Donahaye, E.J., Navarro, S., Bell, C., Jayas, D., Noyes, R., Phillips, T.W. [Eds.] (2007) Proc. Int. Conf. Controlled Atmosphere and Fumigation in Stored Products, Gold-Coast Australia 8-13th August 2004. FTIC Ltd. Publishing, Israel. pp. 455-465

NEW METHOD OF PHOSPHINE AND CARBON DIOXIDE APPLICATION AND ITS OPTIMIZATION

I.C. CHADDA[1], K. JAYRAJ[2] AND A.V. DHURI[3]

[1]Central Warehousing Corporation, 4/1, Siri Institutional Area, August Kranti Marg, Hauz Khas, New Delhi – 110016, India. E- mail: icchadda@indiatimes.com
[2]Indian Grain Storage Management and Research Institute, Rajender Nagar, Hyderabad, India
[3]Excel Crop Care Ltd., 184-87, S.V.Road, Jogeshwari (W), Mumbai- 400102, India. E- mail: dhuri@excelcropcare.com

A B S T R A C T

With the increased dependence on phosphine for disinfestations of grain stocks, a new method of application is developed. A "Fumigation Machine" was designed and fabricated to generate phosphine, mixed with carbon dioxide at the required proportion and deliver the mixture into the bag stack under gas proof cover. This "Fumigation Machine" is portable, convenient and does not require any energy source, which makes it most suitable for use in field conditions of developing countries. To optimize the proportion of phosphine and carbon dioxide, laboratory trials were conducted in specially designed acrylic chambers against adults of *Sitophilus oryzae, Rhyzopertha dominica, Tribolium castaneum, Oryzaephilus surinamensis* and full grown larvae of *Trogoderma granarium, Tribolium castaneum and Stegobium paniceum*. Effective combination was field tested in godowns of Central Warehousing Corporation, at Mehboob Nagar, Andhra Pradesh (India). Rice stacks (> 90 t each) having infestations of *Tribolium castaneum, Cryptolestes spp*. and *Oryzaephilus surinamensis* were fumigated with various proportions of phosphine and carbon dioxide. Additionally, test cages with 10 adults each of T. *castaneum* and *Cryptolestes* spp. as well as full grown larvae of *T. granarium* were kept in the stacks at different levels. It was observed that a combination of 1.35 g phosphine and 35 g carbon dioxide per cubic meter was most effective in controlling all the species of stored grain insects tested.

INTRODUCTION

Fumigation plays a key role in control and management of infestation in commodities stored in tropical countries like India. It has proven to be a versatile technique and great reliance has been placed on it to underpin the success of other pest and quality control measures particularly in countries where admixture of grain protectants is prohibited. It is a curative treatment which adds to storage hygiene by keeping infestation free storage environment to comply with regulatory requirements. India handles more than 200 million tones (Mt) of food grains annually, which need to be preserved using available fumigants. Methyl bromide and phosphine are the most commonly used fumigants. In spite of having some advantages, methyl bromide as a fumigant is on it's way out, as it has been identified as a serious ozone depleting agent with an ozone depletion potential (ODP) of 0.7. The Clean Air Act in the US declares that any product with an ODP of 0.2 or greater will be eliminated. The Montreal Protocol's 120 plus signatory countries have also endorsed the same. This makes phosphine as the most accepted fumigant for stored products. There are several developments in our knowledge of phosphine, which lend positive support to the continued use of phosphine as a fumigant (Banks, 1994). Alternatives to phosphine are more expensive, difficult to use and less acceptable by market.

Formerly it was thought that phosphine could not be recirculated using a fan, because of risk of an explosion. However, the flammability properties of this fumigant have been reinvestigated and it is now apparent that it may be recirculated safely provided certain precautions are taken. The explosion limits of phosphine-air mixtures at 1 atm pressure and 0.39% (v/v) water vapour at 30^0C and 40^0 C are 1.98 % v/v (30.1 g per m^3) and 1.92 % v/v (29.1 g per m^3) of phosphine concentration, respectively. In most fumigations, the concentration of phosphine is unlikely to exceed this limit (Green *et al.* 1984).

