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. 237-253.

NEW PHOSPHINE FUMIGATION POSSIBILITIES USING THE HORN DILUPHOS SYSTEM®, VAPORPH3OS® AND THE FOSFOQUIM PHOSPHINE MONITOR®

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ABSTRACT

The HORN DILUPHOS SYSTEM® (HDS) allows the blending of pure phosphine with air, to obtain a continuous flow of air mixed with phosphine at a concentration of 10,000 ppm at a rate of 19 or 47 grams/minute of phosphine, depending on the model of dispensing equipment used. It is an automatic system that informs the operator on an LCD screen the steps to follow. The equipment is designed to apply the product VAPORPH$_3$OS®, manufactured by Cytec.

VAPORPH$_3$OS® phosphine fumigant is a continuous source of pure phosphine in cylinders, where each cylinder contains 18 kg of gas.

The FOSFOQUIM PHOSPHINE MONITOR® is an infrared continuous monitoring system that measures and registers the phosphine concentration during the whole fumigation period in four different zones, allowing an excellent control of the fumigation.

With these three new tools many new fumigation possibilities are now available and many new possibilities will be discovered in the future.

Only some of them will be summarized:

The H-System for fumigation of silo bins and flat storages without recirculation, is a fumigation method where a phosphine-air mixture is injected into the silo bin at the bottom, at a concentration close to the final one required. This phosphine-air mixture replaces the air in the grain interstices, distributing the gas evenly in only a couple of hours.

A fresh fruit and vegetable fumigation procedure, with pure phosphine, free of ammonia, is being developed in Chile with great success in the control of target pests and with no damage to the fruit. The fumigation is carried out in the same cold storages where the fruit is stored.

Also mills have been fumigated successfully with phosphine, minimizing corrosion, working with the HORN DILUPHOS SYSTEM together with the FOSFOQUIM PHOSPHINE MONITOR, using low phosphine concentrations precisely controlled with the monitor during the whole fumigation period, and re-dosing every time it is necessary.

A new system (JP-System) has been developed for the fumigation of containers without residues and is presently being field-tested.

DESCRIPTION OF THE HORN DILUPHOS SYSTEM®

The HORN DILUPHOS SYSTEM® (HDS) is an automated system, which allows the direct blending of pure phosphine with air below the ignition limit of PH_3 without risk of ignition, allowing the injection of an air and phosphine mixture into the enclosure to be fumigated with concentrations from 0 to 10,000-ppm.

The system includes a series of safety mechanisms, which will avoid damage in any risk situation, and even a power failure.

Only a nitrogen cylinder, a phosphine cylinder and an electrical supply is required to operate the system. Instruction for operation is shown on an LCD screen.

The system injects an air and phosphine mixture at a pressure of 20 to 30 cm water column (depending on the model). This is enough pressure to penetrate and distribute the air-gas mixture in any stored commodity, with the great advantage that the mixture has the same density as pure air, which assures a very fast and good distribution and diffusion.

There are two models commercially available: the HDS 80, that has a capacity of 80 m^3/hour PH_3-Air mixture at a concentration of 10,000-ppm phosphine at a rate of 19 g/min PH_3 with a power consumption of 220 VAC, 4 Amp; and the HDS 200, that has a capacity of 200 m^3/hour PH_3-Air mixture at a concentration of 10,000-ppm phosphine at a rate of 47 g/min PH_3 with a power consumption of 208 VAC three phase, 7 Amp or 380 VAC three phase 4 Amp. The size of both models, without cylinders, is 90 cm long, 68 cm wide and 92 cm high.

Figure 1. The HORN DILUPHOS SYSTEM® setup for fumigation.

Some advantages of HORN DILUPHOS SYSTEM® are:

- It is not necessary to enter into the facility.
- It is not necessary to place the fumigant in various locations of the facility.
- There is no need to collect, deactivate and dispose of spent material, following the fumigation.
- There are no environmental problems, as only hydrogen phosphide is applied, which is readily deactivated by sunlight upon release into the atmosphere.
- Phosphine generation does not depend on temperature or on moisture levels of air.
- The required concentration of gas for the fumigation is reached early during the fumigation period.
- The gas concentration can be changed at any time during the fumigation.
- There are no residues after fumigation.
- The amount of gas applied will be exactly the amount needed. If the concentration is lower than required, it is possible to re-dose from outside, at any time.
- The gas can be applied to a totally sealed structure without increasing the pressure, if the gas from the cylinders is mixed with air taken from the inside of the structure to be fumigated.
- Gas dispensing can be stopped at any time.
- The equipment uses pure phosphine free of ammonia.

