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## VAPORMATE (16.7 wt% EtF in CO<sub>2</sub>): dispensing techniques

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### Abstract

The naturally occurring GRAS food additive, ethyl formate is diluted 6x in liquid carbon dioxide (CO<sub>2</sub>) to formulate the non-flammable VAPORMATE (16.7 wt% ethyl formate in liquid CO<sub>2</sub> = 11 vol% ethyl formate in gaseous CO<sub>2</sub>). VAPORMATE is a patented post harvest fumigant which controls insects in stored grains, fresh produce & food processing equipment. VAPORMATE is dispensed as a fog (particle size ~5-10 microns) or hot (~60°C) gas mixture to assist uniform distribution and optimise efficacy. VAPORMATE [“No Withholding Period” status] applications include: niche alternative for methyl bromide (eg grain, dried fruit, nuts etc); rapid treatment: eg 50-tonne silo of grain: 12 minutes to apply, three hours to fumigate and two hours to air out with no withholding period; disinfestation of food processing equipment containing food residues; modified Atmosphere Package (MAP) treatment for packaged food. VAPORMATE dispensing innovations include: spraying product via a manual hand gun to treat food processing equipment as the resultant “fog” permeated the spaces quickly being propelled by the high cylinder pressure (50 bar = 800 psi). This application is assisted having the VAPORMATE piped to a number of locations throughout the food plant; VAPORMATE is vaporised as a hot gas and dispensed using aeration fans in grain storages (product is dispensed during one air change); VAPORMATE is vaporised as a hot gas and dispensed using

novel mixing devices based on pressure equalisation or venturi principles to dilute the hot gaseous mixture with atmospheric air to optimise use.

*Key words:* Gaseous fumigants; methyl bromide alternative; stored product pests; pest-free & residue-free grain; commodity fumigants.

### Introduction

The BOC formulated, non-flammable, patented VAPORMATE (16.7 wt% Ethyl Formate in Liquid CO<sub>2</sub>) is based on BOC Envirosol technology which uses liquid carbon dioxide (CO<sub>2</sub>) as a solvent-propellant. The unique solvent-propellant property of liquid CO<sub>2</sub> (Ryan et al., 1978) produces a high-pressure (50 bar), non-flammable aerosol (particles size ~5 μ) which is marketed in industrial gas cylinders containing up to 31 kg of product. The small volatile ethyl formate particles vaporise in ambient air and the “fog” is converted to a vapour. In packed fumigation spaces the VAPORMATE is vaporised by passing through a hot water bath and dispensed as a “warm gas” to improve efficacy and distribution (preferably dispensed in one air-change using installed aeration system). In addition to eliminating flammability, the synergistic effects of CO<sub>2</sub> enhance the efficacy of the ethyl formate.

Ethyl formate (EtF), a historical fumigant of dried fruit and packaged food, is naturally

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occurring, found in green apples, cabbages etc. VAPORMATE the BOC registered pesticide for the treatment of stored grain, fresh produce and packaged food, is a new weapon against stored products insects.

### **Ethyl formate**

A fumigant is a chemical which can exist in the gaseous state in sufficient concentration to be lethal to a given pest organism. Fumigants are gases or very volatile liquids because of the requirement of penetrating material to contact the target pests. Prior to commercial use fumigants like all pesticides need to be registered by statutory authorities e.g. EPA (USA), APVMA (Australia).

The development of alternative fumigants has a high level of importance because of threats to the widely used fumigants, methyl bromide and phosphine. Specifically, methyl bromide is an ozone depletor (quotas enforced by the Montreal Protocol) and there is increasing phosphine resistance in insects. Alternative fumigants should be efficacious against a wide range of insect pests, safe to consumers and workers, but not damage the product.

Ethyl formate is a fumigant that satisfies these requirements. Ethyl Formate a volatile highly flammable liquid is a historical fumigant of dried fruit and a rapid acting, GRAS registered food additive. EtF's advantage include: natural occurrence in food; rapid kill of insects (2-4 hours); fast breakdown of residues to natural products; low human toxicity.

Some properties of Ethyl Formate (EtF): Formula:  $\text{HCOOC}_2\text{H}_5$ ; Molecular Weight: 74.08; Boiling Point: 54.1 °C; Solubility in Water: 14.5 % (w/w); Flammability in air: 2.8-16.5 % (v/v) or 90-540 g/m<sup>3</sup>.

However EtF exhibits poor penetration characteristics although it would make a very good spot fumigant for milling equipment similar to ethylene dibromide (EDB) before it was withdrawn from the market. Ethyl formate is currently registered as a fumigant for dried fruit treatment in Australia. High doses of EtF (>120

g/t of grain) are, however, required to control internal developmental stages of rice weevil (*Sitophilus oryzae*), which are higher than the flammable limit of 85 g/t. Therefore, it is necessary to enhance EtF toxicity and reduce flammability by mixing it with carbon dioxide.