Phosphine gas generated by Aluminium Phosphide tablets is used for fumigation in food grain storage godowns in India. The tablets, each weighing 3 g and releasing 1 g of phosphine, are applied at the rate of 3 tablets per tonne of grain stored. Tablets kept in paper or enameled plates are manually distributed on the bagged stacks to be fumigated and the stack is covered by a gas proof cover. The stack is left undisturbed for 7 days, after which degassing is done. The present system involves prolonged applicator exposure to rapidly releasing fumigant and produces potentially dangerous solid waste fumigant, posing disposal problem. Improper fumigation practices also lead to frequent cases of insect resistance to phosphine. In order to improve the efficacy of phosphine treatment of bagged stacks and to reduce human exposure a "Portable Phosphine Generator" was developed by M/S Excel Crop Care Limited, Mumbai in association with Central Warehousing Corporation, New Delhi and Indian Grain Storage Management and Research Institute, Hyderabad.

OBJECTIVES OF TRIALS

To find out the synergistic effect of carbon dioxide and phosphine.
To find out the most appropriate and effective combination levels of phosphine and CO_2.
To reduce the dosage of fumigant.
To reduce the exposure period.

MATERIALS AND METHODS

The Portable Phosphine Generator comprises of a gas tight reactor made of a strong corrosion resistant stainless steel body and mounted on a frame provided with wheels and a handle (Fig.1) The reaction chamber is provided with a sight glass for viewing the reaction. The reactor is provided at the top surface with carbon dioxide inlet line having a control valve and flow indicator; the water inlet passage with a flow regulator; aluminium phosphide tablet feeder with a regulator. The gas outlet is fitted with an impingement column provided with a pressure sensor and further connected to fumigation tubing. This reactor is also provided with a sludge outlet line with a valve at the bottom.

Operation of Portable Phosphine Generator

Water is fed into the reactor through water inlet. The level of water in the chamber can be seen through the sight glass. After removing the gas tight lid from the mouth of the hopper, aluminium phosphide tablets are loaded into it .

Between the hopper and the reactor there is a manually operated valve assembly which helps in regulating the flow of tablets into the reactor. During manual rotation of the valve assembly (Feed Control device) one of the grooves therein faces the hopper and tablets enter the groove. When this groove is rotated 180^0 the tablets in it fall down into the reaction chamber. At the same position the other groove in the valve body faces the hopper and receives the tablets.

Water in the reactor reacts with aluminium phosphide to generate phosphine gas. Carbon dioxide gas from the cylinder is fed into the reactor via the carbon dioxide inlet line. The flow of carbon dioxide is regulated by a valve and metered by a flow indicator. Carbon dioxide gas bubbles through the water in the reactor and stirs the water to help dissolution of the tablets.

The carbon dioxide gas and phosphine gas flow out through the impingement column and get mixed. The pressure sensor monitors the gas pressure in the impingement column. The mixture containing phosphine and carbon dioxide when pumped in gets mixed with air and hence lowers the concentration of phosphine at the place of its introduction, hence eliminating the risk of fire or explosion.

The gas pressure in the impingement column can be controlled by regulating inflow of feed rate of aluminium phosphide tablets into the gas generator. Phosphine and the carbon dioxide mixture is delivered into the fumigation site through the gas outlet line and perforated portion of the delivery pipe inside the stack.

The sludge/sediment at the bottom of the reactor is drained out by opening the valve. The conical shaped bottom of the reactor facilitates drainage of the sludge.

Salient benefits of the portable phosphine generator

It is easy to move around due to the provision of wheels. It can be mounted on a carrier to facilitate transportation.

It comprises of few components with simple construction.

It is compact, not so heavy (75 kg. approx.) and easy to maneuver.

It operates at ambient conditions.

It does not require any electric or thermal energy for its operation.

It does not leave any residues on treated bags /grains.

It involves reduced house keeping.

