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A NEW PHOSPHINE RELEASING BAG PRODUCT BASED ON MAGNESIUM PHOSPHIDE FOR SHORT-TERM FUMIGATION

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ABSTRACT

A new magnesium phosphide-based product for the protection of stored products by phosphine (PH_3) fumigation has several advantages when compared with the usual products. The metallic phosphide formulation is contained in bags made of specially impregnated paper (Tyvek) which are permeable only to water vapor. After complete decomposition of the metal phosphide, the fine dust remains in the bags so no residues can reach the stored, fumigated commodities. The addition of zeolite, a water-absorbing sodium-aluminum silicate, ensures that when the tin is opened for use no uncombined PH_3 can be detected in the packed product. In addition, all danger of self-ignition is precluded. Furthermore, because this adjuvant delays the development of PH_3 at the beginning of the decomposition, there is enough time for the fumigant to diffuse without causing any hygienic risk to the worker who inhales the generating gas. In contrast to similar products based on aluminum phosphide, under normal conditions (20°C/60% r.h.), the new product, "Detia Gas Ex-B Forte," decomposed completely within 48 h. The residue in the bags contained only traces (0.1%) of magnesium phosphide. Because of its prompt decomposition, this product is especially suitable for short-exposure fumigations. This formulation is also remarkable in that it enables fumigations to be carried out at low temperatures (below 5°C) without greatly prolonging the exposure time. Consequently, short-term fumigations in cold weather or in chilled containers are also possible. Using this magnesium phosphide product in bags might open new operational areas for fumigation with PH_3. Good results have already been achieved with the quarantine treatment of bananas, red peppers, mangos, etc.

INTRODUCTION

Considering the three most important aspects in the development of a fumigant formulation for phosphine (PH_3) release, namely storage, application and disposal, raises the possibility of problems at all three stages. When the development of a new PH_3-releasing bag formulation was initiated, the first priority was to achieve greater safety during storage of

the formulation, during application and during retrieval or disposal (when risk should be eliminated entirely). The second objective was to develop a PH_3 product that decomposes faster than other PH_3 formulations presently available on the market. The new formulation was designed to reduce exposure times for commodities during transport and in storage, particularly with regard to container shipments that demand shorter fumigation times.

STORAGE OF THE FORMULATION

Frequently low PH_3 concentrations (in the ppm-range) can be measured outside tubes or tins containing PH_3 formulations. These low concentrations may be attributed to leakage along soldered lines and around tube caps and tin lids.

Recently, part of an American harbour was temporarily closed because of unacceptably high concentrations of PH_3 in an area surrounding one of the transport and storage containers. Both manufacturers and research institutes have repeatedly found up to 1,000 ppm of PH_3 remaining in fumigant packaging. This is not surprising, since the volume of a tube or a tin is very small. If a tube of 9.5 cm^3 contains 1,000 or 2,000 ppm, this means that an employee or technician within about one cubic meter of it could be exposed to a few ppm PH_3 when opening it. However, a special ingredient in the newly developed bags has, for the first time, enabled the manufacture of a PH_3-free package.

This was made possible because when PH_3 is released from the metal (magnesium) phosphide, it is absorbed by a specially added ingredient, sodium aluminum silicate. This silicate, known as zeolite, is a naturally occurring substance, and zeolite mines exist in northern Italy among other places. Zeolite has a very high affinity for PH_3, immediately adsorbing the PH_3 molecules that develop from the metal phosphide.

In the new bag formulations there are two different types of zeolite molecule. One type has small pores which temporarily adsorb PH_3 molecules, and the other adsorbs H_2O molecules. This assures that water vapour molecules combine with the zeolite and are therefore unable to react too rapidly with the magnesium phosphide to form PH_3. It also assures that the first PH_3 molecules to develop are initially retained in the zeolite molecular filter. The packaging itself thus remains PH_3 free.

