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Advancement of Fumigation Technologies on Grain Storage in China

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Abstract: The application technologies of fumigants including choropicrin, methyl Bromide, dichloros, phosphine etc. and research progresses of fumigants such as sulfuryl fluoride, ethyl formate etc. in Chinese grain storage industries are discussed in this paper, with focus on the effective concentration of phosphine, fumigation technologies, application devices and so on. Accumulation of experience for application technologies has played an important role in controlling stored grain insect pests in China.

Key words: fumigants, stored grain insect pests, pest control

As most fumigants possess many advantages, including good diffusibility, permeability, easy gasification, effectiveness for controlling pests, low harmful residuals, low-cost, easy transportation, storage and management, and simple operation they have been regarded as the principal chemicals for controlling pests in grain storage and taken into applications and developments wildly in China. As early as the 11^{th} century BC during the Western Zhou Dynasty, botanical insecticide fumigants have been applied for controlling pests in grain in China. Before the Peoples Republic of China was founded, few fumigants for grain storage had been used in China. Most of them were still in the process of experimentation. Since the 1950s, fumigants such as Choropicrin, Bisulfide Carbon, Methyl Bromide, Aluminum Phosphide, Calcium Phosphide, Cyanhydric Acid, Dichloroethane and Dichloros have been put into production and practice one after the other [1]. Actually, the industry of fumigant production has made rapid progress. Compared with the few dozen fumigant applications in the 1950s, three thousand fumigants are in practice for grain storage at present. Through technology research on fumigants for grain storage, such as fumigation technology utilizing phosphine, anthelminthic and synergism mechanisms, anti-blasting mechanisms, protective measures, equipment for fumigation and so on, much significant progress has been made and lots of experiments for application technologies have been accumulated. Meanwhile, the technical specifications for grain and oil storage and the technical rules for recirculation fumigation with phosphine have been drafted. So many advantages have been created for the proper application of fumigants in China [2].

1 Application Technology Research on Choropicrin

According to GBZ2 – 2002, China's national occupational health standards, the maximum acceptable concentration for Choropicrin is 1 mg/m^3. However, the application dosage usually reached 15 g/m^3 – 20 g/m^3 during fumigation, with fumigation temperatures more successful above 20℃. If Choropicrin was used as a bactericidal agent, the application dosage could take between 20mg/L and 30mg/L. Because of high absorbability to finished products and high residual traces, Choropicrin should not be allowed in fumigation of finished products. In addition, since it has a negative influence on germination rates of some crops, fumigation of grain seeds should also not be allowed. Being uneasy during gas exchange, Choropicrin is not suitable for fumigation in underground granaries. Some experiments carried out with mixture fumigants in China, such as Choropicrin and Phosphine, Choropicrin, dichloroethane and Phosphine, have shown that such general pests as *Sitophilus zeamais*, *Tribolium castaneum* could be controlled completely by fumigation with mixture chemicals. The same results occurred with *Rhizopertha dominica* even though there was high pesticide resistance [3].

However, CCl_3NO_2, inorganic nitrite and nitramine could be produced from chemical reactions in foods, which may have a carcinogenic effect. Because of many disadvantages, such as heavy workload for application, weak diffusibility, slow gas exchange and so on, Choropicrin is in few application at present and will begin to phase-out.

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2 Application Research and Phase-out on Methyl Bromide

Methyl Bromide (MB), one excellent fumigant, has many advantages such as: stable chemical characters, low boiling point, high vapor pressure, well diffusibility, little absorbability for grain, and ease in scattering poisonous gas after fumigation. Besides the above, MB could be used for fumigation at low temperature (beyond 6℃), and does not burn or explode at general concentrations. Gasiform MB does not leave negative effects on such materials as metal, cotton, gloria products, and wood and so on. Since the 1950s, MB had been used to control pests in agriculture, such as sterilizing in soil, plants and their products, and use in quarantine of plant products during international trade. It also has been a fumigant to control pests for all kinds of buildings such as: ancient buildings, granaries, cabins, vehicles, aircraft, and food processing plants and so on. Except some beans with high protein content, MB can be used in fumigation for all kinds of grains, finished products, oils and potato and so on. Generally, every cubic meter of grain needs 30 grams, and space needs 15 – 20 grams for 2 – 7 day fumigation. In 1999, an experiment on fumigation with a mixture of Phosphine and MB for grain storage was made by LanFang Jian. It showed that mixture fumigation could reach the same results in controlling pests as MB alone, but cost lower than MB fumigation alone [4]. In 2000, by fumigating grain bulks in carbin with a mixture of Phosphine and MB, KaiXiang Wang et al did indeed control pests to excellent effect [5].