Initial trials using the phosphine generator (Fig.2) were conducted at Central Warehouse - Muzaffarnagar (U.P.) and at Central Warehouse - Guntur (A.P.) to give confidence to the operators in handling the machine.

Laboratory trials at Igmri, Hyderabad

The test environment was 4 mm clear acrylic cubes (25X25X25cm) (Fig.3 & 4). The cube is closed on 5 sides with one side open. This open side is always kept on a 4 mm clear acrylic sheet of 27 x 27 cm that served as the 6th surface of the cube. The preliminary trials were conducted with wide range of treatment levels of phosphine at 0.20,0.30,0.40, 0.60 and 0.80 g per m^3 and carbon dioxide at 20,30,,40 and 50 g per $m^{3.}$ Thus, he phosphine - carbon dioxide mixture was tested with 20 different combinations.

Test insects were adults of *Sitophilus oryzae, Rhyzopertha dominica, Tribolium castaneum* and *Oryzaephilus surinamensis* and full-grown larvae of *Trogoderma granarium, Tribolium castaneum* and *Stegobium paniceum*. Muslin cloth bags containing broken raw rice (Moisture Content 14%) were kept in the cubes to simulate the conditions of bagged stack. Mixed population containing 5 pairs of unaged and unsexed test insects of each species were kept in separate cloth bags filled with grain and placed in the cube. Calculated amount of phosphine and carbon dioxide were pumped into these cubes by specially designed equipment. After 7 days of exposure period, degassing was done and insect mortality was recorded.

Based on the test results of preliminary trials, further trials were conducted with 10 different combinations of carbon dioxide and phosphine i.e. 0.8 g per m^3 of phosphine with 20,30, 40, and 50 g of carbon dioxide per m^3, 0.6 g per m^3 of phosphine with 20,30, 40, and 50 g of carbon dioxide per m^3 and 0.4 g per m^3 of phosphine with 40 and 50 g of carbon dioxide per $m^{3.}$ These trials were repeated giving 5 days (120 h) exposure period instead of 7 days given earlier.

It was clear from these trials that 0.8 g of phosphine per m^3 in combination with 40 g of carbon dioxide per m^3 for 5 days exposure period is the most effective combination for successful fumigation (Table I). The range of temperature and relative humidity during the trial period was recorded as 34-36^{0}C and 34-35%, respectively.

Final field trials

Final field trials were conducted in the godowns of Central Warehousing Corporation at Mahboobnagar (A.P.) (Fig. 5). Twelve parboiled rice stacks having internal infestation of *Tribolium castaneum, Cryptolestes spp. and Oryzaephilus surinamensis* were selected for these trials. Test cages with 5 pairs each of unaged and unsexed adults of *T. castaneum* and *Cryptolestes spp*. and full grown larvae of *Trogoderma granarium* were kept in the stacks at different levels. Three stacks were fumigated with dosage of 1 g of phosphine (60% of normal phosphine dosage) +35 g of carbon dioxide per m^3; three stacks were fumigated with dosage of 1.18 g of phosphine (70% of normal phosphine dosage) +35 g of carbon dioxide per m^3; three stacks were fumigated with dosage of 1.35 g of phosphine (80% of normal phosphine dosage) + 35 g of carbon dioxide per m^3 with the phosphine generator (Fig.6) and the remaining three stacks were fumigated with normal dosage of 1.71 g per m^3 in conventional method (without addition of carbon dioxide). Sand snakes (2 layers) were used for sealing the stacks.

The range of temperature and relative humidity was recorded as 30 – 32^{0}C and 52- 56%, respectively during the period of trials. After 120 h of exposure period, degassing was done; insect mortality in the test cages and the stacks was recorded (Table II).

