#### Горновская С.В., Федоренко В.П. Вредители посевов подсолнечника в Северной Степи Украины

Установлены доминирующие виды фитофагов в разные фазы развития растений. Уточнён видовой состав вредителей подсолнечника. Установлено вредоносность фитофагов на посевах подсолнечника. Выявлено годы массовых размножений доминирующих видов насекомых. С 2012 года происходит нарастание численности и вредоносности подсолнечной шипоноски, подсолнечного усача и лугового мотылька на посевах подсолнечника в Северной Степи Украины.

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## FEATURES OF PHOSPHINE USE AGAINST PESTS OF GRAIN STOCKS AT DIFFERENT STAGES OF THEIR DEVELOPMENT

It is investigated the toxic effects of phosphine against pests of grain stocks at all stages of their development. It is defined the indicators of product of the mean concentration at exposure time (PMCET), alternative to methyl bromide, which provide the efficiency of fumigation for rice (Sitophilus oryzae L.) and granary (Sitophilus granarius L.) weevils in all phases of development.

#### lethal standards, phosphine drugs, grain stocks pests

Investigations of granary pests in Ukraine, damaging grain and grain products during their storage, has set out their species composition, which comprises 116 species. Among the pests of grain stocks during their storage, the most common are 32 species, of which there are 20 beetles, 7 moths and pylarid moths, 2 ticks, and 3 species of small rodents [6].

The most common of these are: granary (*Sitophilus granarius* L.) and rice (*Sitophilus oryzae* L.) weevils, flour (*Tribolium confusum* Duv.) and fusty flour (*Tribolium castaneum* Hrbst) beetles, saw-toothed grain (*Oryzaephi*-

*lus surinamensis* L.) and rust red grain *(Laemophloeus ferrugineus* Steph.) beetles, grain worm *(Rhizopertha dominica* F.), pea weevil (Bruchus pisorum L.), Indian meal (*Plodia interpunctella* Hb.) and flour (*Ephestia kchniella* Zell.) moths, grain moth *(Sitotroga cerealella* Oliv.), flour mite *(Acarus siro* L.), the usual fluffy mite (*Glycyphagus destructor* Ouds.).

Among less common species are: maize weevil (Sitophilus zea mays Motsv.), flour tenebrionide beetle (Tenebrioides mauritanicus L.), meal beetle (Tenebrio molitor L.), bean weevil (Acanthoscelides obtectus Say.), lentil beetle (Bruchus lentis Frol.), alfalfa chalcid (Bruchophagus gibbus B.), drugstore beetle (Stegobium paniceum L.), whitemarked spider beetle (Ptinus fur L.), larder beetle (Dermestes lardarius L.), elongated mite (Tyrophagus noxius A. Zach.), Caloglyphus Rodionova (Caloglyphus Rodionovi A. Zach.), dust lice (Psocoptera) and others [1].

Dangerous pests of grain and grain stocks, noted below, have not been detected in Ukraine: khapra beetle (*Trogoderma granarium* Ev.), Trogoderma versicolor (*Trogoderma vercicolor* G.), Southern cowpea weevil (*Callosobruchus chinensis* L.), Bruchid beetle (*Callosobruchus quadrimaculatus* F.), pea weevil (*Bruchidius incanatus* B.), broad-nosed granary weevil (*Caulophilus latinasus* Say.) and others. These species of pests are common in Asia, America, Africa, and Europe, with which Ukraine has trade relations; therefore, there is a danger of their importation [5].

Each year, during storage, even in the presence of granaries with modern modifications such as silo type elevators of built-up or all-welded metal construction of various forms and kitting, we lose from 5 to 30% of the harvested grain, and its edibility, forage and seeding characteristics are significantly reduced.