However due to destruction of the ozone layer in the atmospheric stratosphere, and an overall negative effect on living conditions for all mankind on Earth, MB has been labeled an ozone layer deleting substance and is restricted or banned for application by United Nations Environment Program. The Chinese government has approved *the Copenhagen amendment* of *the Montreal Protocol*. According to the agreement, the consumption of MB should be decreased to 80% of the average consumption during the period of 1995 – 1998 in China before the year 2005. By 2015, MB should be phased-out completely except for use in fumigation for quarantine.

With the help of international assistance funds, provided by Multilateral Funds executive committee of *the Montreal Protocol* in July, 2004, the international assistant projects for the MB phase-out was launched officially in Chinese grain storage industries. By the current situation of application with MB in Chinese grain storage industries and granaries' conditions, the practice proposal for MB phase-out has been drafted, and alternative technologies for MB have been identified. The total goal of the proposal was that the consumption of MB would fall off by 50% in 2005 compared to 2003. That is: the amount of consumption would decrease to below 105 tons. Then, MB would fall off to 80% in 2006 of the consumption in 2003, or the amount of about 42 tons. From Dec 31st, 2006, MB was not allowed as a fumigant by any grain depots in Chinese grain storage industries. Until Jan, 2007, MB should be prohibited completely in Chinese grain storage industries, in order to make proper contribution for carrying out the amendment of *the Montreal Protocol* completely in China [6,7].

3 Dichloros and Its Application Research

With strong contact and stomach toxicity effects, good fumigation and to some extent lure effects, Dichloros (DDVP) was one kind of significant pesticide used in the control of grain storage pests in China. The daily allowed intake for mankind was between zero and 0.004 milligrams by the Food and Agriculture Organization and World Health Organization (1967). Because of weak diffusibility and easy adsorption to grain, DDVP has always made some application for fumigation on the surface of grain bulks, empty granary, procession plants, equipment for package, matting materials and so on. Reference data is as follows: a full storage granary could be fumigated with 80% emulsifiable DDVP at concentrations of 0.3 g/m^3 – 0.4 g/m^3, and an empty granary and devices at concentrations of 0.2 g/m^3 – 0.3 g/m^3. A seal should be kept for 2 – 5 days following application with DDVP, and *Sitophilus zeamais*, *Tribolium castaneum*, *Rhizopertha dominica*, all kinds of moth adults or larva and other grain storage pests can be controlled.

Much research on fumigation has laid a stable foundation for pest control in empty storage and grain bulk surfaces with DDVP. In 1964, the Grain Research and Scientific Institute in the GuangDong Province carried on research on pest control with DDVP in empty granaries [8]. In 1965, research on DDVP having a toxic influence on *Sitophilus zeamais*, *Oryzaephilus surinamensis* and *Tribolium castaneum* was carried out by the Research and Design Institute of the grain ministry [9]. In 1966, DDVP was applied to control pests on the surface of grain bulks at the dosage of 0.2 mL/m^3 –0.3 mL/m^3 by the Grain Research and Scientific Institute in ShangHai City [10]. In 1966, the Grain Research and Scientific Institute in ZheJiang Province carried out research on controlling grain storage pests with DDVP by different application methods. It is also worth mentioning that operating staff must be put on canister respirators and armors during the fumigation of the indoors and greenhouse, which should be available to filter poisonous gas.

4 Research on Phosphine Application Technology

It has been over 40 years since self – development, production and application of Phosphine in China occurred in 1965. Lots of researches on fumigation with Phosphine have been conducted, including effective concentration, pharmacodynamic impact factor, and fumigation technologies and devices for application. Their application and promotion has played a significant role on pest control in Chinese grain storage industries.