Through the application of pure phosphine through this HDS, some typical disadvantages of phosphine as a fumigant are now avoided. The high flammability of phosphine is avoided, since the PH_3 concentration never passes the 18,000 ppm limit, the ammonia is eliminated since only pure phosphine without ammonia is applied and it is easier to control corrosion with the HDS, since it allows adding only the exact amount of phosphine needed and it is possible to use and maintain a low concentration in the building.

PHOSPHINE AS A FUMIGANT

Phosphine, has been used for over 70 years as an insecticide, and is presently the most accepted fumigant for stored products. It has a great ecological advantage; its application in pure form does not leave harmful residues in the environment or in treated products.

Nevertheless, because phosphine forms explosive and self flammable mixtures with air at concentrations over 18,000-ppm, it had not been possible to apply phosphine in its pure state by means of direct dilution with air, even though this would be the best way to apply the gas.

The problem then is to manage diluting the phosphine with air from its pure form into concentrations below the limit of self-ignition, without producing ignition in the process. Once the problem was identified, Fosfoquim S.A. systematically studied the phenomenon of spontaneous ignition and how to avoid it.

By carrying out a series of different tests, Fosfoquim S.A. has managed to solve the problem by patenting a system for the phosphine dilution with air, without risk of ignition. This method of dilution is presently known as the HORN DILUPHOS SYSTEM®.

This new tool now allows the commercialization of pure phosphine in cylinders for fumigation purposes.

VAPORPH_3OS®, phosphine fumigant, which is pure cylinderized phosphine, manufactured by Cytec, is the only product that can actually be applied using the HDS system.

FOSFOQUIM PHOSPHINE MONITOR®

The FOSFOQUIM PHOSPHINE MONITOR® is a monitor that uses the patented non destructive infrared absorption method to determine the phosphine concentration. The right wave length, allows perfect readings at intervals of 2 minutes or more at concentrations up to 10,000 ppm, storing 1,000 data per zone.

In this multipoint (4 zones) equipment, the sample is passed continuously through the infrared cell, where the concentration is measured (Fig. 3).

Figure 2. The FOSFOQUIM PHOSPHINE MONITOR®

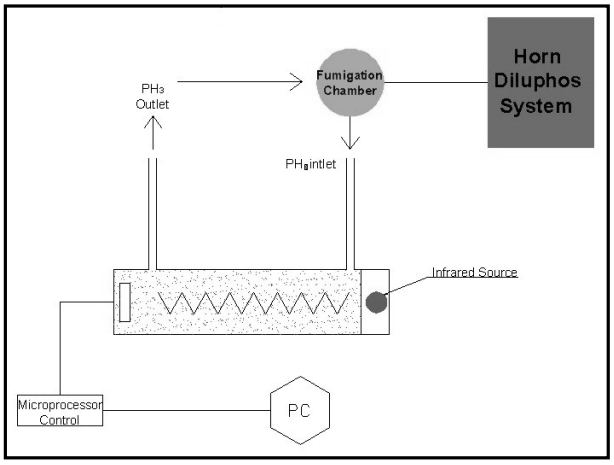

Figure 3. Infrared absorption gas monitoring

The equipment allows the operator to view on the display screen the sampling data in graphic displays and the exact amount of phosphine concentration in terms of ppm, with the time and date that the measurement was taken.

After the fumigation, the data can be downloaded through an RS232 port directly to a computer or printed out directly through a thermal printer.

The features and benefits of this monitor for any phosphine fumigation are that it provides real-time, continuous measurements of phosphine and it eliminates therefore the need for manual analysis.

SPECIFICATIONS OF THE FOSFOQUIM PHOSPHINE MONITOR®:

Technology: Patented mid-infrared multipoint (4 zones) analyzer for automated real-time analysis of phosphine gas during fumigation processes.