### **Registered Pesticide**

VAPORMATE is now a registered pesticide in Australia and New Zealand and is attracting global interest as a niche alternative for methyl bromide, the historical fumigant severely restricted from January 2005 because it is an ozone depletor. VAPORMATE has less OH&S issues than existing fumigants as ethyl formate is 300x less toxic than phosphine. As EtF breaks down on the commodity after fumigation forming naturally occurring breakdown products (ethanol and formic acid), VAPORMATE has been given a "No Withholding Period" status by registration authorities.

### **Non-Flammable**

The non-flammable VAPORMATE overcome the flammability, improves efficacy and penetration of ethyl formate. TestSafe Australia conducted flammability testing of EtF, CO<sub>2</sub> & Air mixtures. Ryan and Pearson (2002) found that 12.5 vol% or 19 wt% of EtF in CO<sub>2</sub> is the maximum amount of ethyl formate that can be mixed with carbon dioxide to maintain a non-flammable mixture for all proportions in air. Allowing additional margin for error the VAPORMATE formulation is 16.7 wt% of EtF in CO<sub>2</sub> i.e. a 6:1 dilution by mass of ethyl formate with liquid carbon dioxide (equivalent to 11 vol% in gaseous carbon dioxide when vaporised).

### **Cooperative team effort**

VAPORMATE had input from a number of supporters. The initial R&D project involved commitment & financial support from the grower organisation, Grain Research & Development Corporation (GRDC); innovation from researchers

at Commonwealth Scientific & Industrial Research Organisation (CSIRO Entomology); and product development from BOC Limited – to develop a fast treatment for small storages (50-200 tonnes). On completion of laboratory and disinfestation grain storages trials in WA, Queensland, ACT and NSW, CSIRO researchers developed a standard concentration for a 50-tonne silo of grain which only takes 12 minutes to apply, three hours to fumigate and two hours to air out. There is no residues issue as VAPORMATE has a “No Withholding Period” status that allows the treated product to be used immediately after aeration (Table 1).

### Efficacy

The approved dosage on the on the registered VAPORMATE label is 420 g/m<sup>3</sup> (~2.3 % v/v ethyl formate & ~21 % v/v carbon dioxide). CSIRO reported VAPORMATE forced flow fumigation of stored grain is safe, efficacious and rapid (very high level of mortality of tolerant insects was achieved in 3 hours). Contrary to expectations lowering the temperature to 15 °C did not affect the efficacy of VAPORMATE.

### Current Registered Label.

Situation	Insect	Application Rate g/m <sup>3</sup>	Critical Comment
Cereal grains and oilseeds in sealed storage	Adult stages of: Rice weevil ( <i>Sitophilus oryzae</i> ); Lesser grain borer ( <i>Rhyzopertha dominica</i> ); Flour beetle ( <i>Tribolium castaneum</i> ); Book lice (Psocids -various species)	420 g/m <sup>3</sup> (24 hours exposure)	Only apply VAPORMATE with BOC LIMITED approved equipment. Only apply VAPORMATE into a gastight closed system for the exposure time period. VAPORMATE is dispensed via fixed high pressure pipe installation into sealed gastight chamber to allow the volatile ethyl formate active ingredient to penetrate deep into the commodity being treated for the recommended exposure period. The storage volume (m <sup>3</sup> ) needs to be calculated so correct VAPORMATE dose can be accurately dispensed. The treatment area should be completely shut for the recommended exposure period (a minimum of four hours) to allow the VAPORMATE to act. The storage should be thoroughly ventilated of ethyl formate vapour (less than 100 ppm) and CO <sub>2</sub> (less than 5,000 ppm) before out loading or re-entry.

Continue...

**Table 1.** Continue.

Situation	Insect	Application Rate g/m <sup>3</sup>	Critical Comment
Grain storage premises and equipment	Adult stages of: Rice weevil ( <i>Sitophilus oryzae</i> ); Lesser grain borer ( <i>Rhyzopertha dominica</i> ); Flour beetle ( <i>Tribolium castaneum</i> ); Book lice (Psocids -various species)	420 g/m <sup>3</sup> (6 hours exposure)	
Horticulture produce (post harvest only) – fruit, vegetables, flowers in sealed storage.	Pacific spider mite ( <i>Tetranychus pacificus</i> ), western flower thrips ( <i>Frankliniella occidentalis</i> ), omnivorous leaf roller ( <i>Platynota stultana</i> ), aphids (eg: <i>Macrosiphum euphorbiae</i> ), mealybugs ( <i>Pseudococcus longispinus</i> ),	420 g/m <sup>3</sup> (4 hours exposure)	

### Proposed new VAPORMATE label rates

Insect tested by Haritos et al. (2004) included highly phosphine resistant field strain of the grain borer, *Rhyzopertha dominica*; laboratory strains of the flour beetle, *Tribolium castaneum* and the rice weevil, *Sitophilus oryzae*. A single dose of 450 g/m<sup>3</sup> is sufficient to obtain high level control (> 99 %) of all stage of *T. castaneum* and *R. dominica* when the grain is held for 24 hours and moderate control (86 %) of *S. oryzae*. In the presence of light infestation of *S. oryzae* the lower rate of application would be sufficient to greatly reduce the insect load in the grain.