4.1 Research on Effective Concentration of Phosphine

During the early period of fumigation with phosphine in China, the dosage of Aluminum Phosphide was used to guide practice. Dosage of each unit or volume of grain and total fumigant consumption was considered alone during fumigation. Generally, 6 g/m^3 – 9 g/m^3 of fumigants were put into practice in full storage. However, many series of problems depended on experience and sensation to practice, such as whether the effective concentration could be reached in the granary or grain bulks after fumigation or not How much time does it take to reach the effective pesticide concentration Is the concentration too high, leading to and increase in pests with protective stupefaction or not Are there fumigation corners and partial districts of low concentration or not Will the effective concentration keep for enough time or not Without inspecting concentration, fumigation could not always get the results desired, and grain storage pests easily developed resistance to Phosphine increasingly. According to LS/T1201 – 2002, the rules on recirculation fumigation with Phosphine issued in 2002, the concentration of Phosphine and anthelminthic effects should be brought forward clearly to guide practice. By different pest rates and temperatures of grain, it was recommended that fumigation with a concentration of 100 mL/m^3 – 350 mL/m^3 over 14 – 28 days was necessary. However, to control some pests with high pesticide resistance, such as *Cryptolestes ferrugineus*, 350 mL/m^3 – 500 mL/m^3 concentrations should be reached during fumigation to control pests completely. From recent applications, reference data has successfully guided fumigation practice in Chinese grain storage industries [1].

4.2 Research on Application Technology with Phosphine

To assure effective and homogeneous distribution of phosphine concentration during fumigation, lots of research on application technologies with phosphine have been made by grain storage staff in China, including such more practical and feasible technologies as slow-release, phosphine generators outdoors, mixture gas in cylinder outdoor applications and so on. Furthermore, by recirculation technologies, phosphine could be distributed quickly and homogeneously into large grain bulks to assure the effect of controlling pests.

To keep an effective concentration to control pests at each stage of sensitiveness, it was by way of intermittent fumigation that pests at a sensitive stage could be controlled ahead, while pests at other stages with strong resistance became sensitive, and all of them could then be killed. The experiment on control pests by way of intermittent fumigation was carried out by ChangJin Zhou et al., and it showed that chemical consumption decreased and labor intensity lightened. What was more important was that lethal rates reached 100%. The whole operation procedure was as follows: during the first application in large granaries, the effective concentration of phosphine should be kept for 6 – 10 days, followed by an interval period of 6 – 10 days, and last, after replenishing for 1 – 2 days, the time for sealing should reach over 21 days [12]. For controlling the speed of phosphine release, Aluminum Phosphide was put into the polyethylene film, which could separate phosphine from moisture, thus slow-releasing fumigation could control the reaction speed of Aluminum Phosphide decomposition and the releasing speed of phosphine. The experiment on slow – releasing fumigation in wheat bulks was carried on by XiangGang Wang et al., it showed that slow-releasing could achieve excellent effects, and mixtures of combinations conventional with slow-releasing fumigation could reach better effects on grain with a few beetles [13]. Application recirculation technologies could improve phosphine distribution homogeneously in large grain bulks, and so assure the effect of controlling pests. For outdoor fumigation, the difference between grain temperature and temperature at the outlet for mixture gas exchange was not over 5℃. What is most important is that the distance between grain bulks with the air outlet is close. It is also worth noting that if granaries have no better sealing performance, effective concentration for control pests in grain bulks could not be reached, so it would not only miss the purpose of controlling pests, but also could induce pesticide resistance of pests [14].

4.3 Application and promotion of Recirculation technology with phosphine

4.3.1 Research on recirculation technology with phosphine

Research and application of recirculation fumigation technologies with phosphine were carried out by LaiLin Zhang et al [15] in 1994, NaiQiang Sun [16] in 1995, Yifu Yu et al [17] in 1997, and Rong Zhang et al [18] in 1998 one after another. Meanwhile, such important devices for fumigation as outdoor phosphine generators, recirculation fumigation devices, sampling devices for phosphine indoors and phosphine inspectors have been researched and developed by research staff in China and implemented in industrialization production. These research results have widely laid down the foundation for promoting recirculation fumigation technologies with phosphine.

