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Test on Recirculation Fumigation under Film with Mixed Gas of $PH_3 - CO_2$ in Steel Cylinder

Yang Xinzhong[1], Song Lishan[1], Li Hailong[2], Xin Liyong[2], Li Guangtao[3], Shi Zhiguo[2], Liu Guihe[2], Li Yanyu[3] and Cao Yang[3]

Abstract: In order to research the applied technology of film sealing technology of the grain surface combined with recirculation fumigation of a mixed gas of $PH_3 - CO_2$ [PH_3 2% + CO_2 98% (w/w)], we performed field tests on recirculation fumigation under film in a warehouse. The warehouse was 54.36m long, 35.26m wide and the loaded grain height 6m. There were 7650t of bulk wheat stored in the warehouse, and five test points of gas concentration and five test-insect cages were located in the warehouse. Supply 250kgs of mixed gas of $PH_3 + CO_2$ and open recirculation ventilator to run for 12 hours, and then stop. Begin to test the gas concentration three hours after application, after that test the gas concentration of PH_3 in the warehouse once a day, degas after 21 days and take the test-insect cages out to check mortality. Culture the tested insects for 30 days (25℃75% RH) and then check mortality. In this research, we used No. 23 warehouse with the same conditions as the control warehouse which used normal aluminum phosphide fumigation with application on grain surface and application on buried bags. The No. 23 warehouse is the same as the tested warehouse in terms of locations of test points of gas concentration and test-insect cages, and sampling and testing methods. The result shows that the pressure half-life of the tested warehouse were 4s (−30Pa to −15Pa), and the average, Min. and Max. concentration of PH_3 at each location of the tested warehouse on the 7th day, 14th day and 21st day were 198 (136 − 266), 132 (86 − 170) and 86 (58 − 115) mL/m^3 respectively, the ratio of Min. concentration and Max. concentration of each gas sampling point was 1∶2. The distribution of PH_3 concentration at each location in the warehouse was uniform and four kinds of tested pests of full-stages (adult, egg, larvae and pupa) pre-buried in grain piles before test were killed completely; the pest control was 100%. The dosage applied to the control warehouse was three times as much as that of the recirculation fumigation under film with mixed gas of $PH_3 - CO_2$; on the 7th day and 14th day after fumigation, the tested gas concentrations of PH_3 at the same location and same depth were 173 (45 − 251) and 101 (26 − 156) mL/m^3 respectively; the ratio of Min. concentration and Max. concentration was more than 1∶5, and the distribution of PH_3 concentration was not very uniform; degas 14 days after end of fumigation and there was no live adult found after sampling and checking, the death ratio of adults being 100%. But after three weeks, live adults were found again in parts of the warehouse, and the density was 7 adults/kg, in which there were two *Rhizopertha dominica* (Fabricius) and five *Cryptolestes ferrugineus* (Stephens); the pest control was worse. Therefore, pest killing technology of recirculation fumigation under film with mixed gas of $PH_3 - CO_2$ not only improves air-tightness and uniformity of fumigation, reducing dosage and improving efficacy, but also saves time and work. It is an easy and safe operation.

Key words: high and flat warehouse, stored − grain pests, hydrogen phosphide, carbon dioxide, recirculation fumigation

Introduction

Our country has invested and built new warehouses with capacity of 50 billion kg in three batches since 1998. The new warehouse has the characteristics of big span, large volume and more loaded grain but it is not very ideal in some aspects such as air-tightness and pest killing by fumigation. There are a good many problems in fumigation:

(1) The duration of effective concentration of PH_3 is short.

(2) Pests can not be killed completely and resistance of pests to fumigant is increased.

