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"VAPORMATE™" AN ALTERNATIVE FUMIGANT FOR QPS TREATMENTS

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ABSTRACT

For the registration of Vapormate™ as an alternative to methyl bromide and for quarantine and post harvest treatments, efficiency tests were conducted at the laboratory, at semi- commercial and commercial trials in Israel. Vapormate™ contains 16.7% ethyl formate mixed with carbon dioxide. The effect of three Vapormate™ dosages 210, 420 and 630 g/m^3 was tested at fixed exposure times of 24 h with control at a temperature of 30°C and 70% relative humidity at laboratory conditions. For laboratory trials, test insects were adults of *Tribolium castaneum* and *Rhyzopertha dominica* and larvae of *Trogoderma granarium* in 3-liter desiccators containing 1 kg of rice or corn. The optimal results were obtained at 24 h exposure of 420 g m^{-3} that caused 100% mortality of *T. castaneum* and *R. dominica* adults and *T. granarium* larvae. Semi-commercial tests were carried out on green coffee beans stored in a 3 m^3 plastic cube fumigated for 24 h exposure to 420 g m^{-3} Vapormate™. Fumigations resulted in total mortality of *T. castaneum* adults with no adverse effects on green coffee beans. Commercial tests were carried out on 20 tonnes of rice stored in bags inside a 33.2 m^3 standard transport container. The rice was fumigated for 24 h by exposure to 420 g m^{-3} Vapormate™. Adults of *R. dominica* and *Sitophilus oryzae* exposed to Vapormate™ resulted in total mortality. Dosage of 420 g m^{-3} and exposure time of 24 h that resulted in high toxicity to the test insects, and the rapid desorption from the commodities, offer Vapormate™ to be a potential fumigant to replace methyl bromide in QPS treatments and when rapid disinfestations of storage commodities is essential.

Key words: Vapormate™, ethyl formate, QPS, fumigation, insect control, methyl bromide, *Rhyzopertha dominica*, *Tribolium castaneum*, *Orazophilus surinamensis, Trogoderma granarium, Sitophilus oryzae*

INTRODUCTION

Methyl Bromide (MB) alternatives were considered for quarantine and pre-shipment (QPS) treatments throughout the world before and after its phase out in 2005 in all the developed countries. In Israel, the only alternative fumigant for treatment of post harvest of durables remained phosphine. A fumigant that most exporters or importers as well as their pest controller are reluctant to use because of the long exposure time needed for successful implementation and the resistance that many pest insect have developed to this fumigant.

The global concern from the introduction of new pests or new resistant strains of known grain storage insect pest increased the interest in additional alternatives. A fumigant that will be user friendlier to environment, effective, rapid action and at the same time should be on an acceptable cost basis. One of the fumigant of choice considered was ethyl formate (EF) known in its commercial formulation as Vapormate™.

Vapormate™ is a low human risk fumigant formulated by BOC Australia, a member of the Linde Group, and contains 16.7 wt% EF in liquid carbon dioxide (CO_2) (Ryan and Bishop, 2003). The CO_2 in Vapormate^{TM} has been added to eliminate the flammability of the EF and to enhance efficacy by its synergistic effect in reducing the time required to kill insects (Haritos et al., 2006). EF occurs naturally in many natural products as orange juice, honey, apples, pears and wine. It is used as a synthetic flavoring agent in the food industry and as fragrances; it is also a GRAS registered food additive (Ryan et al., 2006). It decomposes slowly in water releasing formic acid and ethanol. Laboratory tests as a fumigant against insect pests of food commodities and field trials on bagged cereals, spices, pulses, dry fruits and oilcakes have been carried out (Muthu et al., 1984). EF is currently registered as a fumigant in Australia as ERANOL® by Orica Chemnet for the elimination of insect pests in packed dried fruits like raisins. It is toxic to storage insects including psocids (Annis et al., 2000). It was registered for use in grain and horticultural products in Australia, and in New Zealand for use in grain and for quarantine treatment of bananas (Krishna et al., 2002). It is registered in Israel for dates disinfestation and control of nitidulid beetles (Finkelman et al., 2010). In this work we report on the efficiency tests that were conducted at the laboratory, at semi-commercial and commercial trials to register Vapormate^{TM} in Israel for QPS treatments as an optional MB alternative fumigant**.**