4.3.2 Application and promotion of recirculation fumigation technology with phosphine

As recirculation fumigation technologies have been promoted and applied in large warehouses and squat silos, built since 1998 [21~23], development of technologies for controlling grain pests have been promoted rapidly in China. During the actual application, these technologies have developed to such advanced levels as recirculation fumigation technologies with phosphine under film [24], recirculation fumigation technologies by dynamic and nature deliquescence [25], recirculation fumigation technologies by application of chemicals at combination grain surface with air outlet, partial recirculation fumigation technologies in grain bulks and so on [26]. Hundreds of papers on these fields have been published one after another, and rapid strides have been made in China in these fields.

4.4 Research on Combination Fumigation Technology with Phosphine

4.4.1 Fumigation technology by combination phosphine with carbon dioxide

The application of carbon dioxide has increased the phosphine diffusion binding and speed, decreased grain absorption consumption of phosphine and been in favor of its well – distribution. Furthermore, it could postpone the exposure time at maximum concentration than single fumigation. By stimulating the respiration of pests and increasing pesticide's consumption in pests, the lethal speed of pests has been raised [27,28]. It has been reported that by many experimental steps, such as 16% concentration of carbon dioxide for 24 hours, ventilation for 10 minutes, and then fumigation for 24 hours at 0.009 mg/m^3 of concentration, the mortality ratios of *Sitophilus granarius*, *Tribolium confusum* reached 88.3% and 98.0% respectively. When fumigating with a single kind of fumigant, both moralities of pests were below 44%.

4.4.2 After recirculation fumigation by combination phosphine with DDVP, some difficulties on controlling pests in large granaries could be settled excellently. It had an especially complete effect on *Cryptolestes ferrugineus*, booklouse and grain storage mites with certain resistance, and made the idea of fumigation at low concentration one time every year possible [30-32]. The process of mixture fumigation using a combination of phosphine with DDVP could overcome some disadvantages of fumigation with DDVP simply, such as slow diffusion and weak penetration abilities. Depending on recirculation fumigation by combination of phosphine with DDVP, application alcohol accelerating diffusion in large bulks had been taken by XinHua Lai et al; it was shown that there were excellent practice effects.

5 Fumigants in Development and Research

As pesticide resistance development and environment impact from chemicals is increasing, many kinds of pesticide have been prohibited. Most experts agree on the development of new, more effective fumigants for controlling pests by fumigants other than phosphine. However, not only is there great cost for promotion of a new kind of chemical into markets and limited resource of material, but also excellent fumigants with bioactivity are rather rare. There is no optimistic prospect to research and develop new fumigants.

5.1 Ethyl Formate(EtF)

EtF, one regularly practiced fumigant, has been used for the fumigation of dry fruit for the past many years. Many stored products produce natural EtF during storage, including many kinds of vegetables, fruits, corn and animal products. EtF degrades into formic acid and ethanol after fumigation, both substances existing naturally in many kinds of food, so it would not have a negative effect on grain qualities and germination after fumigation.

At ordinary temperatures, EtF decreases to original concentrations quickly, and has no residual effect. With Methyl Bromide phasing-out and phosphine resistance increasing recently, EtF, as one kind of environmentally-friendly fumigant, will arouse people's concern again.

PeiAn Tang et al, from Southwestern University, made systemic research on the lethal effect on such important grain storage pests as *Sitophilus oryzae* and *Tribolium castaneum* by fumigation with EtF at different temperatures, concentrations and fumigation times. It was shown that EtF had excellent immediate and lethal effect to both of these pests at their immature stages, and is better for the fumigation of the young larvae of *Sitophilus oryzae*. Pupa and egg both possess excellent resistance to pesticide. The best lethal effect of EtF against Tribolium castaneum was obtained in egg developmental period [35]. By fumigating wheat, maize, and paddy bulks at a concentration of $70g/m^3$ in simulation granaries, it was shown that the best effect was observed during fumigation of wheat bulks with EtF. The lethal rates of four such kinds of test pests, *Sitophilus oryae*, *Tribolium castaneum*, *Rhizopertha dominica* and Liposcelis were at 100%. There was also excellent fumigation effect in maize bulks. However, the effect to paddy bulks was worse. It was found that there were strong penetration effects in maize and wheat bulks, thus having an excellent fumigation effect. Therefore, EtF has been regarded as one alternative fumigant for use in control of *Sitophilus oryze*, , *Tribolium castaneum*, *Rhizopertha dominica* and Liposcelis in wheat or maize granaries. Because of poor fumigation effect in paddy bulks, EtF could be used in combination with carbon dioxide to carry on mixture fumigation [36]. This research has supplied many pieces of scientific evidence for application of EtF during full storage.