RESULTS AND DISCUSSION

The laboratory trials indicated that there are critical levels of the gases to be used for a successful fumigation (Table I). Within each of the phosphine level, the insect mortality was higher with increase in carbon dioxide level. Out of the six test insects, it was found that *T. granarium* larvae were most difficult to control. The final field trials (trials conducted at CWC, Mahabubnagar) indicate that fumigation with 1.35 g of phosphine per m^3 (80% of the normal dosage) in combination with 35 g of carbon dioxide per m^3 with an exposure period of 120 h (5 days) gives 100 % mortality of *Tribolium casasneum*, *Crytolestes* spp. and *Oryzaephilus surinamensis* and full grown larvae of *T.granarium*. The entire fumigant mixture needed for the

TABLE I

Efficacy of phosphine and carbon dioxide mixture at various concentrations against different stored grain insect pest under laboratory conditions

Experi -ment No.	Dosage in (g/m^3)		Mortality percentage of insects						
	PH_3	CO_2	A	B	C	D	E	F	G
1.	0.40	40	13.33	6.66	16.66	20.00	0.00	16.66	13.33
2.	0.40	50	20.00	16.66	26.66	30.00	20.00	36.66	16.66
3.	0.60	20	46.66	26.66	26.66	36.66	0.00	30.00	30.00
4.	0.60	30	43.33	36.66	30.00	36.66	0.00	36.66	36.66
5.	0.60	40	50.00	56.66	60.00	63.33	16.66	50.00	53.33
6.	0.60	50	90.00	80.00	73.33	76.66	56.66	76.66	80.00
7.	0.80	20	63.33	43.33	30.00	46.66	0.00	36.66	46.66
8.	0.80	30	66.66	53.33	46.66	50.00	0.00	46.66	66.66
9.	0.80	40	100.0	100.0	100.0	100.0	100.0	100.0	100.0
10.	0.80	50	100.0	100.0	100.0	100.0	100.0	100.0	100.0

A = *Sitophilus oryzae* B = *Rhyzopertha dominica* C = *Tribolium castaneum*
D = *Oryzaephilus surinamensis* E = *Trogoderma granarium* larvae
F = *Tribolium castaneum* larvae G = *Stegobium paniceum* larvae.

TABLE 2
Efficacy Of Phosphine And Carbon Dioxide Mixture At Various Concentrations Against Different Stored Grain Insect Pests Under Field Conditions At Central Warehouse Mehboob Nagar , A.P., India

Stack No.	**Weight (Mt)**	**Dosage (g /m^3)**		**Initial Infestation**		**Final Infestation**	
		PH_3	**CO_2**	**Test cage**	**Internal**	**Test Cage**	**Internal**
1.	92.360	1.01	35.00	C,E,H,(10 each)	C1,H1	E9	NIL
2.	106.95	1.01	35.00	C,E,H,(10 each)	C1,H2	E8	NIL
3.	92.340	1.01	35.00	C,E,H,(10 each)	C4,J3	E7	H2
4.	88.750	1.18	35.00	C,E,H,(10 each)	C1,H2	NIL	NIL
5.	131.45	1.18	35.00	C,E,H,(10 each)	C2,H3	NIL	H1
6.	92.380	1.18	35.00	C,E,H,(10 each)	C3,H1,D1	NIL	NIL
7.	92.390	1.35	35.00	C,E,H,(10 each)	C2,H2	NIL	NIL
8.	131.44	1.35	35.00	C,E,H,(10 each)	C2,H3,D1	NIL	NIL
9.	92.365	1.35	35.00	C,E,H,(10 each)	C5,H3	NIL	NIL
10.	92.340	1.70	NIL	C,E,H,(10 each)	C3,H2	NIL	NIL
11.	131.34	1.70	NIL	C,E,H,(10 each)	C3,H2	NIL	NIL
12.	92.350	1.70	NIL	C,E,H,(10 each)	C3, H2	NIL	NIL

C = *Tribolium castaneum*, D = *Oryzaephilus Surinamensis*
E = *Trogoderma granarium* larvae H = *Cryptolestes* spp.