Phosphine Range: 10-10,000 ppm

Ports: 4 zones

Memory Capacity: up to 1000 test cycles per zone.

NEW FUMIGATION PROCEDURES

These three new tools described above enable the fumigation business to develop a lot of new different fumigation procedures and technologies that will change the way to undertake fumigation. In this case only a few new fumigation procedures will be shown, but it is understood that there are many more being actually used.

The H-System for fumigation of silo bins and flat storages without recirculation

A fresh fruit and vegetable fumigation method, with pure phosphine free of ammonia

Mill fumigation with phosphine minimizing corrosion

The JP-System, for the fumigation of containers **without leaving residues**

THE H-SYSTEM FOR FUMIGATION OF SILOS AND STORAGES WITHOUT RECIRCULATION

The standard way of application of phosphine through the HDS for silo bins and grain stores is the H-SYSTEM. The H-SYSTEM is a new fumigation method in which the air inside the storage to be fumigated, is replaced with a diluted mixture of phosphine with air at a concentration close to the final required concentration, distributing the gas evenly in only a couple of hours. This is done using the HORN DILUPHOS SYSTEM® as a constant source of phosphine (19 g/min or 47 g/min of PH_3 depending on the model). Using this distribution method, no recirculation is required to maintain the required gas concentration.

Also an additional fan can be used to lower the PH_3 concentration of the mixture that enters the facility, or the PH_3 air mixture of the HDS can be injected into the air stream of a recirculation fan installed at the site.

The gas mixture is introduced from the bottom of the storage structure or bin through the existing ventilation system or a system installed for the gas injection, by pushing the air without phosphine up as shown in Fig. 4.

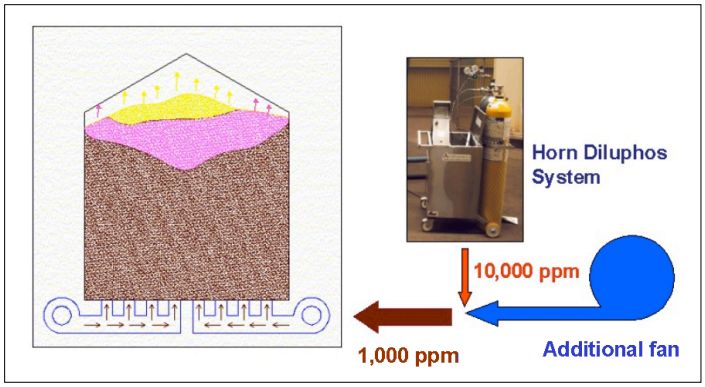

Figure 4. Silo fumigation with the H-System During fumigation an opening must be left open at the top of the bin, in order to allow the air without phosphine, that is pushed up by the phosphine-air mixture, to escape to the atmosphere and to avoid a pressure increase in the bin.

Figure 5. Connection of HDS and additional blower to ventilation system of silo

The above Fig. 5 shows how an additional fan is connected to the ventilation system of a silo bin. The blue pipe comes from the outlet of the HDS unit with a concentration of 10,000 ppm and is diluted with the additional fan to 1,000 ppm.

The ventilation system of the bin is sealed and is not activated during fumigation.

After distribution, which is achieved early after starting fumigation, no recirculation is required to maintain the concentration.

After injection the top and the bottom of the bin must be sealed off in order to avoid gas leaks.

The following graph shows the gas concentration during the injection of the gas and some hours after injection in a silo bin fumigated with the Horn Diluphos System. The first blue curve to reach the 1,000 ppm level, shows the concentration of the phosphine-air mixture in the ventilation system after being diluted with the additional fan. The second red curve to reach the 1,000 ppm level, is the concentration measured at half the height of the bin in the middle of the grain mass. The third green curve to reach the 1,000 ppm level, is measured at the top of the bin over the grain.