5.2 Carbon Disulfide

Carbon Disulfide was tested and proven to have abilities to control all grain storage pests in 1958. With good penetration abilities and ease in evaporation in places with high temperature, Carbon Disulfide had more practical values. According to GBZ2 – 2002, national occupation health standards in China, many contact poison limitations were as follows: the Carbon Disulfide average allowed concentration time weighted was $5mg/m^3$ in vitro skin permeation, contact allowed concentration in short time was $5mg/m^3$ in vitro skin permeation [37].

The preliminary test on fumigation with carbon disulfide to control Sweet potato black rot and the experiment on controlling grain storage pests with carbon disulfide were carried out in 1966 and 1967 one after another. Meanwhile, the research on carbon disulfide residual standards allowed in grain was carried out as well. However, carbon disulfide has not been in practice for grain fumigation for many years. Recently it has been reappraised as a substitution for Methyl Bromide. With many advantages, such as convenience of use, fumigation at low temperatures of below 10℃, and low residuals there is the excellent desired effect of controlling pests by fumigation by combination carbon disulfide with carbon tetrachloride mixture at certain proportion, especially to *Rhyzopertha dominica* with strong phosphine resistance [38].

5.3 Carbonyl Oxysulfide

Carbonyl Oxysulfide, which is a chemical material that exists naturally in the atmosphere and has important ingredients for sulfur cycling in the earth, was used for synthesis of oxycarbide, sulfoacid, thiosulfate and thiazole in many industries. Therefore, it was regarded as a patent of one new fumigant by John Stooker, Australian. According to research made by XianChang Tan in 1994, paddy had more resistance than wheat and maize with 7 day fumigation at a temperature of 39℃ and concentration of $25\ g/m^3 - 39\ g/m^3$. After fumigation at $25\ g/m^3$, prophase germination rate decreased to 6.29%, 28.4%, 20.3% respectively. With dosage acceleration, both prophase germination rate and germination ratio have been decreased accordingly.

The dosage for fumigating barley and oil seeds by Carbonyl Oxysulfide was recommended at $17\ g/m^3$, $15\ g/m^3$ respectively. During fumigation, gas is distributed equally and the concentration is decreased to 8% 6 hours later, with the average concentration in barley and oilseed granary being 13 g/m^3 and 12 g/m^3 respectively 7 days later. After fumigation for 7 days, six kinds of test beetles, three kinds of booklouse, and one kind of moth and carpet beetle larvae were killed completely. By ventilation for 2 – 4 hours by 0.4kW ventilators after fumigation, the residual of Carbon Oxysulfide in grain was at maximum residual standards of 0.2 mg/kg, Australian ruled.

5.4 Ethylene Oxide

Ethylene Oxide has been taken into practice widely for cold sterilization of medical treatment materials and devices, as well as for prevention of food and flavoring from mold. It has always been used for paddy, miscellaneous grain crops and some plants products. At actual concentrations, it has homicidal poisoning abilities to many kinds of bacteria, fungi and viruses. However, it also had rank poison to plants and a negative effect on the germination of seeds. As it was easy to burn, in practice it was usually used in a combination with carbon dioxide. For hydrocarbylation and inducing mutation, it could also have potential carcinogenic effect. The toxicity against pests was about at a middle degree. In China, it has been allowed only for fumigation wheat with *Tilletia contraversa* Kuhn.

