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Report on Tests of Aluminum Phosphide Fumigation through Different Application and Recirculation Methods

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Abstract: In order to control the resistance of stored grain pests to PH_3 in the high temperature and high humidity areas of our country, improve the pest killing effect of recirculation fumigation and reduce the cost of control, Wuzhou Grain Depot, State Grain Reserves has performed the tests of recirculation fumigation in the whole warehouse and recirculation fumigation under sheet through the application of aluminum phosphide on the surface of grain mass and the application of aluminum phosphide in the vent of ventilation duct for many times since 2000, these tests were performed in three horizontal warehouses separately of which lengths were 51.2m , the widths were 20.5m, the eaves height were 7.8m, and there were eight fumigation tests performed with different application dosages, different application ways, different air-tightness, different recirculation ways early or late.

This article reports summary and analysis according to the results of these tests; test results showed that when air-tightness of the warehouse was not changed, holding time of the PH_3 concentration and unit dosage showed a positive correlation, i. e. the less unit dosage, the shorter holding time of certain concentration. Fumigation efficacy was not good when PH_3 fumigation time was less than 28 days; the recirculation fumigation through intermittent application had certain advantage under the same air-tightness condition compared with recirculation fumigation through single application, and the control effect of the former was better obviously; the air-tightness half-life time of the No. 6 warehouse was increased from 60s to 98s and the unit dosage of the fumigation was reduced from 6g to 5g; for the recirculation fumigation through single application, the holding times of the concentrations above 300 mL/m^3 and 200mL/m^3 were prolonged obviously and reached 21 days and 40 days, respectively. No live pest was found two months after the fumigation, the interval between two fumigations was prolonged to more than 257 days and obtained better effect of control; performed the test of the recirculation fumigation through intermittent application which combined application on the surface of grain with the secondary application in door of ventilation duct on the floor in the No. 10 warehouse, holding times of the concentration above 300 mL/m^3 and 200mL/m^3 were 38 day and 48 days, respectively. The interval between two fumigations was prolonged to 317 days, the fumigation effect was better than that of the No. 6 warehouse; for the recirculation fumigation under film in the No. 18 warehouse, the air-tightness (-300Pa) half-life time was 135s, when we used intermittent application by combination with the secondary application in vent of ventilation duct, the holding time of the concentration could be longer and the fumigation effect would be better; therefore, this method has useful value in management of the resistance of stored grain pests to PH_3. This article also presented the requirement for the operation of recirculation fumigation through application in vent to ensure safety and effectiveness.

Key words: aluminum phosphide, stored grain pests, recirculation fumigation

1 Preface

Wuzhou Grain Depot, State Grain Reserves is located in the centre of high-temperature and high-humidity South China region. Because of the humidity weather of plum rain in March and April and strong rainfall formed by tropical storm from May to September every year, the above 28℃ annual daily mean temperature and humidity between 60% -95% can reach to 120 days. This weather and environment condition is most beneficial for the growth and reproduction of stored grain pests. The common stored grain pests are *Sitophilus zeamais Motschulsky*, *Rhizopertha dominica F*, *Gelechiid moth*, *Cryptolestes ferrugineus*, *Cryptolestes pusillus*, Psocoptera. [1] Grain department in Wuzhou area has performed pest killing with PH_3 fumigation since late 1960s. Since PH_3 has high pest killing toxicity and less residual, it is safe for human and animals. PH_3 exhaust gas degrades naturally, so it is safe for the environment. Therefore, aluminum phosphide is still the stored gain pesticide which is used extensively at present[2]. Since the relationship between "threshold concentration" and "fixed death time" , i. e. relationship of Ct value when performed pest killing by PH_3 fumigation and influences of some factors such

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as limitation of facility condition of warehouses, inappropriate application dosage and holding time of effective concentration have resulted in big resistance of stored grain pests. The phenomenon that pests are not killed happens frequently. Generally, two fumigations are needed in one year. Three fumigations are needed for individual warehouses. The results of investigations for resistance of stored grain pests in this region performed by national experts such as Yang Xiaoping show that resistance multiple of *R. dominica* F was 70.5 – 260.7[3] and the resistance multiple of *C. ferrugineus* was 110 [3]; the research performed by Bai Qingyun and Cao Yang showed that the resistance multiple reached 165[4]. These kinds of stored grain pests belong to the high resistance and very high resistance series. Liu Chunhua reported test results of PH_3 fumigation for *C. ferrugineus*; the normal application dosage was 6.0g/m^3; 27 days after application with the concentration above 315 mL/m^3, the pests were not killed completely. [5] It showed that the PH_3 resistance of *C. ferrugineus* was very serious, and the improvement of fumigation technology and development of comprehensive controlling for resistance of stored grain pests were necessary.