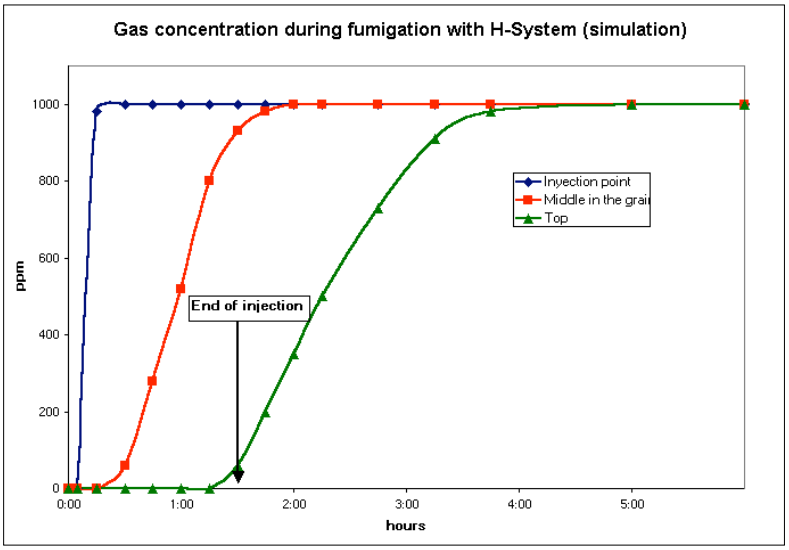

Figure 6. Gas concentration during fumigation of silo bin with H-System

The applied dosage for each case must be calculated with the following formula starting from the required concentration:

$$Dosage\left(g/m^3\right) = \frac{concentration\ (ppm)}{718} = \frac{grams\ PH_3}{m^3}$$

$$grams\ PH_3 = \frac{Empty\ Space\ (m^3)\ x\ Concentration\ (ppm)}{718}$$

The second equation can be used to calculate the amount of phosphine to be delivered to achieve the target concentration at a given empty space volume. The empty space is the sum of the headspace and interstitial space as in the following equation.

$$Empty\ Space = Headspace + Interstitial\ Space$$

The interstitial space is calculated using the percentages of the total grain volume as shown in the following Table:

TABLE 1
Interstitial spaces for different grain types

Type of Grain	Interstitial spaces,%	Moisture Content, %
Rice	50.4	11.9
Oat	47.6	9.8
Barley	45.4	9.8
Rye	41.2	9.7
Yellow corn	44.0	25
Yellow corn	40.0	15
Sorghum	36.8	9.9
Soya	33.8	7
Hard wheat	42.6	9.8
Soft wheat	39.6	9.8

The phosphine dosage can be affected in each case by different factors such as:

- The sealing of the structure
- Temperature of the stored good.
- Pest species and local regulations.
- Phosphine degradation characteristics of commodity.

FRESH FRUIT AND VEGETABLE FUMIGATION PROCEDURE

This fumigation method is for fresh fruit treatment where pure phosphine, free of ammonia is used at low temperature for the control of pests in fresh fruit. The gas is applied in fumigation chambers, cooling chambers or controlled atmosphere chambers at low temperatures.

It was determined that this can be done successfully if the fumigation is carried out at a temperature between –1.5 and 15ºC with a concentration of pure phosphine free from ammonia, between 700 and 3,500 ppm (1-5 grams /m^3) in a sealed enclosure, with an exposure time of between 36 and 72 hours. The gas used for the described fumigations is VAPORPH_3OS®, manufactured by Cytec and applied through the HORN DILUPHOS SYSTEM®. Preferably, 1,500 ppm are used for 48 hours at 0° C.

No damage to the fruit has been detected if the fumigation is carried out under the above conditions, and the shelf life of the fruit after treatment was found to be similar to non treated fruit.

Some small off-taste of fumigated fruits was observed following fumigation, but this disappeared after 5 or 6 days of storage at low temperatures.

For several years, phosphine has been investigated as a fumigant for the treatment of fresh fruit and vegetables. The research has shown good results with regard to mortality of insects. However, acceptable results were not obtained with regard to the quality of treated fruit, which always suffered damage. This damage was caused by two main factors: the presence of ammonia, and the relatively high fumigation temperature of over 15°C, under which the tests were carried out.

Aluminum phosphide or magnesium phosphide based products have the great disadvantage that, when they are used at low temperature, they produce phosphine very slowly and they always produce ammonia as a by-product and ammonia is known to be very phytotoxic. For this reason, damage to the fruit is to be expected when using metal phosphides.

