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COMPARISON OF RATE OF RELEASE OF PHOSPHINE FROM SOME COMMERCIAL FORMULATIONS GENERATED UNDER 75% RELATIVE HUMIDITY AND FOUR TEMPERATURES

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ABSTRACT

There is a paucity of data on the influence of temperature and the availability of water on the rate of gas production by commercial preparations used to generate phosphine. The rate of phosphine production by five materials - Magphos tablets (Mg_3P_2), Celphos tablets - aluminium phosphide (AlP), Phostoxin tablets (AlP), Celphos pellets (AlP), and Phostoxin pellets (AlP) - were studied at temperatures of 15, 20, 25, and 32°C, and 75% relative humidity (r.h.). Trials were carried out in 1-m^3 chambers and the evolution of phosphine was measured by a passive electrochemical cell at hourly intervals. This technique provides an accurate measurement of the decomposition curve. Results showed marked differences in the rate of reaction among materials under the different conditions. The respective times required by Magphos tablets, Celphos tablets, Phostoxin tablets, Celphos pellets, and Phostoxin pellets to reach 90% decomposition were:

at 15°C: 22, 38, 42, 21, and 20.5 hr (total available water: 9.7 g/m^3)

at 20°C: 17, 30, 30.5, 18, and 17 hr (total available water; 13 g/m^3)

at 25°C: 12, 24, 25, 15, and 13 hr (total available water: 17.4 g/m^3)

at 32°C: 10, 19, and 20 hr (total available water: 25.4 g/m^3); no results for pellets.

Magnesium phosphide tablets and aluminium phosphide pellets were shown to have the same rate of release, that is twice the speed of aluminium phosphide tablets. Differences among the aluminium phosphide formulations were slight.

INTRODUCTION

Phosphine (PH_3) used for fumigation is generated by the hydrolysis of a formulation containing one of the active ingredients: aluminium phosphide or magnesium phosphide. Commercial preparations contain additional ingredients that are included to reduce the risk of ignition and moderate the rate of phosphine release. It is necessary to know the rate of release under the prevailing conditions in order to model the rate of concentration change that can be expected during a fumigation. There are two types of factors that determine the rate of release of phosphine:

- Nature of the formulation including the type of active ingredient, type and quantity of other ingredients, and the degree of compression.
- External factors that may affect the rate of release such as the nature of the commodity, location of application, etc.

The aim of the work presented here was to find a way of measuring the rate of release of phosphine from commercial formulations.

Banks (1991) describes a method of determining rates of release involving the control of the physical conditions: temperature, water vapour content, and airflow. The latter, airflow, is problematic because airflow rates are difficult to measure and are therefore rarely known under real conditions. In order to avoid the problems of airflow, we decided to compare formulations using a set of conditions in which there was no forced airflow.

MATERIALS AND METHODS

The experiments were carried out in four 1.0-m^3 stainless steel chambers. The relative humidity (r.h.) in the chambers was controlled at 75% r.h. by trays of saturated sodium chloride (NaCl). Preliminary trials showed that r.h. equilibrium could be reached in about 2 hr by exposure of a surface to volume ratio of 0.3 m^2/m^3 NaCl. The actual water content of the air depended on the temperature and r.h. The quantities of formulation necessary to give 1 g/m^3 PH_3, i.e., 1 tablet or 5 pellets, were placed in an open 7-cm diam. petri dish on a narrow shelf at the centre of the chamber. The concentration of phosphine in the chamber was measured continuously with an electrochemical cell placed in the chamber. (Ducom and Bourges, 1987). Concentrations were recorded once per hour on a data logger until a maximum value was recorded. The data were transferred to a computer and analyzed using a Lotus spreadsheet. Formulations were obtained from a French representative of suppliers and no further information was available as to their exact origin. The formulations tested were round tablets of Celphos (AlP from Excel Industries Ltd.*) and Magphos (from Detia-Degesch*), pellets of Celphos (AlP), and Phostoxin (AlP from Detia-Degesch*), and flat

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* Names cited do not constitute recommendations for use of these products.

tablets of Phostoxin (AlP). Round tablets and pellets of Celphos were new candidates for registration in France.

All treatments were replicated four times.

RESULTS

Shape of the decomposition curve

The data were modeled well by the best fit polynomial (Fig. 1) with a noticeable improvement in fit as the degree increased.

x^2 correlation coefficient
0.99 ($y = -60.7 + 27.9x - 0.3x^2$)

x^3 correlation coefficient
0.999 ($y = 33.05 + 21.99x - 0.026x^2 + 0.0033x^3$)

x^5 correlation coefficient
0.9999 ($y = -1.21 + 11.11x + 0.86x^2 - 0.03x^3 + 0.00024x^4$)

Rates of release

As can be seen from Fig. 1, the first section of the curve is represented well by a straight line plot. This relationship was used to simplify the comparisons of release rate among temperatures.