The newly-built horizontal warehouse of Wuzhou Grain Depot, built in 1998, was put into use in March 2000. Outside-storage fixed recirculation fumigation equipment have been installed for each warehouse. From May 2000, in order to improve the effect of PH_3 fumigation, we have performed tests of recirculation fumigation in the whole warehouse and recirculation fumigation under film through the application of aluminum phosphide on the surface of grain and the application of aluminum phosphide in ventilation ducts many times to reduce dosage, fumigation cost, relieve labor intensity of chemical prevention personnel and improve fumigation efficacy.

2 Materials and Methods

2.1 Materials and Equipments

2.1.1 Tested warehouse

No. 6, No. 10 and No. 18 horizontal bulk storage warehouses of Wuzhou Grain Depot were selectedas test warehouses. Their structure and specifications were the same, with length 51.2m, width 20.5m, eaves height 7.8m and volume 8 186.9m^3. Tested field air-tightness of warehouses by positive pressure method: half-life pressure reducing from 300Pa to 150Pa. No. 6 warehouse was 60s before 2004 and increased to 98s after sealing improvement. No. 10 warehouse was 110s. Tested No. 18 warehouse with grain surface sealed by film by negative pressure, half-life was 135s.

2.1.2 Base situations of the stored grain in the tested warehouse

See Table 1 for test serial number, type of fumigation test, No. of tested warehouse, base situations of the stored grain in the warehouse.

2.1.3 Fumigant

56% (1.0kg/bottle) aluminum phosphide tablets produced in Jining, Shandong.

2.1.4 Equipments

Fixed recirculation blower produced by Shenzhen Dashi Co., Ltd.; power: 350W; air volume: 600m^3/h; static air pressure: 900Pa; tip speed of blade: 37m/s.

NHL(HL – 210) PH_3 concentration tester produced in Beijing;

HL – 200 PH_3 alarm system produced in Beijing.

DS – 97 computer detection control system for stored grain produced in Zhuzhou, Henan.

2.1.5 Ventilation/aeration ducts on the floor

There were three sets of one-sided reducing ventilation ducts for each warehouse, two of three ducts for one aeration blower and one of four ducts for a second aeration blower. There were nine air distributors for each duct, which are half-round, full perforated and shingle shaped to overlap. Size of outer joint of: 640mm 560mm; size of inner joint of each duct: 500mm 510mm; volume of: for three ducts for one aeration blower, about 9.5m^3; four ducts for second blower, about 13.0m^3.

2.1.6 Status of pests in the tested grain piles

The pests in the tested warehouses were the common insects existing in field warehouses. The sampling points were set at four corners of each warehouse and its centre of longitudinal central axis(two points), totally 6 sampling points. Performed sampling at 300mm below the surface of grain when testing, used the depth where density was maximal as the representative value. See Table 2 for the kinds and densities of pests before fumigation test in each tested warehouse.

2.1.7 Other tested materials

0.14mm and 0.08mm polyvinyl chloride film, plastic slot (outer width: 14mm, notch: 6mm, inner diameter of slot: 10mm), plastic

dish, cotton flour bag, woven bag, pest screen.

2.2 Method

2.2.1 Sealing and air-tightness improvement of the warehouse

Installed plastic slots on all gates, entry doors, grain inspection doors, and windows, and sealed them with 0.08mm polyvinyl chloride film. In order to improve the air – tightness of the warehouse, we have performed continued improvement on all warehouses in the whole depot.

Improvement process of the air – tightness for the No. 6 warehouse: At beginning of 2004, changed the glass windows with steel wood frame into double – faced colorful steel sandwich air tight windows, after improvement, there were rubber seal rings added all around the windows and doors. At the beginning of 2006, after the improvement of the vent of ventilation duct, the fixing of cover board by twenty screws (Φ12mm) was changed into fixing of leaf rotating type by four screws (Φ12mm), and it made the application in vent more convenient and changed the cover board from straight board type (seal rings were asbestos bars) to impacted rotating door (seal rings were tube-type rubber bars); changed 90^0 butt joint of the corners of plastic slots in gate, grain inspection doors and windows into circular arc butt joint; performed sealing of joints between plastic slot and wall body and cracks of walls and roofs of the warehouse.