Phosphine is generated, when using aluminum phosphide or magnesium phosphide, by the following reactions:

$AlP + 2H_2O \quad \lozenge \quad PH_3 + AlOOH$

$Mg_3P_2 + 6H2O \quad \lozenge \quad 2PH_3 + 3Mg(OH)_2$

And together with the above reactions there are always ammonia generating reactions:

$NH_2CO_2NH_4 \quad \lozenge \quad 2NH_3 + CO_2$

$AlN + 2H_2O \quad \lozenge \quad AlOOH + NH_3$

$Mg_3N_2 + 6\ H_20 \quad \lozenge \quad 3Mg(OH)_2 + 2NH_3$

But on the other hand, because of the pyrophobic characteristics of the product, until the HORN DILUPHOS SYSTEM® was developed, it was not possible to apply pure phosphine for fumigations. Therefore, until that moment, the only possible way to apply phosphine was through a reaction of hydrolysis of metallic phosphides like aluminum phosphide or magnesium phosphide.

Since, during the last few years pure phosphine, free of ammonia has become available, it has been possible to carry out fresh fruit fumigation at low temperatures and with high gas concentrations using the HORN DILUPHOS SYSTEM®, with the surprising discovery that the quality of the fruits is not damaged, and it is possible to eliminate the main pests of fruits.

It was discovered that when lowering the temperature, it is possible to carry out the fumigation with a very high concentration of phosphine with no damage to the fruit, since at low temperature, the metabolic activity of the fruit is slowed down.

This high concentration compensates for the reduced activity of the insects at low temperatures, thereby controlling the pests.

The best way to do the treatment with phosphine is to fumigate the fruits directly in the cooling chambers where the fruit is stored after the selection process, leaving the cooling system working during the whole fumigation period. With three phase inductive motor ventilators, and ammonia cooling systems, no corrosion has been observed.

The fruit is preferably treated at the cold storage temperature of each fruit. For example, for apples, grapes, kiwis and berries, pears, nectarines, peaches, etc., it is preferred to undertake the treatment at temperatures from –1,5 to 2°C. Other fruits like avocados, citrus fruits and mangos, are preferably treated at their corresponding cold storage temperatures.

In this procedure, using the HORN DILUPHOS SYSTEM®, no increase of pressure is generated inside the enclosure to be fumigated, since the air of the inside of the enclosure is recirculated through the HDS system.

The use of pure phosphine has as its main advantage, that after liberated to the atmosphere, phosphine is oxidized into phosphoric acid by the action of sunlight.

yIt has been demonstrated that it is possible to control the major pests of fruit, such as the mealybugs, *Pseudococcus spp*; the apple moth, *Cydia pomonella*; eulia, *Proeulia spp*; the fruit tree weevil, *Naupactus xanthographus*; the mediterranean fruit fly, *Ceratitis capitata*; fruit flies such as, *Rhagoletis spp, Bractocera spp, Anastrepha spp*; the Chilean false spider, *Brevipalpus chilensis;* and *Thrips spp*.

TABLE 2.
Phosphine fumigation results on infected apples compared with non fumigated apples

TREATMENT	INSECT	STAGE	Description	Insects	Alive	Dead	Rate %
Exposure to 2.1 grs. of phosphine/m^3 at a temperature between -1 a –0.3º C during 62 hours and 44 minutes	*Pseudococcus viburni*	Adult	FUMIGATED	160	0	160	100.0
			NOT FUMIGATED	65	55	10	15.4
		Crawler	FUMIGATED	819	0	819	100.0
			NOT FUMIGATED	335	305	30	9.0
		Egg	FUMIGATED	360	1	359	99.7
			NOT FUMIGATED	120	108	12	10.0
	Cydia pomonella	1st state larva	FUMIGATED	16	0	16	100.0
			NOT FUMIGATED	5	5	0	0.0
		5t state larva	FUMIGATED	7	0	7	100.0
			NOT FUMIGATED	6	5	1	16.7