At present, our country is using normal pest prevention and control with aluminum phosphide fumigation, whose use ratio is around 80%; because of long-term and illegitimate use of aluminum phosphide, the resistance for PH_3 of stored-grain pests has increased, and the ma-

1. *China Grain Reserves Corporation Beijing Branch*, *Beijing* 100045
2. *State Grain Reserves Sanhe Depot*, *Hebei* 065206
3. *Academy of State Administration of Grain*, *Beijing* 100037

jor reason is the blind increasing or decreasing of dosage of aluminum phosphide during use and ignorance of air-tightness of warehouse and duration of effective concentration of PH_3. After repeated failed fumigations, the pests can not be killed completely, even the resistance of pests increased. Therefore, normal pest prevention and control of aluminum phosphide fumigation can not be applied to the new high and flat warehouse any more. If the pest control can not be resolved in time, it will result in considerable reproduction, spread of stored-grain pests and heat-releasing, mildewing of stored grain, and will influence safety of stored grain directly. Therefore, in order to ensure safety of stored grain, increase technical level of storage, improve and research use method of PH_3 and prolong its service life, the systematic and practical pest killing application experiment should be performed. This research performed the experiment for the application effect of mixed gas of $PH_3 - CO_2$ in steel cylinder in a high and flat warehouse and performed the comparison with normal PH_3 fumigation in a high and flat warehouse to provide control for effective application of PH_3 in high and flat warehouse.

1 Materials and Methods

1.1 Materials

1.1.1 Base situations of the tested warehouse and the control warehouse

We used No. 19 warehouse as the tested warehouse and used No. 23 warehouse as the control warehouse. No. 19 warehouse and No. 23 warehouse were all high and flat warehouses which were brick and concrete structure, and whose roofs were aerated concrete slabs, frames were steel frames and floors were concrete, east to west; the lengths were 54.36m, widths were 35.26m, loading heights were 6m, eaves heights were 9.8m, top heights were 11.6m. There were two gates and two wickets of upper warehouse equipped on the north and south separately; and there were two mobile PH_3 recirculation fumigation systems equipped on the north and south separately; the ventilation systems were cages on the gourd, one machine one passage, and there were 10 passages on the north and south separately, total 20 passages. Their geographic positions, trends of warehouses and construction materials were the same. The volume, kinds, quantities and stacking forms of stored grain were same basically. (Table 1)

Table 1. Stored grain status of the tested and control warehouse

No. of warehouse	kinds	Quantity (kg)	Grain storage volume (m^3)	Stacking form
19	wheat	7650	9563	Bulk
23	wheat	7530	9256	Bulk

1.1.2 Test – insects

The test-insects were *Cryptolestes ferrugineus* (Stephens), *Sitophilus oryzae* (Linnaeus) and *Oryzaephilus surinamensis* (Linnaeus) provided by Academy of State Administration of Grain.

1.1.3 Mixed gas of $PH_3 + CO_2$ in steel cylinder

Developed and produced by Hangzhou Tongyi Gas Research Institute. 25kg of mixed gas of $PH_3 + CO_2$ in each steel cylinder. The ratio of gas concentration was PH_3 2% + CO_2 98% (w/w).

1.1.4 Equipments and Devices

Pipelines of recirculation fumigation under film for grain surface in No. 19 tested warehouse were designed and provided by Henan Weilai Machine and Electric Project Co., Ltd. The layout of pipelines is shown in figure 1. Related equipments used in the experiment are shown in table 2.

Table 2. Equipments used in the experiment and the manufacturers

Name	Manufacturer
Pipelines of recirculation fumigation under film for grain surface	Henan Weilai Machine and Electric Project Co., Ltd.
Pipelines of recirculation fumigation	
Application cars and recirculation machines special for steel cylinders	Beijing Zhonggu Grain and Oil S&T Research Institute
Measuring device of PH_3 concentration	Drager, Germany

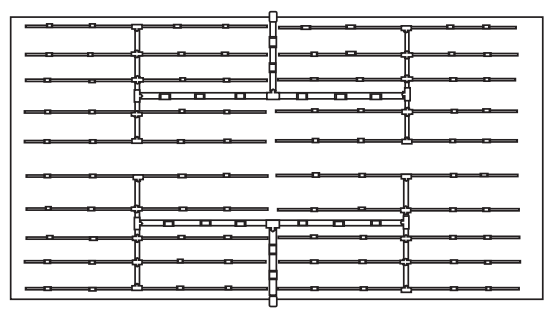

Fig. 1 Layout of pipelines of recirculation fumigation under film for grain surface in No. 19 tested warehouse

CQMY air – tightness determination device consists of car body, ventilator, U – type pressure gauge, butterfly valves, seconds-counter, connection soft tubes, connection flanges and etc., produced by Henan Weilai Machine and Electric Project Co., Ltd. The main parameters are shown in table 3.