5.5 Sulfuryl Fluoride (SF)

Advantages of Sulfuryl Fluoride (SF) include excellent diffusion, broad-spectrum anthelminthic abilities, low drug consumption, low residual content, rapid speed of taking into practice, short time of diffusion, practical convenience at low temperatures, difficulty in burning and exploding, noncorrosive to metals in the gas stage, and no influence to germination ratios of seeds. As such it has been used for controlling pests or termites widely in some places, such as granaries, cargo boats, containers and buildings, water reservoirs dams, gardens and arbor vitae. SF has been regarded as an alternative substance to Methyl Bromide in some industries, such as plants quarantines, healthy quarantines, agriculture storage and building industries and so on.

Since the 1970s, after the project founded by Chinese agriculture ministry, SF has been developed by 21 units including the Plants Quarantine Institute. Application of SF in grain industries has been researched widely by such Chinese scholars as GuoGan Xu, WangChang Li, XianChang Tan et al [39]. At present, SF has been registered for fumigating such materials as wood, official files, books, embankments and buildings, and was already taken into application in more ranges of buildings and quarantine ministries.

Due to the notable pharmacodynamic action of SF, there was excellent effect on control of pests such as: bark beetles, longicorn, termite, *Trogoderma granarium*, *Sitophilus oryza*, *Sitophilus zeamais*, *Tribolium castaneum*, *Sitophilus granaries*, *Callosobruchus chinensis*, *and Lasioderma serricorne*. Pharmacodynamic tests against about 30 species of pests have been carried out on over 30 units including the Plants Quarantine Institute of Agriculture Ministry. These tests showed that the mortality effect against pests could reach 100% at concentrations of 20 g/m^3 – 60 g/m^3 and fumigations of 2 – 3 days, especially against pests at postembryonic period. It also has a shorter explosive time, lower chemical consumption, more rapid gas diffusion.

Research on acute and subacute inhalation toxicity has been carried out by the Healthy Institute of China Academy of Medical Science. They have shown that LC50 of SF against Mus musculus albus was 800 mL/m^3, and the lethal concentration against house rabbit was 3 250 mL/m^3. After narcotics tests against an albino rat for 2 hours at a concentration of 55.6 mL/m^3 by subacute tests, there was no obvious hurt to the important organs of the rat. There was also a lower toxicity against higher animals compared to others fumigants.

The temporary residual and permanent residual on SF has been researched by GuoGan Xu et al. The temporary residual could be disadsorbed by ventilation. Compared with fumigation of soya bean and maize with Methyl Bromide, the consumption of SF only was 36% of consumption of Methyl Bromide during fumigation of soya bean, and 20.3% during fumigation of maize. The speed of SF disadsorption was higher than Methyl Bromide after fumigation. There was also no residual poison inspected by gas chromatographic analysis during fumigation analysis of the granary after 8 hours, and no residual poison inspected by the gas detector during fumigation of cotton granaries in large shipments with diffusions of about 4 – 12 hours. However, the permanent residual could not be disadsorbed after chemical reactions with fumigants. The permanent residual of SF was lower than that of Methyl Bromide as well.

In the experiment on residual inspection after fumigation of grain with SF at high concentrations by GuoGan Xu and Guang Li et al. ,it was shown that the residual of SF would increase with increasing consumption, and the residual of fluorine in powder grain was higher than in original grain. According to GB2762 – 2005 *Maximum levels of contaminants in foods*, the maximum levels of fluorine in grain should be below 1. 5 mg/kg, in rice and flour below 1.0 mg/kg, and in beans and their products below 3. 0 mg/kg. Furthermore, according to GB5009. 18 – 2003, *Fluorine inspection in foods*, the official main inspection used was colorimetry by diffusion-fluorine reagents, and the maximum level of fluorine inspection was 0. 1 mg/kg.

Following the experiment on the fumigation of several dozen plants seeds such as bean, mung bean, black bean, cucumber, eggplant, Chinese cabbage and so on with SF at concentrations of 70 g/m^3 and 100 g/m^3 respectively, there were no evidence of SF influencing the germination ratios of these plants seeds.

At present, temporary registration certification for SF use has been approved to take into practice in grain.

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