Remarks: The dosages of phosphine (PH_3 in stack 1 to 3, 4 to 6 and 7 to 9 was 1.80 g per MT, 2.10 g per MT and 2.4 g per MT, respectively which represent 60, 70 and 80% of normal dosages which is 3 g per MT as applied in stack No. 10 to 12. The dosage of carbon dioxide (CO_2) was 62.14 g per MT in stack No. 1 to 9.

fumigation was pumped into the stack at one time instead of the conventional method of placing required tablets at different levels in the stack. This also indicates that the exposure period can be reduced to 120 h (5 days) from 168 h (7 days).

Mueller (1994) reported that insects are stressed by the increased levels of carbon dioxide and heat, which allows lower levels of phosphine to be more effective in achieving 100% mortality of all life stages including the egg stage in shorter periods of time. Increased carbon dioxide accelerates respiration of the insects thereby

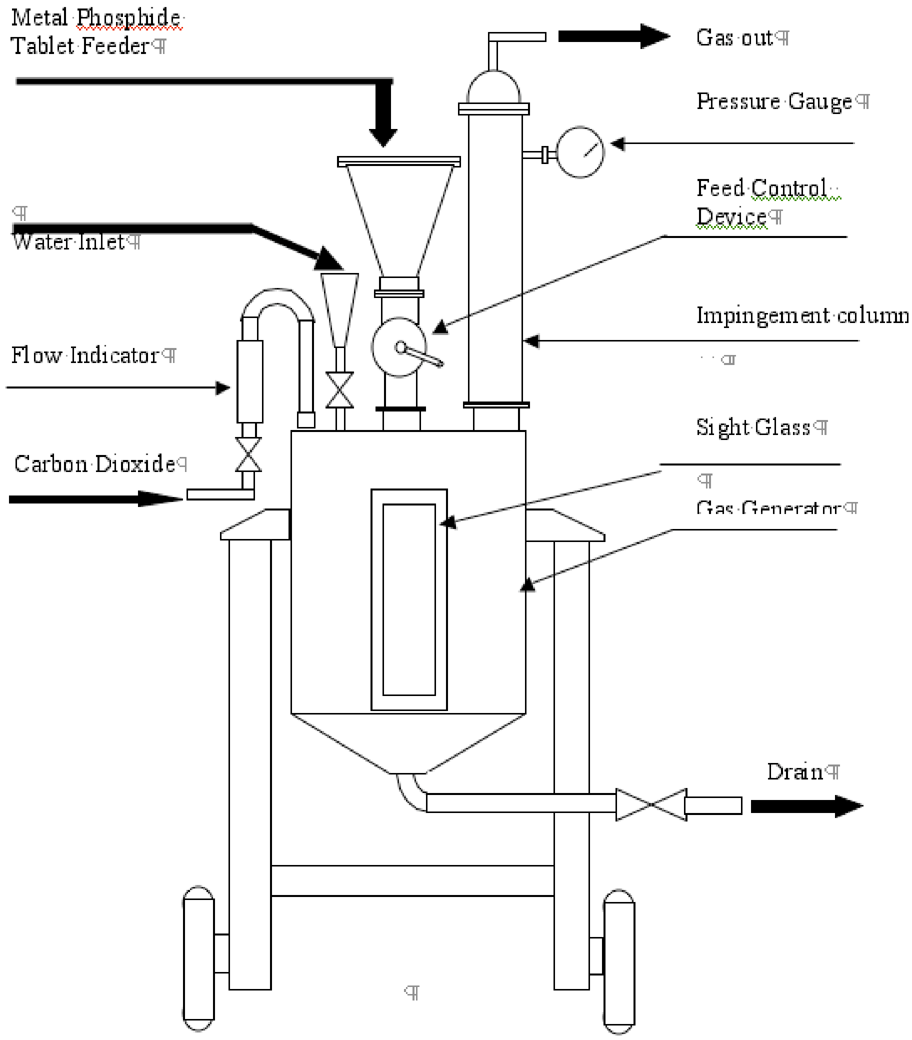


Figure 1. Line diagram of Portable Fumigator

making them more susceptible to phosphine. A combination method of fumigation maintaining lower levels of phosphine, moderate heat and higher level of carbon dioxide for a period of 24 h in sealed structures has the potential for replacing many methyl bromide applications. In China, adding carbon dioxide into the headspace during release of phosphine from a preparation placed on the grain surface assists distribution of phosphine in silo bins. A phosphine generator based on adding acid to a mixture of zinc phosphide and sodium bicarbonate is in use in China (Champ, 1985). The present phosphine generator developed by M/S Excel Industries Limited, Mumbai and its team also works on the same lines where phosphine is generated by putting aluminium phosphide tablets in a water tank instead of adding acid, which is more cost effective.