Studies have shown that in warehouses of the second half of the last century, and in the old elevators of reinforced concrete structures, the equipment of which trails greatly to modern technology against pests of grain stocks, in some cases almost 50% of grain production was lost. According to the results of the research, technological and hygienic indicators on the extent of infestation and contamination of grain stocks in these types of granaries were the highest, sometimes exceeding the permitted limit, and constituted IV–V degree of infestation; such grains cannot be used for food [6].

Today in the world, the single most efficient and economically rational method of grain stocks protection against pests is fumigation.

Previously, for many years one of the main means of protection against pests of grain stocks were drugs based on gaseous substances like methyl bromide. Methyl bromide (CH<sub>3</sub>Br bromomethane, methyl bromide) is a substance, halogen derivative of methane, a colorless gas with a boiling point of  $3,6-4,5^{\circ}$ C. Vapor of methyl bromide is heavier than air, it penetrates deep into the sorbing materials, but is absorbed by them, remaining in the form of related inorganic bromides, the number of which depends on the

concentration of the drugs used and the duration of exposure. Raised humidity of products does not prevent the penetration of steam.

To use this material, preferably against quarantine facilities, there have been developed appropriate fumigation modes and lethal standards of gramequivalents for decontamination of agricultural products depending on thermal behavior of cargo and decontamination environment, species of pests and, that is very important, stages of their development.

Relevant standards of gram-equivalents allowed using just the right amount of the fumigant, according to the species composition of the pests, which would not exceed the possible accumulation of the active substance and its metabolites in agricultural products, thereby solving the problem of environmental protection.

Nevertheless, by the decision of the participants of the Fourth Conference of the Montreal Protocol [7, 2], methyl bromide was banned due to its negative impact on the ozone layer of the stratosphere. The only effective fumigant, which was officially registered in Ukraine and is quite widely used against pests of grain stocks, is phosphine (PH<sub>3</sub>). Highly toxic substance with a molecular weight of 34,04, in the gaseous state is 1,5 times heavier than air, with the boiling point of 87,4°C, the freezing point of 133,5°C, the lower threshold of explosiveness by volume of air is 1,79%, reminiscent of the carbide smell. Able to auto-ignition in contact with the dripping-liquid moisture. The lower threshold of auto-ignition is 26–28 mg/l. The smell of gaseous phosphine is felt at its concentrations of 0,002–0,004 mg/l. It has no effect on steel, galvanized metal, wood, silk and cotton fabrics, and other materials. Causes severe oxidation of copper pieces of equipment.

However, despite the heavy use of drugs on phosphine, the issues of their toxic effect on harmful organisms are insufficiently studied for today; namely, there is no data on the necessary thanatophoric standards for the most common types of pests of grain stocks considering their stage of development. In addition, three are only few instructional materials that offer the variability of the required indicators of product of the mean concentration at exposure time on phosphine according to the species of many pests of grain stocks for post-embryonic development stages.

In addition, it is important to study the problem concerning the use of phosphine in different types of granaries and facilities during transportation of product stocks: wagons, ships` holds, containers that is associated with various indicators of phosphine sorption by products in a certain amount of fumigation and the necessary number of reaching lethal standards of the number of gram-equivalents.

Considering the above, nowadays it is extremely necessary to develop modern methods of protection against entomological complex of grain stocks pests by means of the drugs based on phosphine using modern methods and tools, such as gas detection sensor devices for continuous monitoring of the air of the working area, including the use of bellows-sealed aspirators, only in some cases. This also applies to the use of modern means of individual protection, thanks to the new modifications of protective filters against harmful concentrations of phosphine and convenient panoramic gas masks that allow professionals monitoring the fumigation works in more detail, especially in harsh conditions of fumigation (high dust content or insufficient illumination). When creating new, modern techniques of phosphine use, we will significantly reduce the likelihood of manifestations of pest resistance to the active ingredient.

It is known that the main cause of resistance in insects is considered unsatisfactory conduct of fumigation work, usage of imperfect instruments for measuring the concentration or often lack thereof, insufficient hermetic sealing of objects, fumigation in transit, non-observance or absence of fumigation modes [4].