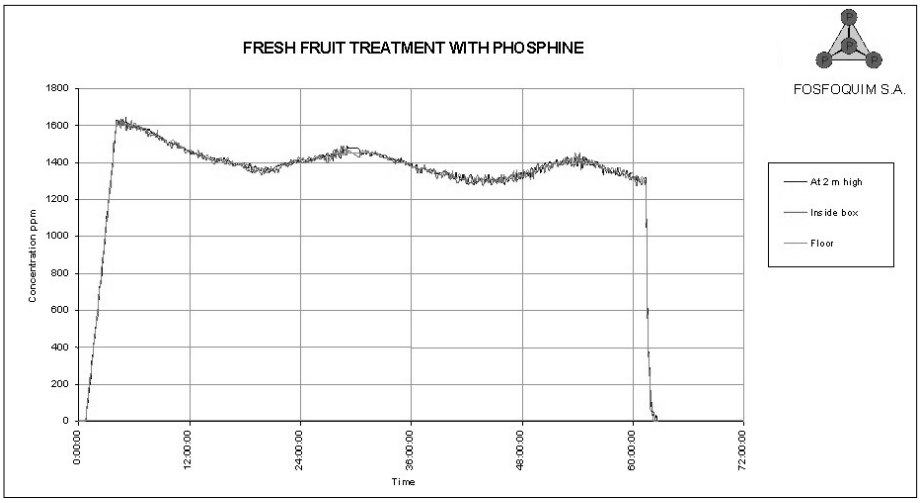

Figure 7. Phosphine concentration graph during whole fumigation period

Many mill fumigations have been carried out using the HORN DILUPHOS SYSTEM® with phosphine concentrations close to 150 ppm for 48 hours at temperatures of 25-30° C, using VAPORPH$_3$OS®, phosphine fumigant with very good results and without problems of corrosion. This has been monitored by placing partially covered copper strips at strategic places.

This fumigation procedure will be effective against adults, but it will not kill every egg in the fumigated facility. This means that the fumigation should be repeated every 3 to 4 months in order to maintain a low level of insects.

To be able to carry out a fumigation of a mill, it is necessary to take special care in trying to obtain a good distribution of gas in the entire facility, in order to avoid areas with high gas concentrations where corrosion could be a problem.

Temperature and moisture are important factors to be considered when evaluating corrosion risk.

The gas levels should be continuously monitored in order to assure a low phosphine concentration, but high enough to be effective against the insects. A good tool for the continuous monitoring of phosphine concentration is the FOSFOQUIM PHOSPHINE MONITOR®.

The HDS unit allows one to re-dose from outside every time it is necessary or to lower the concentration of the phosphine-air mixture at the outlet of the equipment to maintain a continuous flow of 150 ppm that will counteract the leaks of the enclosure.

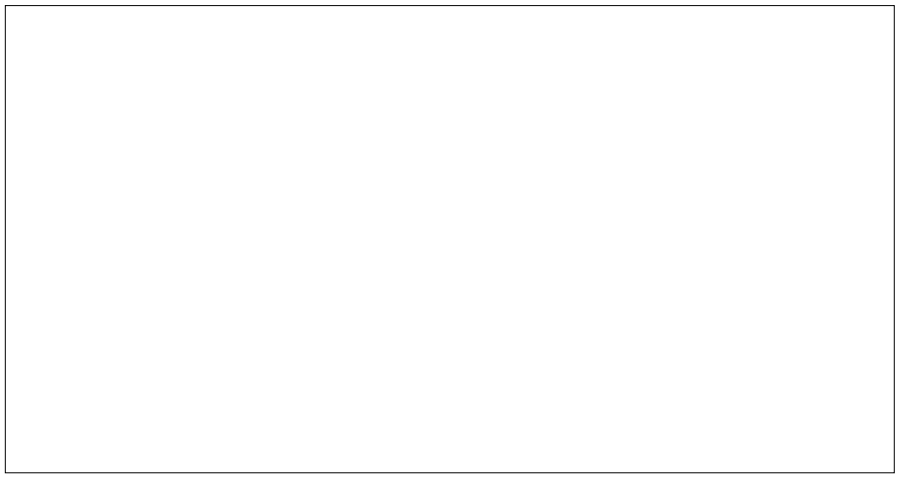

Figure 8. Phosphine concentration during mill fumigation, at Nos, Chile

The above concentration graph shows the PH_3 concentration taken with a FOSFOQUIM PHOSPHINE MONITOR® during a 72 hour mill fumigation in Chile in a very leaky facility. Approximately every 12 hours it was necessary to re-dose from outside with the HDS unit, in order to maintain an average concentration of about 170 ppm.