Table 3. main parameters of CQMY air – tightness determination device

Item	Type of blower	Wind pressure (pa)	Air volume (m^3/h)	Diameter of wind pipe (mm)
Parameter	4 – 72 – 123kw	989 – 1578	2664 – 5268	200

1.2 Method

1.2.1 Culture of full – stages test – insects

\Put test – insects into 250g of related feed separately and cultured them under the conditions of 28 ± 1℃ and 70% ± 5% RH for 42 days, then put the test – insects and feed into cages for use.

1.2.2 Locating of pre-buried cages and PH_3 test points

Placed the sampling points for measuring of PH_3 concentration as quincunx, i. e. set one point at each corner (four corners) and one center point, which are 0.5m far from surface of grain mass. Gas sampling tube connected the outside of the warehouse to measure the concentration of PH_3.

There were five cages pre-buried in the warehouse, and their locations corresponded with that of test points of gas concentration, i. e. 0.5m far from surface of grain pile.

1.2.3 Sealing of the warehouse

No. 19 warehouse: installed recirculation pipelines at 30cm under the surface of grain, and performed plastic film sealing of grain surface after locating of cages and test points was finished. Both sides of warehouse body were sealed with PVC plastic film and the recirculation pipelines under the warehouse were sealed with adhesive tape.

No. 23 warehouse: performed film sealing of pipe chases of windows and doors.

1.2.4 Determination of air-tightness of warehouse

No. 19 warehouse: used CQMY determination device and U-type pressure gauge, performed air-tightness determination of negative-pressure half-life by suction type. Opened blower to run for about 60 min., then closed the butterfly valve and measured the static pressure of gas in the warehouse with U-type pressure gauge, repeated these processes for three times and used the average value as the result of air-tightness determination.

No. 23 warehouse: used L4 – 72 – 11 No. 4.5A centrifugal blower produced by Shijiazhuang Blower Factory, whose power was 7.5 kw; performed air-tightness determination of positive-pressure half-life by press-in type. Opened blower to run for about 30 min., then measured the static pressure of gas in the warehouse with U-type pressure gauge which was connected with gas sampling tube of fumigation. Repeated these processes for three times and used the average value as the result of air-tightness determination.

1.2.5 Application and recirculation outside of the warehouse

No. 19 warehouse: charged the mixed gas of $PH_3 + CO_2$ into application car special for gas in steel cylinder, and connected to application mouth of recirculation blower with high-pressure soft tube (pressure > 10kg); opened the recirculation blower at first, then opened on-off valve on the steel cylinder to apply. Applied at both sides of warehouse for 15 minutes each bottle. During application, opened the recirculation blower at both sides of warehouse to recirculate under the film for continuous 24h, and then turned off the recirculation blower.

No. 23 warehouse: used normal whole-warehouse fumigation, and application methods were grain surface and pipe outlet medicament tray methods, each tray applied 150g. Total dosage of aluminum phosphide was 46kg. Tested the concentration 24 hours after apply and tested once a day.

1.2.6 Measuring of PH_3 concentration

During the first week of fumigation, measure the PH_3 concentration of each point every four hours and every 24 hours after the week.

1.2.7 Checking of death of pests

Degas 21 days after application and fumigation, then take the pre-buried cages out and separate the adults out, put the adults and 10g of feed into insect culture room to culture (temperature: 28 ± 1℃, relative humidity: 70% ± 5% RH), check the death status of adults in each point after 14 days and record the data.

The remaining wheat feed after separation of adults was put into other culture bottles, 15g of fresh feed was added into each bottle and bottles were cultured for 42 days under the same conditions, then checked if there are adults appeared.