Information given indicates the expediency of studying the use of phosphine as a single and available alternative fumigant. However, during the decontamination of any product, it is obligatory to use fumigant against those stages of the pests' development, which, depending on storage conditions, may be present in this product. Modes of use and lethal standards are developed separately for different stages of the pests' development because any species has its own standards of relevant product of the mean concentration at exposure time at the appropriate temperature and air humidity of the working area.

*Methods of research.* The research was conducted in 2012–2014 on the premises of the enterprise for storage and processing of cereals: LLC «Factory pf processed foods», Skvyrskyi region, Skvyra. Sealed adapted compartments were used for fumigation. Lethal standards of gram-equivalents were determined by the generally accepted method, used for gaseous fumigants [3].

Testing of fumigants was performed on the most widespread test subjects such as imagoes of non-quarantine species of grain stocks pests: rice (*Sitophilus oryzae* L.) and granary (*Sitophilus granarius* L.) weevils, and their pre-imaginal stages of development.

Among the drugs on the basis of phosphine, there was chosen: magtoxin (based on magnesium phosphide), the manufacturer of the formulation is Detia Degesch GmbH, Germany. This drug is degraded more rapidly than drugs containing aluminum phosphide. At a humidity of 60% and a temperature of  $20^{\circ}$ C, 75% of phosphine exhales already in 24 hours. To conduct the appropriate research, the following materials and equipment are used:

- sensory gas analyzer (manufacturer: Draeger, Germany) Draeger X-Am 5000, adapter for the pump, telescope probe with extension for gas-air sample collection;
- overflow launder for fumigant;
- sensory thermohygrometers testo 608 H1(TESTO AG, Germany);
- panoramic gas mask for respiratory protection;

- gas filters for gas masks to protect against phosphine;
- sealants: adhesive tape, sealed mass, sealing foam, polyethylene film for sealing vapors gaseous substance;
- special protective overalls "ZM" 4530;
- special protective footwear (Нм, K<sub>20</sub>);
- protective rubber gloves «ostadkar» K80;

Experiments were reconducted three times; during each repetition, 30 insects were used. The contaminated products with pests in latent form were fixed in holding cages separated to control the obtained PMCET. Non-fumigated specimen, which were kept in the same conditions as the tested ones, were used as means of control.

#### Variants of experiments:

Modes of decontamination were used in accordance with the guidance material, the requirements of the state sanitary-epidemiological expertise conclusion to the drug as well as the recommended standards of the fumigant manufacturer regarding the use of the drug.

However, to address the major environmental problem concerning the study of pesticide load and reduce the accumulation of fumigants and their metabolites in the production stocks, we used the modes with the minimum dosage rate. The research was conducted under the three temperature modes: interval No.  $1 - 25^{\circ}$ C, No.  $2 - 20^{\circ}$ C and No.  $3 - 16^{\circ}$ C. Under the mode No. 1, the exposure was - 96 hours, under the mode No. 2 - 120 hours, under the mode No. 3 - 144 hours. Concentration range for the mode No.  $1 - \text{from } 224 \text{ mg/m}^3$  to  $1120 \text{ mg/m}^3$ , for No.  $2 - \text{from } 203 \text{ mg/m}^3$  to  $1092 \text{ mg/m}^3$ , for No.  $3 - \text{from } 154 \text{ mg/m}^3$  to  $756 \text{ mg/m}^3$ . Nonfumigated specimen were used as means of control.

**Research results.** Conducted researches have shown that lethal standards of the relevant gram-equivalents under the same conditions of use have different indicators according to the species of pests. In addition, we determined the dependence of the concentration on the exposure at the appropriate temperature and air humidity conditions of the working area. One of the most important and the main factors prior to fumigation work under the required temperature and air humidity of the working area is sealing of the premises. Therefore, first it is necessary to pay attention to sealing, taking into account the ventilation openings.