MATERIALS AND METHODS

Test insects

All test insects were reared at FTIC laboratory at 30º±1C and 70±2% r.h. Test insect species were: *Rhyzopertha dominica* (F.)*, Tribolium castaneum* (Herbst), *Trogoderma granarium* Everts, *Sitophilus oryzae* (L.) and *Oryzaephilus surinamensis* (L.)

Laboratory trials

Adults of *R. dominica* and *T. castaneum* were placed into a 22 mL glass vials together with about 3 g of ground wheat. Each glass vial together with the test insects was placed into a 3 L gas-tight desiccator used as a fumigation chamber. Each desiccator contained either 1 kg of polished rice (11.5% m.c.) or corn (11.0% m.c.). The Vapormate^{TM} was introduced into the desiccator to achieve concentration of 630, 420 and 210 g m^{-3} at 30±1ºC or 24 h. Dosage calculations were converted to the gaseous phase and the required volume of Vapormate™ was obtained by evacuating the desiccator to the desired pressure, followed by restoration of atmospheric pressure using Vapormate™ supplied from a pressurized cylinder. The desired pressure was first calculated by converting the dose into a percentage of the desiccator volume to be treated, then desiccator was evacuated to the desired absolute pressure using a laboratory vacuum pump and the pressure measured using a portable transducer manometer (SE-2000, Celesco, Chatsworth, CA, USA), and then the equivalent to the partial pressure of in air was supplied by restoration of atmospheric pressure using the Vapormate™ supplied from the pressurized cylinder. The same process of evacuatingto the desired pressure was carried out in the control desiccator but instead of the gas mixture, the pressure was restored using ambient air at atmospheric pressure (Finkelman et al., 2010). At the end of the exposure time, the glass vials with the test insects were removed from the fumigation chamber and placed in an incubator at 30±1ºCfor 24 h before mortality counts were made. For every test 4 replicates were used.

The efficiency of Vapormate^{TM} was tested on non-diapausing larvae of *T. granarium*, since this species is considered one of the most important quarantine pests. The larvae were exposed to 420 g m^{-3} at the same conditions as the other tested insects in the desiccator. The desiccator was then placed at 30ºC for the predetermined exposure times. The effectiveness of Vapormate^{TM} on *T. granarium* larvae was tested at three exposure times: 12, 16 and 24 h. At the end of each exposure time, the glass vials with the test insects were removed from the fumigation chamber and placed in an incubator at 30ºC and 70±2% r.h. for 24 h before mortality counts were made.

Semi-commercial trials

Two semi-commercial trials were carried out using two types of flexible fumigation chambers to test the efficiency of Vapormate^{TM}. In the first trial 1.2 tonne of polished rice stored in 50 kg bags were fumigated with 420 g m^{-3} Vapormate^{TM} at 26^{o}±2C for 24 h. The rice bags (11.85±0.85 m.c.) were placed in a 2 m^3 cube consisted of welded PE-PP laminated with aluminum foil barrier sheets. Test insects were placed at the top, middle and bottom of each chamber. In each test location at least 20 adults of *R. dominica*, *S. oryzae* and *O. surinamensis* were placed in glass vials of 22 mL together with about 3 g of flour. Each test was replicated four times. In the second trial 12 bags containing green coffee beans (60 kg each), imported from Vietnam, were arranged on a pallet and the pallet was placed in a 3 m^3 Rentokil flexible PVC fumigation chamber. Test insects were placed at the top, middle and bottom of the chamber among the bags. In each test location three glass vials of 22 mL, each containing three developmental stages of *T. castaneum*; adults, pupae or larvae were placed with the glass vials contained about 3 g of flour and 20 individual insects. The bags were fumigated using 420 g m^{-3} Vapormate^{TM} at 27^{o}C for 24 h. Vapormate™ supplied from the pressurized cylinder was mounted on a scale while the pressure tube was hold inside the sealed liner and secured to prevent movement of the injection tube due to back pressure of the gas. During the injection the opposite top of the chamber was kept open to release excessive pressure and to prevent sudden ballooning of the fumigation chamber. A gas-sampling opening in the chamber was used to measure gas concentration. An initial dosage of 420 g m^{-3} was used and concentrations were measured immediately after the gas release using a CO_2 gas analyzer. After exposure to fumigants the glass vials were taken to the laboratory and placed in an incubator at 30ºC and 70±2% r.h. for 24 h before mortality counts were made.