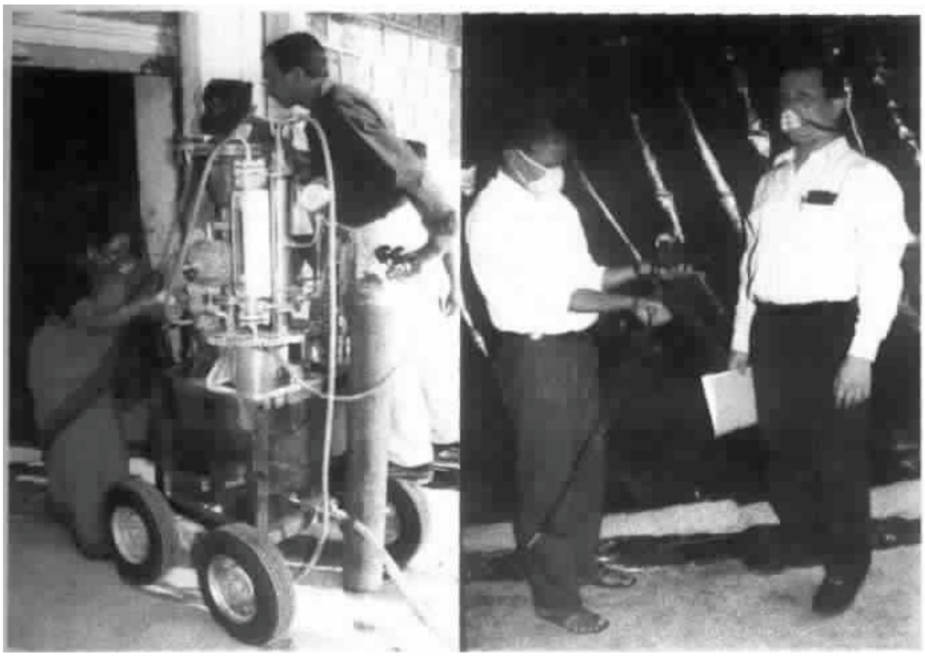
Casella, (1998) reported that the effective control (100%) of all developing stages of *Sitophilus spp*. was achieved with the synthetic atmosphere containing 21% CO_2 and 79% N_2 and 0.50 g phosphine, for an exposure period of 120 h. El – Lakwah *et al*. (1989) in their experiments on control of diapause larvae of *Trogoderma granarium* found that the addition of carbon dioxide increased the mortality by phosphine for an exposure period of 48 and 72 h at 30^0C. The present trials also indicate that addition of carbon dioxide enhances the effect of phosphine on insects at the same temperature.

Rajendran (1990) in his experiments on control of 1 day and 2 day old pupae of *Tribolium castaneum* found that 40% of carbon dioxide in air enhanced the toxic action of phosphine.
When phosphine fumigation experiments were conducted in tower (4.15 m high) containing soft red winter wheat, it was found that when carbon dioxide was applied with aluminium phosphide, phosphine penetrated the wheat faster and accumulated in higher concentration than when aluminium phosphide was applied alone. The effects of carbon dioxide were more pronounced as the depth in the column increased. At the end of the exposure time, the concentration of phosphine was more evenly distributed when carbon dioxide was applied with aluminium phosphide (Leesch 1992). In the light of these experiments, the phosphine generator under testing can also be used for fumigation in the silos/ towers.