In conducting research under the mode No. 1, it was found that the necessary lethal standards for imago of a rice weevil (*Sitophilus oryzae* L.) is a measure of the total PMCET<sub> $\Sigma$ </sub> equal to 15 gram-equivalents with an exposure of 42 hours.

However, according to the results of the research, this figure of the total concentration product at the time is not effective for the other stages of this species' development (Fig. 1).

Lethal standards for pre-imaginal stages were effective when achieving



appropriate indicators of PMCET. For example, the larval stage was the most susceptible to phosphine; the total figure for  $PMCET_{\Sigma}$  was equal to 9 gramequivalents with the exposure of more than 28 hours. Necessary PMCET for the pupal stage were 17 gram-equivalents with the exposure of more than 49 hours. In addition, the egg stage was the most resistant to phosphine with the indicator 22 gram-equivalents and the exposure of more than 52 hours.

Dependence of toxic action on phosphine concentration and duration (of the exposure) required for the achievement of the relevant lethal standards of gram-equivalents under the mode No. 1 amounted to the following indicators:  $224 \text{ mg/m}^3 - 1120 \text{ mg/m}^3$  (Fig. 2).

In conducting research under the mode No. 2, it was found that the indicators of the total PMCET<sub>2</sub> were equal to 15,4 gram-equivalents with the exposure over 47 hours were the necessary lethal standards for imago of a rice weevil. Lethal standards for pre-imaginal stages under the mode No. 2 were as follows: the larval stage was the most susceptible to phosphine, the total figure of PMCET<sub>2</sub> was equal to 10,3 with the exposure over 31 hours. Effective lethal standards for the pupal stage reached 19 gram-equivalents with the exposure of 51 hours. For the egg stage, lethal standards were as follows: 22,6 gram-equivalents with the exposure of more than 55 hours.

Dependence of concentration on the exposure under the second mode of use demonstrated some changes (Fig. 3).

It was found that under the mode No. 3, the indicators of the total  $PMCET_{\Sigma}$  equal to 17 gram-equivalents with the exposure of more than 58 hours were the necessary lethal standards for imago of a rice weevil. Lethal standards for pre-imaginal stages under this mode were as follows: the larval stage -11 gram-equivalents with the exposure of more than 48 hours. The





indicator of 22 gram-equivalents with the exposure of more than 68 hours was the necessary PMCET for the pupal stage. For the egg stage, lethal standards reached 24 gram-equivalents with the exposure of more than 69 hours. Concentration indicators under the relevant mode also had the other parameters (Fig. 4).

When achieving lethal standards for all stages of a granary weevil (*Sitophilus granarius* L.), there was observed almost a similar relation of resistance to phosphine; however, they still had different figures (Fig. 5).

For the mode No. 1, PMCET indicators were as follows: for imago - 17 gram-equivalents with the exposure over 49 hours, for the pupal stage - 18 gram-equivalents with the exposure of 51 hours. The egg stage proved to



be the most resistant with lethal standards indicator of 23 gram-equivalents with the exposure of 55 hours. The larval stage was the most susceptible to phosphine, with PMCET indicators of 9,5 gram-equivalents and the exposure of more than 30 hours.

For the mode No. 2, the indicators were as follows: for imago -19 gram-equivalents with the exposure over 55 hours, for the larval stage -21 gram-equivalents with the exposure over 57 hours. The egg stage was the most resistant, with the indicators of 24 gram-equivalents and the exposure over 58 hours. For the larval stage, the total indicator was equal to 10.7 gram-equivalents with the exposure over 32 hours.