2 Results and Analysis

2.1 Result of Air-tightness Determin Ation in the Warehouse

Air-tightness determination results of No. 19 tested warehouse and No. 23 control warehouse are shown in table 3. For the tested warehouse, used film sealing of grain surface and used CQMY air-tightness determination device to perform negative pressure determination. Although we took some measures, the air-tightness was not very good, and the negative pressure only could reach −30Pa and pressure half-life was only 4s. For the control warehouse without film sealing and determined air-tightness by positive pressure method, and increasing of pressure was very small when determined with CQMY air-tightness determination device. The other fun with L4 −72 −11 (7.5kW) used for determination, and the pressure only could reach 350Pa and the half-life was 20s. From above, we can get that the air-tightness of these two warehouses are not good for fumigation. Overall improvements of warehouse should be performed to improve the air-tightness.

2.2 Changes of PH_3 concentration

The average, Min. and Max. concentrations of PH_3 measured at each location in warehouse on 7th day, 14th day and 21st day after fumigation of the tested warehouse were 198 (136 −266), 132 (86 −170) and 86 (58 −115) mL/m^3 separately, and the ratio of the Min. concentration and Max. concentrations of each sampling point was basically the same at each position which was 1∶2; the distribution of PH_3 concentration was relatively uniform. In the control warehouse, the average, Min. and Max. concentrations of PH_3 measured at each location in warehouse on 7th day and 14th day after fumigation were 151 (79 −202) and 31 (10 −72) mL/m^3 respectively, and the ratios of Min. concentration and Max. concentrations were 1∶2.6 and 1∶7.2; the uniformity of PH_3 concentration of each sampling point in the warehouse was worse than that in the tested warehouse.

Table 4. determination status of air −tightness in the tested warehouse

No. of warehouse	Pressure measuring method	Timing pressure (Pa)	Pressure half −life (s)			
			1	2	3	Average
19	Negative pressure	−30	4	5	4	4
23	Positive pressure	350	21	20	18	20

From the average concentration of PH_3 measured every day, the PH_3 concentration in the tested warehouse under the test on recirculation fumigation under film with mixed gas of PH_3 − CO_2 in steel cylinder is always higher than that of the control warehouse which uses normal fumigation, and from the 6th day after fumigation, the PH_3 concentration in the control warehouse reduced rapidly; see figure 2 and table 5. After 14 days, the concentration reduced to 31 mL/m^3. Degas and stop fumigation. But in the tested warehouse, the decreasing trend of PH_3 concentration become slow and the PH_3 concentration is still at 86 mL/m^3 after 21 days. It shows that the air-tightness of the warehouse after film sealing of grain surface is clearly improved.

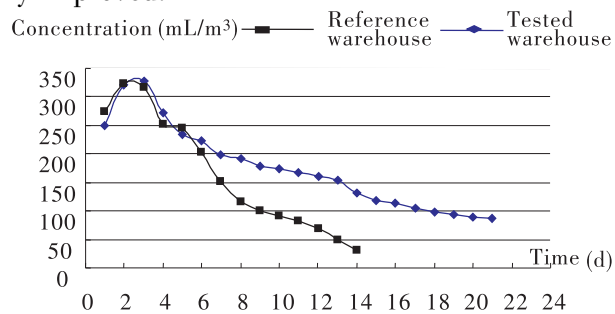

Fig. 2 changes of PH_3 concentration in the tested and the control warehouse

2.3 Efficacy offumigation

For the tested warehouse, 21 days after treatment by recirculation fumigation under film with mixed gas of PH_3 + CO_2 in steel cylinder, various pests in each pre-buried cages in the warehouse were killed completely. 30 days after culture (25℃ and 65% RH) of pests and feed in each cages, there was still no live pest found; pest mortality was 100%. At the same time, there was no live pest found when samples from the grain warehouse were checked.

Pest status before fumigation in the control warehouse; in field inspection, the density was 30 pests/kg, in which there were eight *Sitophilus zeamais* Motschulsky, thirteen *Rhizopertha dominica* (Fabricius) and nine *Cryptolestes ferrugineus* (Stephens) (no test-insect cage placed) founded on grain piles of which the surface was above 1.5m. Degas 14 days after sealing, checked the fumigation effect, there was no live adult found in checking, and the estimated death ratio of adults was 100%. But after three weeks, the live adults were found again in parts of the warehouse, and the density was 7 adults/kg, in which there were two *Rhi-*

zopertha dominica (Fabricius) and five *Cryptolestes ferrugineus*. (Stephens). It shows that the efficacy of fumigation is not good. The major factors are non-uniform distribution of PH_3, poor air-tightness, relatively low gas concentration short treatment period and rapid loss of concentration in the control warehouse which uses normal fumigation.