PROTECTION AND SAFETY FOR FUMIGANT OPERATORS

This unique property of sodium aluminum silicate also protects the fumigant operators. This is due to the delayed emission of PH_3 from the new bag when compared to the bag currently in use, without sodium aluminum silicate (Fig. 1). This figure shows emissions during the first 2 h, about the period of time normally needed for applying the fumigant. From this it is clear that there is a marked delay in the decomposition of the formulation with the zeolite ingredients. This delay is normally about 20 min before the first PH_3 concentrations — in very small quantities — can be measured. It continues for up to about 6 h, after which the efficacy of the silicate is diminished and the curves of decomposition approach each other. This delay in decomposition would be an important contribution to the safety and protection of the workers applying the fumigation bags. It should be noted

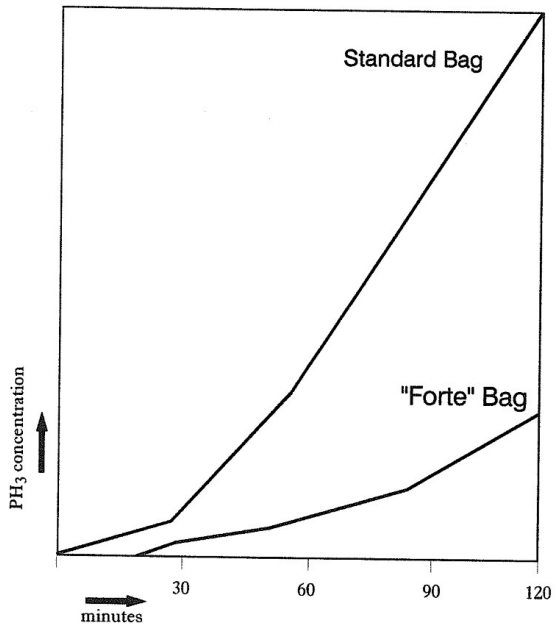

Fig. 1. Rates of initial PH_3 evolution from the standard and from the new "Forte" fumigation bags.

that the MAC-value, or TLV, for PH_3 is almost universally between 0.1 and 0.3 ppm, and such values can easily be reached when tubes or tins containing liberated PH_3 are opened.

RATE OF PHOSPHINE PRODUCTION

Magnesium phosphide is known to decompose faster than aluminum phosphide. Furthermore, the rate of metal phosphide decomposition within a fumigation bag is dependent upon both the temperature and the humidity gradient between the outside and the centre of the bag. Therefore, the reaction can be speeded up by making the bag thinner. The standard 6-mm thick bag can be compared with the 3-mm thickness of the new fast-decomposing bag, and clearly decomposition in the standard bag is much slower. The standard bag contains 34 g of phosphide mixture and generates 11.3 g PH_3, whereas the new magnesium phosphide bag contains only 9 g of phosphide mixture and generates only 3 g PH_3. An additional factor influencing the rate of reaction is the ratio between surface area and weight of the bag. The standard bag is 9×9 cm, with a surface area of 162 cm^2, whereas the new bag is 5×9 cm, with a surface area of 90 cm^2. The weight-to-surface-area ratios of the standard and new bags are 0.21 and 0.1, respectively. This smaller ratio also contributes to a much faster decomposition of the new bag.

Rates of PH_3 concentration build-up over a 48 h period are given in Fig. 2. At 20°C, differences in humidity (between 60% and 75% r.h.) do not significantly affect the rate of PH_3 release.

Magnesium phosphide also has the remarkable property of decomposing rapidly, even at low temperatures. Figure 3 shows decomposition at 3°C and 32% r.h. Even at such low temperatures, considerable decomposition is reached after about 3 d. However, fumigations at such extremely low temperatures should be the exception since it is well known that stored-product pests reduce their metabolic activity drastically at low temperatures.

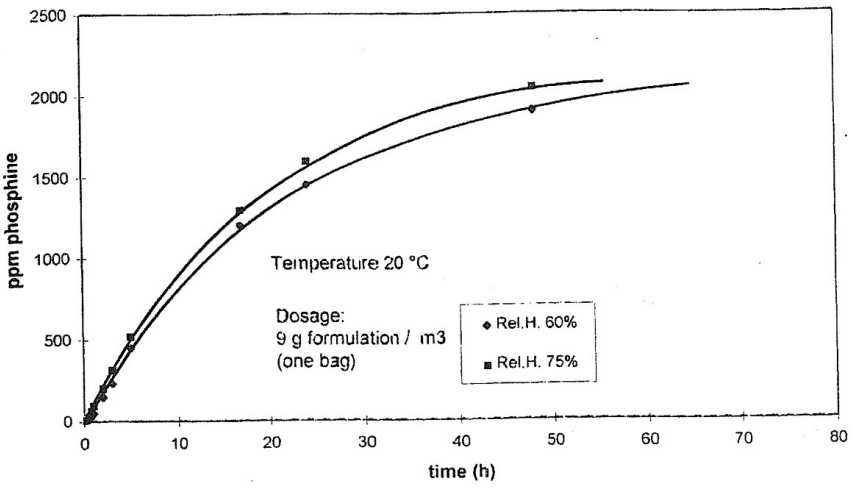

Fig. 2. PH_3 concentration build-up over a 48 h period at 20°C.