For the mode No. 3, air conditions of the working area for the use of phosphine were significantly different from the previous modes No.1 and No.2, and lethal standards indicators were as follows: for imago -19,5 gram-equivalents with the exposure of more than 65 hours, for the pupal stage -26 gram-equivalents with the exposure over 60 hours. The egg stage proved to be

the most resistant with the total  $PMCET_{\Sigma}$  indicator of 27 gram-equivalents and the exposure of more than 76 hours. For the larval stage, the total indicator was 12 gram-equivalents with the exposure of more than 53 hours.

These data show that under different temperature intervals, the egg stage was more resistant to phosphine as compared with larvae, pupae and imago. This is due primarily to the difference in the physiological activity of insects, which strongly depends on the temperature and humidity of the habitat. Eggs and pupae were the most resistant to the fumigant. Larvae were the most susceptible to phosphine.

Analyzing the toxic effect of the fumigant on the above grain stocks pests, it should be said that the proposed modes of decontamination for the use of drugs containing phosphine were based solely on dosage by the fumigant weight on the defined volume, as required by the conclusion of the state sanitary-epidemiological expertise for the drug and recommended standards of use of the drug of the fumigant manufacturer. However, as a result of our investigations it was found that these data are not sufficient considering the fact that some factors may change the concentration ratio that affects insects. The most important among them were the following: temperature and air humidity of the working area, gas sorption of products and gradual loss of active ingredient, especially when reaching the maximum value of concentration in the fumigant space. That is, the effectiveness of the toxic effect depended on the amount of gaseous substance that affected the insects over a certain period of exposure.

Lethal standards of gram-equivalents for each research subject were different based on temperature changes. This especially depended on their phasic development that was controlled by specific modes of gram-equivalents at the appropriate temperature. The higher the temperature, the lower PMCET indicator for pests, besides, pre-imaginal stages, including egg and pupal, showed greater resistance to fumigant than larval and imago.

Most importantly, when conducting our research, it was found that with minimal standards of use of the drug, depending on its conditions of use, we achieved the effectiveness for research subjects at significantly reduced exposure. This fact allows us to solve a major environmental problem aimed at reducing pesticide load, significantly reducing the accumulation of fumigant and its metabolites in the production stocks and gaining significant economic benefits due to substantial decrease in the consumption rate of expensive drug.

### CONCLUSION

- 1. It was discovered, that the larvae of rice (*Sitophilus oryzae* L.) and granary (*Sitophilus granarius* L.) weevils were the most susceptible to phosphine, the maximum PMCET for which was 12 gram-equivalents.
- 2. It is defined the dependence of toxic action on phosphine concentration and exposure that ensured the achievement of appropriate lethal standards of gram-equivalents. That is, the effectiveness of the toxic

effect depended on the amount of gaseous substance that affected the insects over a period of exposure.

3. Lethal standards of gram-equivalents at low temperatures for all tested insects were significantly higher than at high temperatures. It is found that at substantial decrease of the recommended standards of use of the drug, depending on the conditions of use (temperature, humidity and maximum tightness), the required lethal standards for test subjects were achieved at significantly reduced exposure.

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# Середняк Д.П., Федоренко В.П. Особливості використання фосфіну проти шкідників хлібних запасів на різних фазах їх розвитку

Досліджено токсичну дію фосфіну проти шкідників хлібних запасів на всіх стадіях їх розвитку. Визначено альтернативні бромистому метилу показники добутку середньої концентрації на час експозиції (ДСКЧ) при яких забезпечується ефективність фумігації для рисового (Sitophilus oryzae L.) та комірного (Sitophilus granarius L.) довгоносиків на всіх фазах розвитку.

# Середняк Д.П., Федоренко В.П. Фумигация фосфином против вредителей хлебных запасов

Исследовано токсическое действие фосфина против вредителей хлебных запасов. Определены альтернативные бромистому метилу показатели произведения средней концентрации на время экспозиции (ПСКВ) при которых обеспечивается эффективность фумигации для рисового (Sitophilus oryzae L.) и амбарного (Sitophilus granarius L.) долгоносиков во всех фазах развития.