2.2.2 Recirculation under grain surface cover film sheeting

Used single – face sealing with 0.14mm polyvinyl chloride film in the No. 18 warehouse, and fixed and sealed with the plastic slots on the surface of grain, see Fig. 1 for the PVC piping diagram buried at 300mm under the surface of grain.

The diameter of the major solid transverse pipeline in the centre was Φ150mm and the diameters of eleven rows of perforated pipes were Φ120mm; the diameters of pipes at the sides of wall (left, right, upper and lower pipes-not showen in the figure) were Φ80mm.

2.2.3 Setting of the test points of PH_3 concentration

There were 6 PH_3 gas sampling test points in the whole warehouse: at four corners (spaced 1.5m away from wall) and centre of grain piles, totaling 5 points which were buried at 300mm – 500mm under the surface of grain; the 6^{th} sample tube was located midpoint above grain surface in the warehouse to sample the headspace gas concentration.

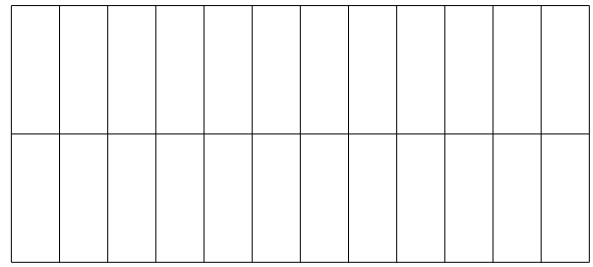

Fig. 1 Diagram of PVC piping pre – buried 300mm under the warehouse grain surface

2.2.4 Fumigation and application method for each tested warehouse

See Table 3 for application dosage and method of aluminum phosphide in each test.

2.2.5 Operation of recirculation blower during the test

See Table 4 for the opening status of recirculation blower in each test.

3 Result and Analysis

3.1 Control Effect of the Application Technology Improvement in the No. 6 Warehouse

See Table 5 and Table 6 for the test result of PH_3 concentration and control effect in each test. Since the air – tightness of the warehouse was not very good, the holding times of PH_3 concentration in the warehouse were different. In the same No. 6 warehouse, in the first normal fumigation test (serial number: A), the unit dosage reached $9g/m^3$, the holding time of the concentration above 300 mL/m^3 was 21 days; in the second and third tests (serial number: B and C), performed with recirculation, the methods for fumigant dosage application on grain surface and application in vent separately, the unit dosages were reduced to 6 and 3 (g/m^3) and the holding times of the concentration above 300 mL/m^3 were reduced to 15 and 5 days, the holding times of the concentration above 300 mL/m^3 were 28 and 20 days separately. The control effects were not very ideal after the three fumigations, where live pests were found the first week after degassing in the third test (serial number: C). This showed that when the air – tightness of the warehouse was not changed, the holding time of the PH_3 concentration and the unit dosage showed the positive correlation, i.e. the less unit dosage, the shorter holding time of certain concentration; the fumigation effect was not good when the PH_3 fumigation time was

less than 28 days (Table 6).

In order to improve the fumigation effect, we improved the application method from single application to intermittent application in the No. 6 warehouse, i. e. total dosage was divided into two applications. Serial number D, Table 3- for the same 6 g/m^3, although the holding time of the concentration above 300 mL/m^3 was 5 days less, the holding time of the concentration above 200 mL/m^3 was 14 days longer than that of serial number B. The efficacy was good and no live pests were found 2 months after degassing. The interval between two fumigations was prolonged to 236 days. Therefore, the fifth fumigation test, serial number E, also used intermittent application and its control effect was also good (Table 6). The recirculation fumigation with intermittent application has certain advantages and the control effect is obvious. We suggest that basic grain warehouses extend and apply this technology, including our excellent sealing technology.

In order to improve the control effect further, we performed air – tightness improvement in the No. 6 warehouse; the air pressure half – life time of the warehouse increased from 60s to 98s. Good fumigation effect was achieved after recirculation fumigation through single dosage application on grain surface. The holding times of the concentrations above 300 and 200mL/m^3 were 21 and 40 days separately (Table 5). No live pests were found 2 months after degassing and the interval between two fumigations was over 257 days (Table 6). The test results showed that improvement of air-tightness in the warehouse was the best way. We suggest that basic grain warehouses pay strict attention to detail and actively perform air-tightness improvement of horizontal warehouses, improving sealing and testing technologies of grain piles in the warehouses. Excellent sealing will provide twice the result with half the effort, with reduced dosages for major improvements of fumigation effect.

3.2.10 Control effect of the fumigation through intermittent application which combined application on the grain surface and a secondary application in vent.