In order to carry out a good fumigation, it is recommended to make a PVC pipe installation that allows distribution of gas to the different levels and areas, as is shown in following drawing.

This installation should include, besides the injection and distribution pipe for the phosphine air mixture from the HDS, - a connection for the air inlet of the HDS to take the fresh air out from inside the facility. The end of this air inlet pipe should be located far enough from the points where gas is injected to avoid the situation where a high concentration of gas returns to the equipment.

It is very important to achieve a good sealing of the structure to avoid leaks and thus, the necessity to re-dose phosphine too often.

JP System for container fumigation

The JP-System (pat. pending) for container fumigation was developed by Fosfoquim (Jerry Sullivan and Pedro Horn) as an easy way for container or truck fumigation with the HORN DILUPHOS SYSTEM®.

The advantage of this system is that it allows the fumigation of a sealed container or truck, without having to open the doors or be concerned with a pressure differential. The fumigation is carried out with pure phosphine gas and therefore, there are no residues to be removed and deactivated following fumigation.

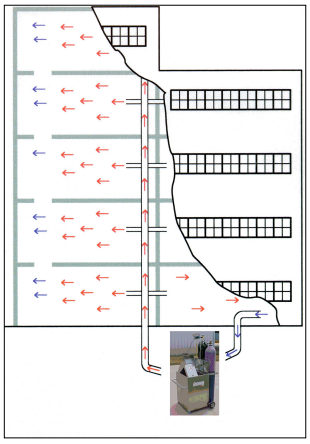

Figure. 9. Gas distribution system for mill fumigation.

The characteristics of the HORN DILUPHOS SYSTEM®, called the HDS, allow one to add the exact amount of gas needed for the fumigation.

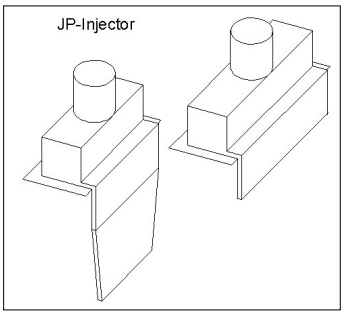

Figure 10. JP-System

The JP-injector can also be used for ventilation of the fumigant and for absorption in a charcyoal filter, by recycling the air from inside the container through this device to the scrubber.

In this case it isy not necessary to open the container prior to ventilation, since the device is easily introduced into the space between the gasketed or roll-up doors.

Advantages of the JP- System:

- No residues in the container since only pure phosphine is applied.
- No need to deactivate spent material.
- It takes only a few minutes to get an even gas distribution in the entire container.
- The device is easily introduced between the gasketed or roll-up doors without opening them.
- Also locked containers can be fumigated without breaking the seal.
- Low cost device that can be used for many containers.
- The container can be aerated using the same device.
- The device for the injection of the gas can be easily extended with flat plastic tubing.
- The device is introduced between the gasketed doors and should be tight enough to hold the gas. For additional sealing, tape can be used.
- Can be used on most modern containers and trucks.

Figure 11. Container being fumigated with the HDS together with the JP- System.

CONCLUSIONS

The HORN DILUPHOS SYSTEM®, together with the FOSFOQUIM PHOSPHINE MONITOR®, allows the development of many new phosphine fumigation techniques using Cytec's VAPORPH$_3$OS®, phosphine fumigant gas. Only a few new techniques were described in this paper, such as the H-System for silo fumigation, the new fresh fruit fumigation procedure, the flourmill fumigation with controlled concentration and the JP-System for container fumigation.

Many other techniques are being developed, such as the bunker storage fumigation using the HDS System, a residue-free in-transit flour railcar fumigation in the USA using VAPORPH$_3$OS® with the HDS system, and short-term greenhouse fumigation.

And surely many unknown possibilities will be recognized in the future for employment of this new constant source of pure phosphine in cylinders, diluted directly with air below the explosion limit, without risk of ignition.