro et al., 2007)

CONCLUSIONS

Almost 25 years after modern hermetic storage systems were first developed, the use of hermetic storage is now becoming widespread using modern low permeability plastic materials that are light-weight, can be used indoors or outdoors, have long lives (10-15 years in the case of Cocoons) and are now, in the case of SuperGrainbags, transportable when full. Pesticide-free Hermetic storage technology has already been found suitable for a number of markets. This is especially true where conventional storage, such as in hot humid climates, fails to adequately protect the stored commodity for the desired time and this results in large losses in quantity and quality.

Hermetic storage is sustainable; it is user-friendly and it is an environmentally benign technology that does not necessitate the use of chemical pesticides (Villers *et al.* 2001; Navarro *et al.*, 1996). The technology can be adapted to the protection of commodities in sizes ranging from that of conventional grain bag size to many thousands of tons.

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