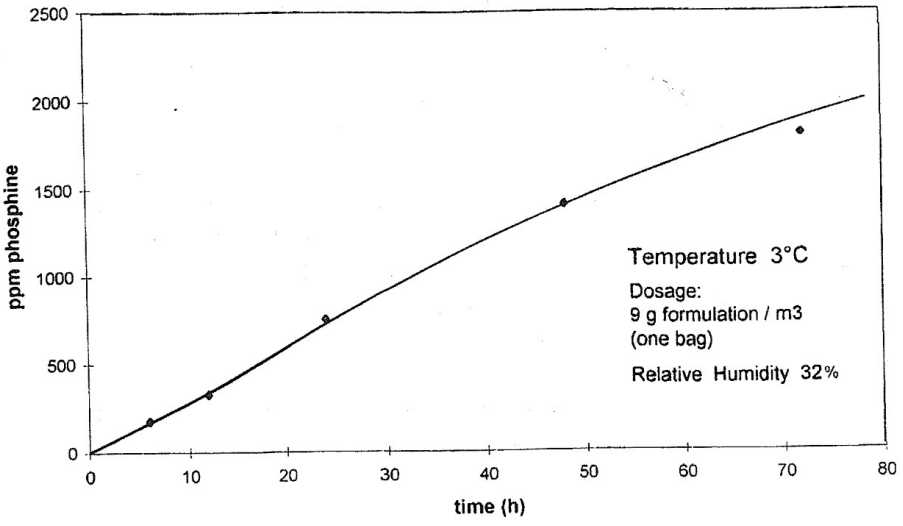

Fig. 3. PH_3 concentration build-up at 3°C.

Fig. 4. Application of the bag chains.

Their respiration is reduced and thus only small amounts of PH_3 are inhaled. Consequently, often only the most susceptible stages, particularly adults, are killed; developing stages, especially when they are inside commodities, survive.

DISPOSAL

Disposal of the decomposed materials has recently received special attention and an increasing number of countries have enacted laws or regulations for handling the waste products. In this important respect also, the new improved bags have decisive advantages. Because the chemical reaction of aluminum phosphide with water to produce PH_3 and aluminium hydroxide only reaches 98% completion, 2% of the original aluminum phosphide remains in the technically spent bags. Magnesium phosphide, on the other hand, decomposes faster and farther than aluminum phosphide. Due to the special adjuvents, in the new magnesium phosphide bags the decomposition rate is further improved, leaving a residue of no more than 0.1% Mg_3P_2.

This new bag is called "Gas-Ex-B forte." It is at present being registered in Germany, Italy, Greece, Austria and Japan for use in the control of stored pests in spices, tobacco, teas, cocoa, dried fruits, seeds, flour and raw coffee. The recommended dosage is 3 g/t or 2 g/m^3. The bags are available in chains, facilitating their use in containers, store-rooms, etc. (Fig. 4).

TREATMENT OF FRESH FRUITS

Preliminary tests carried out with this new fumigation bag for quarantine treatment of various fresh fruits were quite successful. In a survey of literature conducted by the manufacturer, it can be seen that even with high dosages (some with relatively long exposure times) and at different temperatures, the tested fruits were not damaged. These tests are, however, preliminary and they must be confirmed by further studies (Table 1).

TABLE 1
Fresh fruit fumigation with PH_3: preliminary experimental findings

Fruits	Dosage (ppm)	Time (h)	Temperature (°C)	Fruit damage
Grapefruit	500	48–72	15	no
Oranges	1000	72	20	no
Avocados	500	72	21	no
Mango	500	48	21	no
Papaya	2800	24	12	no
Bananas	1000	72	10	no
Grapes	800	72	4	no

The newly developed PH_3 bag product based on magnesium phosphide can possibly replace some of the present methyl bromide (MB) applications. This is of particular importance in those countries where in the near future MB will be partly or completely banned.