In order to explore new application methods, we have performed recirculation fumigation through intermittent application combined with application on the grain surface and the secondary application in vent in the No. 10 warehouse. The 300Pa half-life of this warehouse was 110s which was better than that of the No. 6 warehouse. The test results showed that the holding times of the concentrations above 300 and 200mL/m^3 were 38 and 48 days separately (Table 5). No live pest was found within 2 months after degassing and the interval between two fumigations was prolonged to 317 days (Table 6). The fumigation efficacy was better than that of the No. 6 warehouse, test serial number G. The intermittent application combined with application on the grain surface and the secondary application in vent can improve the value of maximum pest killing concentration of PH_3 and prolong the time of the effective concentration further, realize outside-storage supplemental application, relieve labor intensity of operation personnel. The control effect is obvious, especially for the first fumigation of freshly stored grain. We, strongly suggest basic grain warehouses extend and apply this new technology.

3.3 Control Effect of Recirculation Fumigation under Film in the No. 18 Warehouse

In order to improve the air – tightness of grain piles further, we used film sealing technology on grain surface in the No. 18 warehouse. The test result of the air – tightness showed that the 300Pa half – life under the surface sealing PVC film was 135s. The test result showed that the holding times of the concentrations above 300 and 200mL/m^3 were 32 and 56 days separately (Table 5). No live pests were found within 2 months after degassing, the interval between two fumigations was prolonged to over 180 days, and secondary fumigation has not been required to the present. We see that using film sealing technology on grain surface can improve air-tightness of grain piles, fumigation efficacy is better. Higher efficacy has much value and important meaning in controlling resistance of stored grain pests to PH_3. We strongly suggest basic grain warehouses apply this new technology.

4 Discussion

In the high temperature and high humidity grain regions of China and other countries, when performing the first recirculation fumigation in the whole warehouse after fresh grain loading, we suggest using recirculation fumigation combined primary dosage application on the grain surface with the secondary dosage application in floor aeration ducts.

In the warehouse with less well sealed roof and upper sidewall conditions, we suggest that by using recirculation fumigation combined with film sealing technology on grain surface with the

secondary application in floor aeration ducts, the fumigation efficacy will be better.

When using application in floor aeration or ventilation ducts, start the recirculation blower immediately after dosage application. Do not stop the blower; test the PH_3 concentration in the warehouse every day, the recirculation blower should be not be stopped until the PH_3 concentration reaches the maximum concentration and begins to decrease. Carefully remove the residual phosphine dust from the aeration or ventilation floor ducts 24 hours after the recirculation blower has been stopped to ensure the operation is safe and effective.

Table 1. Base situation of warehouse and stored grain

Warehouse	Grain	Loadtime	Unload time	Quantity (t)	Pile Ht. (m)	Quality status
6	Latehsien Rice	2000.3	02.3	2430	3.6	Husked rice yield: 75.3%; Water Content: 12.8%; impurity: 0.8%
6	Late hsienRice	2002.5	05.2	3787	6.0	Husked rice yield: 75.7%; Water Content: 13.3%; impurity: 0.9%
6	Canadian Wheat	2006.1	In storage	4839	5.3	Volume: 808; water content: 12.8%; Impurity: 0.3%
10	Yellowcorn	2006.5	In storage	5011	6.0	Volume: 735; water content: 13.6%; Impurity: 0.8%
18	Yellowcorn	2007.4	In storage	4660	6.0	Volume: 712; water content: 13.8%; Impurity: 0.8%

Table 2. Kinds and densities of pests in each warehouse before fumigation test

Test No.	Warehouse	Kinds and densities of the pests in tested warehouse (kg)
A	6	Rhizopertha dominica F.: 3, Sitophilus zeamais Motschulsky: 6, Cryptolestesferrugineus: 23, Psocoptera: 63
B		Rhizopertha dominica F: 5, Sitophilus zeamais Motschulsky: 5, Cryptolestesferrugineus: 15, Psocoptera: 46
C		Rhizopertha dominica F.: 1, Sitophilus zeamais Motschulsky: 3, Cryptolestesferrugineus: 17, Psocoptera: 65
D		Rhizopertha dominica F: 1, Sitophilus zeamais Motschulsky: 1, Cryptolestesferrugineus: 28, Psocoptera: 53
E		Gelechiid moth: 2 Sitophilus zeamais Motschulsky: 2Cryptolestesferrugineus: 22, Psocoptera: 41
F		Sitophilus zeamais Motschulsky: 2 Indian grain moth: 2Cryptolestesferrugineus: 15, Psocoptera: 27
G	10	Gelechiid moth: 1 Sitophilus zeamais Motschulsky: 2Cryptolestesferrugineus: 12, Psocoptera: 62
H	18	Sitophilus zeamais Motschulsky: 2 Indian grain moth: 2Cryptolestesferrugineus: 18, Psocoptera: 49