Table 5. the average, Min. and Max. concentrations (mL/m^3) of PH_3 in two warehouses

days (d)	No. 19 warehouse	No. 23 warehouse
1	249 (166 – 346)	274 (324 – 151)
2	320 (250 – 500)	324 (382 – 266)
3	327 (255 – 430)	317 (331 – 288)
4	272 (202 – 318)	252 (281 – 202)
5	233 (192 – 297)	245 (281 – 202)
6	224 (183 – 290)	202 (238 – 166)
7	198 (136 – 266)	151 (202 – 79)
8	191 (141 – 248)	115 (180 – 36)
9	178 (140 – 220)	101 (137 – 58)
10	175 (124 – 214)	92 (115 – 43)
11	167 (116 – 204)	83 (94 – 36)
12	160 (110 – 196)	68 (72 – 22)
13	153 (98 – 196)	50 (78 – 25)
14	132 (86 – 170)	31 (72 – 10)
15	119 (73 – 161)	
16	114 (71 – 153)	
17	105 (68 – 142)	
18	97 (65 – 133)	
19	94 (64 – 125)	
20	89 (63 – 121)	
21	86 (58 – 115)	

3 Discussion

Under the condition of not good air-tightness in high and flat warehouse, and under the basically same warehouse and grain storage conditions, we had used two different methods of recirculation fumigation under film with mixed gas of $PH_3 + CO_2$ in steel cylinder and PH_3 normal fumigation to perform practical application comparison experiment. In the experiment, the PH_3 concentration in the warehouse measured by recirculation fumigation under film with mixed gas of $PH_3 + CO_2$ in steel cylinder is effective for the storage pests, which shows that the major reasons for improving pest killing effect may be improving the air-tightness and the synergism of CO_2 for PH_3 fumigation. This experiment proves that: use recirculation fumigation under film with mixed gas of $PH_3 + CO_2$, reticulate for 5 hours in high and flat warehouse; the distribution of PH_3 concentration in each location of the warehouse is uniform and the ratio of Min. to Max. concentration of each sampling point is 1∶2. The average, Min. and Max. concentrations of PH_3 of each location measured on 7^{th} day, 14^{th} day and 21^{st} day are 198 (136 – 266), 132 (86 – 170) and 86 (58 – 115) mL/m^3 separately. Four kinds of full – stages (i. e. adult, egg, larvae and pupa) pests preburied in grain piles before experiment were killed completely. If the PH_3 normal fumigation method is used, the uniformity of distribution of PH_3 concentration in the warehouse is worse and the ratio of the Min. to Max. concentration is 1∶7. The dosage in normal fumigation is three times more than that of recirculation fumigation under film with mixed gas of $PH_3 - CO_2$ and also the air-tightness of the warehouse is worse; the PH_3 concentrations measured at the same location and same depth on 7^{th} day and 14^{th} day after fumigation were 173 (45 – 251) and 101 (26 – 156) mL/m^3 separately; although the adults in grain piles have been killed completely, but the larvae and pupa may have not been killed completely, and there were adults found again after three weeks. It shows that the pest killing effect is worse. If one used CO_2 (no PH_3 added) only to prevent and control stored-grain pests, the concentration of CO_2 should be determined by kinds of pests, stage of pest and fumigation duration in practical application; generally, the concentration of CO_2 required is 35%; but for some kinds of pests or the pests which are in the growth stage, the concentration of CO_2 should be increased to about 80% to improve mortality rate. If there is 8% oxygen gas, some stored-grain pests still can survive and reproduce. Therefore, using CO_2 alone to prevent and control stored – grain pests is valuable in special places and departments only under the capability which can be supported by recent economy level of our country.

The experiment proved that recirculation fumigation under film with mixed gas of $PH_3 - CO_2$ can be applied to pest killing by fumigation in high and flat warehouse; it not only can improve air-tightness and uniformity of fumiga-

tion, reduce dosage and improve pest killing effect of fumigation significantly, but also saves time and work, and is an easy and safe operation.

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