Field trial by Haritos et al. (2006) showed VAPORMATE is a fast and safe treatment for stored grain. The Field trials data supports the label rate for the control of flour beetle and lesser grain borer and recommend an increase in label rate to achieve the required high mortality (99.8 %) of all life stages of rice weevil [even a

20 % increase of current label dose achieved 99.3 % mortality of all life stages of rice weevil]. The researchers recommended the method of “Active application” ie using aeration fans to ensure distribution of gas throughout the silo despite rapid losses due to sorption.

From this work the following recommendations were made:

“Complete control of all stages of lesser grain borer (*Rhyzopertha dominica*), flour beetle (*Tribolium castaneum*), Psocids - table will include storage moths (*Espehstia* spp., *Plodia* spp.) *Trogoderma variabile*, *Oryzaephilus* spp., *Collosobruchus* spp., *Bructus pisorum*, in cereal grain and oilseeds:

*Dose: 660 g/m<sup>3</sup> held for 4hours or 420 g/m<sup>3</sup> held for 24 hours.*

Complete control of all stages of Rice weevil (*Sitophilus oryzae*) in cereal grains and oilseeds: *Dose: 940 g/m<sup>3</sup> held for 72 hours.”*

### Effect on barley germination

VAPORMATE is seen as an ideal fumigant for malt and malting barley.

While the maximum dose on the registered VAPORMATE label is 420 g/m<sup>3</sup>, the preliminary barley germination test were conducted at ~ 5x this dose to determine any germination issues. A 3 Litre S/S vessel 90 % filled with barley was purged with VAPORMATE at 1 gram/sec to expel all the air and the vessel sealed for 24 and 72 hours. Treated barley was sent to Barrett Burston for germination testing. Germination test are given (Table 2).

**Table 2.** Percentage of germination energy (GE) test results - BBM Barley Laboratory. 100 seeds in each Petri dish; Arapiles barley - 2004 season; Tested Feb 2006.

Sample	24 hr		48 hr		72 hr	
	4 ml	8 ml	4 ml	8 ml	4 ml	8 ml
No treatment	59	98	94	100	100	100
Purged with 11 % EtF in CO <sub>2</sub> , 24 hrs exposure.	74	96	90	100	96	100
Purged with 11% EtF in CO <sub>2</sub> , 72hrs exposure	86	90	97	95	100	96

These preliminary results suggest VAPORMATE is suitable on malting barley as reported by Nischwitz (2006) “Although the control results produced better germination after 72 hours of testing the results do not appear to indicate a significant difference in germination energy”

### Disinfesting food processing equipment

The cleaning of the intricate internals of food storage & processing equipment is not always perfect and pockets of food dust are frequently left behind. This residual food is an attractive breeding place for stored product insects. Pest Control of internal spaces is difficult as treatment with conventional liquid pesticides is not acceptable because of high pesticide residuals levels in food dusts or on the internal surfaces.

VAPORMATE having no residue issues makes possible the disinfestation of enclosed food equipment spaces. As reported by Ryan et al. (2005) trials were conducted at SUNRICE Rice Mill, Deniliquin, NSW where the VAPORMATE was sprayed via a manual hand gun through 3 mm holes in the processing equipment for the calculated time and the resultant “fog” quickly permeated the spaces being propelled by the high cylinder pressure (50 bar). Successful similar trials were conducted on empty flour storage at Arnott’s Biscuit Plant, Huntingwood, NSW.

VAPORMATE also can be used as a Modified Atmosphere Package (MAP) treatment for packaged food. The key is the product has “No Withholding Period” as the chemical quickly breaks down to naturally occurring levels found in foods.

### Summary

VAPORMATE is a fast and safe treatment for stored grain. Field trial data supports the label rate for the control of flour beetle and lesser grain borer. Increase in label rate is required for high mortality (99.8 %) of all life stages of rice weevil (a 20 % increase of label dose achieved 99.3 % in field trials). Active application using aeration fans ensures distribution of gas throughout the silo despite rapid losses. Preliminary results suggest VAPORMATE is suitable on malting barley. VAPORMATE is uniquely suited to the disinfesting of food processing and storage equipment.

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