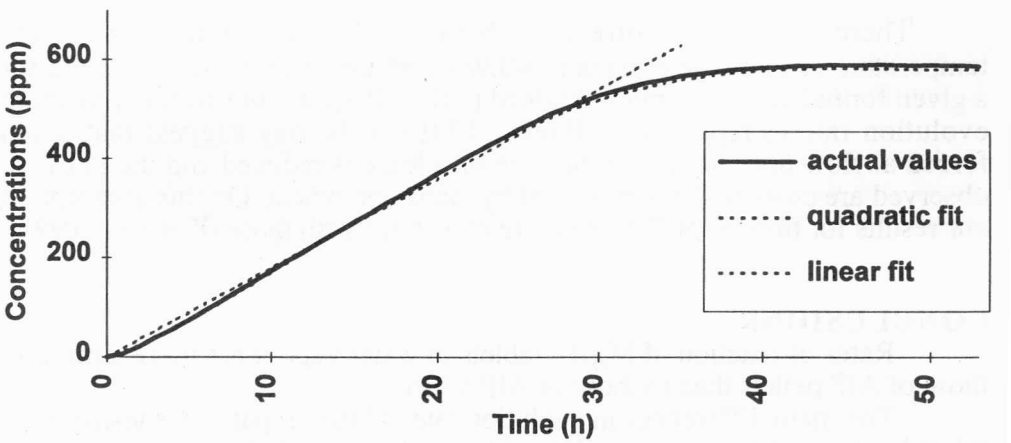

Fig 1: Typical decomposition curve demonstrating cumulative concentrations obtained from an initial dose of 1 g/m^3 of phosphine released from one Phostoxin tablet at 20°C and 75% r.h.

Table 1 shows the average rates of production at different temperatures based on the straight portion of the production curve and the corresponding time to reach 90% of the total release of phosphine. The rates vary for each formulation: a threefold increase for an increase from 15 - 32°C for Magphos, a twofold increase for AlP tablets, and a one-and-a-half time increase for pellets. For a given temperature, Mg_3P_2 and pellets of AlP had approximately the same rate, and temperature appears to have had more of an effect than was the case for AlP tablets.

Table 1: Rate (ppm/hr) of phosphine release and time (hr) to reach 90 % decomposition.

Temperature		15°C		20°C		25°C		32°C	
$[H_20]$ (g/m^3)		9.7		13		17.4		25.4	
		Rate of release ppm/hr	Time to 90% (hr)	Rate of release ppm/hr	Time to 90% (hr)	Rate of release ppm/hr	Time to 90% (hr)	Rate of release ppm/h	Time to 90% (hr)
Tablets	Magphos	24.4	22	35.3	17	56.6	12	72.1	10
	Celphos	15	38	21	30	25	24	31	19
	Phostoxin	13	42	18	30.5	23	25	29	20
Pellets	Celphos	30.7	21	41	18	49	15	-	-
	Phostoxin	26.1	20.5	33.8	17	48	13	-	-

There is a linear correlation between the rate of hydrolysis and temperature or moisture content (r^2=0.98) with the lines being very close for a given formulation. The rates obtained (Table 2) are about half the maximum evolution rate as reported by Banks (1991). This may suggest that when forced airflow does not occur, the rate of release is reduced and the rates we observed are close to those observed by Banks on wheat. On this assumption our results for time-to-50% release are consistent with those of Banks (1991).

CONCLUSIONS

Rates of reaction of Mg_3P_2 tablets to water vapour are more similar to those of AlP pellets than to those of AlP tablets.

The main differences in evolution rates of the preparations tested were related to formulation type (pellet, tablet, and round tablet) and composition of the active ingredient (AlP or Mg_3P_2).

The rates of release up to the 50% release level reported in this paper are similar to those recorded previously by Banks (1991), but differ at higher levels of release. It may be that the lack of forced airflow accounts for the

differences and consequently, the rates of release in this paper will predict more closely those obtained in practice.

Table 2: Maximum evolution rates observed at different temperatures and 75% r.h. based on average values obtained for Celphos and Phostoxin tablets in comparison with values obtained by Banks (1991).

	Rate of release observed (Average of Celphos & Phostoxin tablets)		Expected values*
Temp. (°C)	ppm/hr	g/hr	g/hr
15	14	0.02	0.040
20	19.5	0.029	0.050
25	24	0.034	0.068
32	30	0.048	0.093

* values according to Banks, 1991.

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