Table 3. Application dosage and application way of aluminum phosphide in each test

Serial No.	Ware house	Applic. time (y/m/d)	Dosage (g/m^3)	Application method
A	6	2000.4.28	9.0	Application on grain surface: grain surface cloth application dish, 0.5kg/dish. Applied 1.0kg/vent, Applied 1.0kg inside film of earch warehouse door
B	6	2002.6.5	6.0	Application on grain surface: grain surface cloth application dish, 0.5kg/dish

Serial No.	Ware house	Applic. time (y/m/d)	Dosage (g/m^3)	Application method
C	6	2003.6.10	3.0	Application in vent, 8.0kg/vent, total 24kg. loaded dosage in cotton flour bags, 4.0 kg/bag, after application into vent, spread out flat with club, opened bag, closed vent door.
D	6	2003.10.10 2003.11.18	3.0 3.0	Applied dosage into vent twice: each dosage was same, .8.0kg/vent, total 24kg. loaded dosage in old woven bags 4.0kg/bag, after application into vent, spread out flat with club, opened bag and closed vent door.
E	6	2006.6.25 2006.7.19	3.0 3.0	Same as D。
F	10	2006.7.11 2006.8.6	4.0 3.0	Application on grain surface which was same as B. Secondary application and supplemental application into the vent was same as D. tested air – tightness, half – life = 110s
G	6	2007.2.28	5.0	Application on grain surface which was same as B. tested air – tightness; half – life = 98s
H	18	2007.7.24 2007.8.13	3.0 3.0	Applied dosage into vent at twice – same as D. tested air – tightness; half – life = 135s. performed recirculation fumigation under film.

Note: performed secondary application when PH_3 concentration reduced to $200mL/m^3$

Table 4. Operation status of recirculation blower during fumigation in warehouse

SerialNo.	Warehouse	Airtight time of fumigation(d)	Operation status of recirculation blower during test	Time of start-up(h)
A	6	22	Recirculation blower was not started – performed normal fumigation	0
B	6	37	Started recirculation blower 72 hours after application for 3 hours/day.	36
C	6	32	Started blower immediately after dosage finished – 24 hours continuously, stopped blower when PH_3 concentration started dropping	290
D	6	67	Started up after secondary application which was same as C	1st :241 2nd :332
E	6	56	Same as D	1st:243 2nd:403
F	10	55	The first application was same as B; the secondary application was same as C	1st:33 2nd:368
G	6	49	Same as B	42
H	18	74	Same as D	1st:432 2nd:384

Table 5. Test result of the PH_3 concentration in the tested warehouse

Serial No.	Warehouse	Dosage (g/m^3)	Max. gas level (mL/m^3)	Holding time of concentration(d)		oncentration when degassing (mL/m^3)	Test method
				Above 300 mL/m^3	Above200 mL/m^3		
A	6	9.0	>1000	21		421	Began at the second day after the application, tested once every day
B	6	6.0	>1000	15	28	100	
C	6	3.0	378	5	20	100	
D	6	6.0	365	10	42	100	
E	6	6.0	540	17	50	100	
F	10	7.0	835	38	48	100	
G	6	5.0	>1000	21	40	100	
H	18	6.0	558	32	56	100	

Table 6. Control effect of each test in the tested warehouse

SerialNo.	Warehouse	Efficacy	Inspection within 2 months after degassing (once every week)	Re – fumigation time after test	Interval between two fumigations
A	6	Mortality 100%	Live pests found at test points from 6th week: R. dominica F: 1; C. ferrugineus: 2; Psocoptera: 5	2000.8.24	96d
B			Live pests found at test points from 8th week: C. ferrugineus: 3; Psocoptera: 5	2002.9.29	79d
C			Live pests found at test points from 1st week: C. ferrugineus: 4; Psocoptera: 3	2003.10.10	90d
D			No live pests in 2 months	2004.8.19	236d
E			No live pests in 2 months	2007.2.28	192d
F	10	Mortality 100%	No live pests in 2 months	2007.7.18	317d
G	6	Mortality 100%	No live pest was found within 2 months	No secondary fumigation	Over 257d
H	18	Mortality 100%	No live pest was found within 2 months	No secondary fumigation	Over 180 d

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