Commercial trials

The trials were conducted at the sea port of Haifa as part of scheduled fumigation activities in 33.2 m^3 containers on imported commodities. Three commercial containers each loaded with 20 tonnes of polished rice in bags were prepared to accommodate the test insects which were placed in the front at the four corners of the container among the bags. In each test location two glass vials of 22 mL were placed with adults of *R. dominica* and *S. oryzae* arranged separately to contain about 3 g of flour. Vapormate™ supplied from the pressurized cylinder as in the semi-commercial trials as well as the method of measuring of gas concentration. After fumigation the glass vials were taken to the laboratory and placed in an incubator at 30ºC and 70±2% r.h. for 24 h before mortality counts were made.

RESULTS AND DISCUSSION

Laboratory trails

Exposing adults of *R. dominica* and *T. castaneum* to 630 and 420 g m^{-3} Vapormate^{TM} at 30^{o}C for 24 h resulted in 100% mortality both in rice and in corn. *R. dominica* adults were more sensitive to the fumigant then *T. castaneum* adults and at 210 g m^{-3} only 3.2% of *T. castaneum* died in comparison to 70.5% *R. dominica* adults. Furthermore the mortality of *R. dominica* adults was higher when they were exposed in rice to the fumigant then in corn, resulting in 70.5% and 42.9%, respectively. These differences are probably due to the lower r.h. % in rice that may have caused higher desiccation rate to enhance mortality (Table 1).

Table 1. Laboratory trials on mortality of *R. dominica* and *T. castaneum* adults after exposure to 630, 420 and 210 g m^{-3} of Vapormate^{TM} at 30ºC for 24 h (average of 4 replicates)

Vapormate^{TM} dose (g m^{-3})	Type of grain	*R. dominica*		*T. castaneum*	
		Average number of adults	Average mortality (%)	Average number of adults	Average mortality (%)
630	rice	23.8	100	20.5	100
control	rice	20	5	23	0
630	corn	22	100	20.8	100
control	corn	23	26.1	21	9.5
420	rice	28.5	100	28.8	100
control	rice	20	25	23	8.7
420	corn	28	100	20.3	100
control	corn	19	4	21	3.2
210	rice	23.5	70.5	21.5	3.2
control	rice	20	0	20	0
210	corn	21	42.9	21	4.4
control	corn	21	0	26	0

Khapra beetle (*T. granarium*) is one of the most important quarantine grain pest beetles mainly because they developed a high resistance to phosphine. When the larvae of the of Khapra beetle were exposed for 12 h to 420 g m^{-3} of Vapormate^{TM} at 30ºC, the average mortality was 76.3% and after 16 h mortality was 97.5%. Only when the exposure time was extended to 24 h the target mortality of 100% in all 4 test replicates was achieved (Table 2).