The mixtures of phosphine and carbon dioxide (10 or 20%) reduced the resistance levels to phosphine in populations of *R. dominica* and *S. oryzae* with high levels of resistance to phosphine, although a clear pattern could not be determined (Athie et al. 1998). This could be another advantage of phosphine and carbon dioxide mixture. Ren *et al*. (1994) reported that when insects were exposed to greater than 20% (v/v) of carbon dioxide, intake of phosphine was more than doubled. It is also confirmed that phosphine toxicity increased with increasing concentration of carbon dioxide but decreased beyond 35% of carbon dioxide. It was found that the effect of carbon dioxide on toxicity of phosphine is an apparent synergistic effect. This revelation adds more strength to the present experiments.

CONCLUSION

It can be concluded from the above trials that phosphine in combination with carbon dioxide is more effective than conventional phosphine fumigation where no carbon dioxide is added. The most effective combination of the gases is 1.35 g phosphine (80% of normal phosphine dosage) + 35 g carbon dioxide per m^3 to control all test populations consisting of *Tribolium castaneum, Cryptolestes spp. and Oryzaephilus surinamensis* and full grown larvae of *Trogoderma granarium* It was also concluded that 1.0 g phosphine (60% of normal phosphine dosage) + 35 g carbon dioxide per m^3 is sufficient to produce lethal concentration to induce 100% mortality in test pest population consisting of *Tribolium castaneum and Oryzaephilus surinamensis*. When these gases are pumped into the stack being fumigated with the phosphine generator designed and developed by M/s Excel Industries Limited, Mumbai and its team, the exposure period can be reduced to 5 days instead of 7 days. There is a need to establish ovicidal effects of phosphine – carbon dioxide combinations to find out viable alternative to Methyl Bromide.



Phosphine generation Measurement of phosphine concentration

Figure 2 field trials in a warehouse

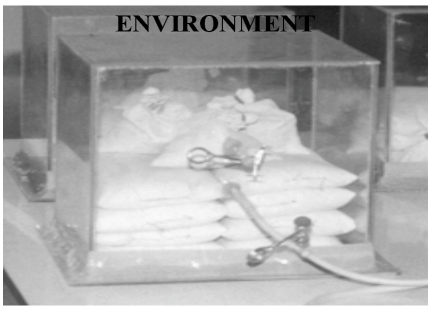
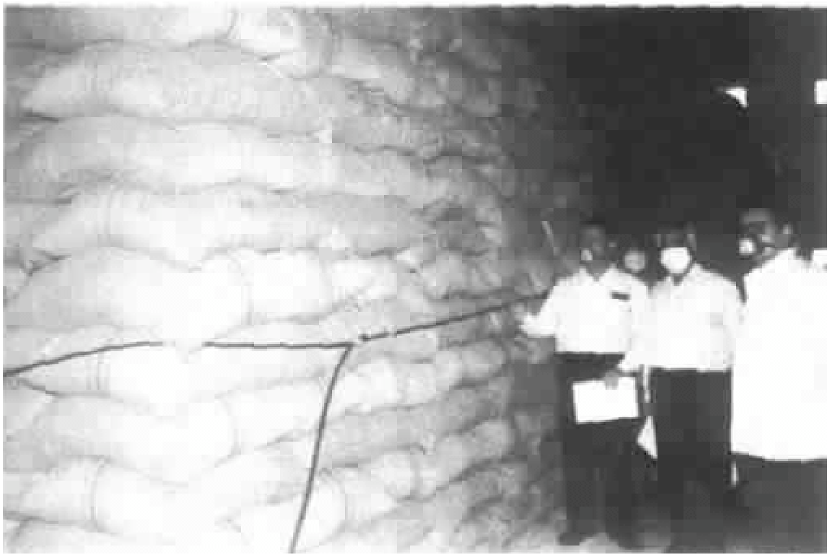


Figure 3. Lab. environment

Figure 4. Lab. experiment in progress



rubber tubing for insertion of phosphine and carbon dioxide

Figure 5, Field trials in a warehouse

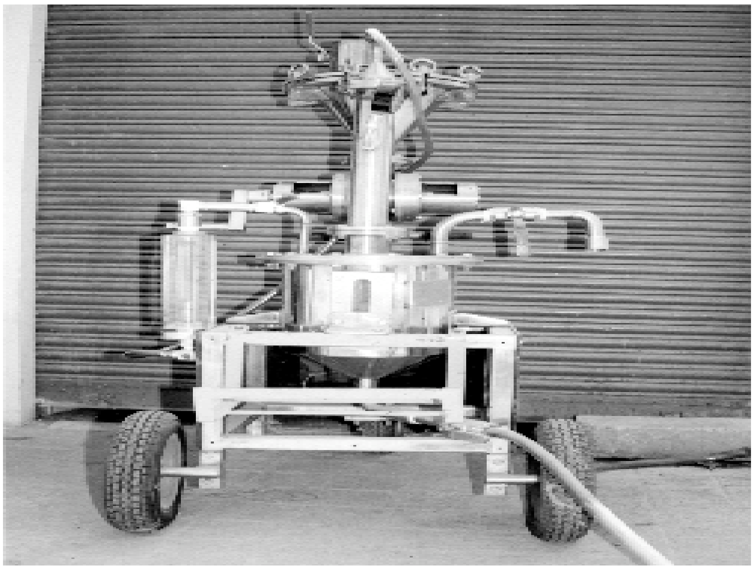


Figure 6, Final view of phosphine generator

REFERENCES

Athié I, Gomez, R.A.R. Bolonhezi, S. Valentini, SR.T. and M. Fernanda Penteado M. de Castro (1998) Effects of carbon dioxide and phosphine mixtures on resistant populations of stored grain insects, *Journal of Stored Products Research*, **34:1**, 27-32.

Bank H.J. (1994) Fumigation – an endangered technology? In: *Proceedings of the 6th International Working Conference on Stored product Protection,* Vol. I, (Edited by Highley E., Wright, E.J., Banks, H.J. and Champ, B.R.) CAB International, Canberra 2-6.

Champ, B.R., Murray, W.J., and Jefferies, M.G. (1981) Grain Storage and Pest Problems in China. *Bulk Wheat*, **15**, 21-26.

Casella T.L de C (1998), Carbon dioxide associated with phosphine in the control of the maize weevil (in Portuguese). *Revista Brasileira de Engenharia Agrecolae Ambiental*, **2:2**, 179-185.

El–Lakwah, F.A., Wohlgemuth R. and Khattab M.M. (1989) Efficiency of phosphine and combinations of phosphine with carbon dioxide against Khapra Beetle larvae *Trogoderma granarium* Evests (Col. Dermestidae). *Anzeiger fur schadilingskunde, Pflanzenschutz, umweltschutz* **62**: 5, 85-88

Green A.R. et al, (1984) The flammability limit of pure phosphine air mixture at atmospheric pressure, In: *Controlled Atmosphere and Fumigation in Grain Storage*, (Edited by B. E. Ripp) Elsevier, Amsterdam 433-449.

Leesch J. G. (1992) Carbon dioxide on the penetration and distribution of phosphine through wheat, *Journal of Economic Entomology*, **85:1,** 157-161.

Mueller D.K. (1994) A new method of using low levels of phosphine in combination with heat and carbon dioxide, In: *Proceedings of the 6th International Working Conference on Stored product Protection*, Vol. I, (Edited by Highley E., Wright, E.J., Banks, H.J. and Champ, B.R.) CAB International Canberra. 123-125

Rajendran S. (1990) The toxicity of phosphine methyl bromide, 1,1,1, trichloroethane and carbon dioxide alone and as mixture to the pupae of red flour beetle, *Pesticide Science*, **29 :1,** 75-83.

Ren. Y.L., O' Brien, I.G. and Whittle, C.P. (1994) Studies on the effect of carbon dioxide in insect treatment with phosphine, In: *Proceedings of the 6th International Working Conference on Stored product Protection*, Vol. I, (Edited by Highley E., Wright, E.J., Banks, H.J. and Champ, B.R.) CAB International, Canberra. 173-177