Table 2. Laboratory trials on mortality of Khapra beetle larvae (*T. granarium*) after exposure to 420 g m^{-3} of Vapormate^{TM} and three exposure times of 12, 16 and 24 h, at 30ºC (average of 4 replicates)

	12 h		16 h		24 h	
	Mortality (%)	Number of larvae	Mortality (%)	Number of larvae	Mortality (%)	Number of larvae
Treatment	76.3	141	97.5	50	100	121
Control	2.2	45	NA	NA	0.1	60

Semi-commercial trials

Using portable flexible fumigation chamber made of welded PE-PP laminates or using the PVC fumigation chamber was effective. Fumigation of 1.2 tonnes of polished rice in 50 kg bags stored was carried out in the PE-PP laminated chamber using 420 g m^{-3} Vapormate^{TM} at 26±2ºC for 24 h resulted in 100% mortality of *R. dominica*, *S. oryzae* and *O. surinamensis* adults (Table 3). The same successful control of 100% mortality of larvae, pupae and adults of *T. castaneum* was obtained when fumigated green coffee beans using 420 g m^{-3} Vapormate^{TM} at 27^{o}C for 24 h in Rentokil flexible fumigation PVC chamber (Table 4).

Table 3. Semi-commercial trials on mortality of *R. dominica* and *T. castaneum* adults after exposure to 420 g m^{-3} of Vapormate^{TM} for 24 h in stored rice (average of 4 replicates)

Test insect		Vapormate^{TM} (420 g m^{-3})		Control	
		Average number of adults	Average mortality (%)	Average number of adults	Average mortality (%)
R. dominica	Top	21.3	100	21.5	16.0
	Middle	21.0	100	NA	NA
	Bottom	21.0	100	21.0	4.0
S. oryzae	Top	20.8	100	22.8	11.0
	Middle	22.5	100	22.8	27.0
	Bottom	21.0	100	20.8	9.0
O. surinamensis	Top	19.5	100	17.3	7.0
	Middle	19.5	100	NA	NA
	Bottom	20.3	100	20.8	7

Table 4. Semi-commercial trials on mortality of *T. castaneum* adults, pupa and larvae after exposure to 420 g m^{-3} of Vapormate^{TM} for 24 h in green coffee beans (average of 4 replicates)

Position in the chamber	Average mortality (%)			Control		
	Adult	Pupa	Larvae	Adult	Pupa	Larvae
Top right	100	100	100	NA	NA	NA
Top left	100	100	100	NA	NA	NA
Top middle	100	100	100	0	0	10
Middle	100	100	100	0	0	5
Bottom middle	100	100	100	0	10.5	5

Commercial trials

Commercial fumigation was carried out as part of the fumigation activities at the sea port of Haifa. A container of 33.2 m^3 was used for importing the 20 tonnes of polished rice stored in bags. The rice was fumigated with 420 g m^{-3} Vapormate^{TM} for 24 h fumigation of the three containers resulted in 100% mortality of *R. dominica* and *S. oryzae* adults (Table 5).

Table 5. Commercial trials on mortality of *R. dominica* and *S. oryzae* adults after exposure to 420 g m^{-3} of Vapormate™ for 24 h in rice (average of 3 containers)

Test insect	Vapormate™ (420 g m^{-3})		Control	
	Average number of adults	Average mortality (%)	Average number of adults	Average mortality (%)
R. dominica	68.3	100	85	4.7
S. oryzae	92.3	100	82	62.1

CONCLUSIONS

The results of this work indicate that exposure to Vapormate™ at the concentration of 420 g m^{-3} at 30ºC for 24 h is an effective fumigation treatment. This treatment was found successful for QPS treatments of grain and other product that are sensitive to infestation by stored products insects. Although, the exposure time needed for Vapormate™ is longer than the time needed for MB, but it is faster and more effective then the use of phosphine. Vapormate™ can be implemented using the same facilities or techniques used by the pest controllers for MB fumigation. Vapormate™ is registered in Israel for the use by the date industry as an alternative to MB since 2008 and is registered for grain treatment since 2010. It is important that it will be implemented for the use of QPS to replace the use of MB or provide an effective substitute.

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