VAPORMATE: Update – a new fumigant for stored grain

V. Haritos, K. Damcevski, G. Dojchinov (CSIRO Entomology); R. F. Ryan (BOC Limited)
PO Box 288, Chatswood, NSW Australia. Email: robert.ryan@boc.com

Fumigants:

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. Some candidate chemicals have been eliminated because of unfavourable properties (corrosive, reactive, produce unpleasant odours, physiological active) however flammability or toxicity is not usually a cause for exclusion. A practical requirement and barrier is the need for fumigants to be registered by statutory authorities e.g. EPA [USA], APVMA [Australia].

The unique solvent-propellant property of liquid CO_2 [Ryan et al, 1978] described a high-pressure (50 bar) aerosol spray based on the low cost liquid, fire retardant CO_2 which enables the formulation of non-flammable products. The unique features of the liquid CO_2 based products include;

* Non-flammability - carbon dioxide solvent-propellant.
* Ultra-fine particle size - range from 2 to 20 microns.
* Sized for commercial and industrial needs - 6 kg and 31 kg cylinders.
* Automatic, fixed or portable space spray systems.

Alternative Fumigant Need:

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:

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. Its 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: $HCOOC_2H_5$; 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^3.

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 by mixing it with other natural products like carbon dioxide or vacuum to reduce the effective dosage and flammability.

VAPORMATE:

The non-flammable VAPORMATE [16.7wt% ethyl formate in liquid carbon dioxide] overcome the flammability, improves efficacy and penetration of ethyl formate. VAPORMATE is now a registered pesticide in Australia & New Zealand.
In addition to eliminating flammability, the CO_2 in the VAPORMATE formulation has a synergistic effect which enhances efficacy. This recently registered pesticide is based on BOC Envirosol technology which uses liquid CO_2 as a solvent-propellant to dispense chemicals. The volatile ethyl formate aerosol particles rapidly vaporise in the ambient air and the aerosol "fog" is converted into a vapour. For application in packed fumigation spaces, such as grain silos and shipping containers, the VAPORMATE is preferably vaporized and discharged as a "warm gas" to improve efficacy & distribution.

R&D Input:

VAPORMATE is a new fumigant assessed and developed by CSIRO Entomology with the support of the GRDC as a fast treatment for small storages (50-200 tonnes). Five years ago CSIRO Entomology started focusing on using the naturally occurring ethyl formate found in green apples and cabbages as a replacement for methyl bromide and phosphine. For the past three years the GRDC-funded project has worked in collaboration with private enterprise to develop a commercial product for the disinfestation of grain storages which also has post harvest application with fresh produce. CSIRO reports 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). Insect tested include a highly phosphine resistant field strain of the grain borer, *Ryzopertha dominica*; laboratory strains of the flour beetle, *Tribolium castaneum* and the rice weevil, *Sitophilus oryzae*. A single dose of 450 g/m^3 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. Contrary to expectations lowering the temperature to 15^oC did not affect the efficacy of VAPORMATE. After disinfestation of grain storages trials in WA, Queensland, the ACT and Walla Walla, CSIRO researchers have developed a standard concentration for a 50-tonne silo of grain which takes 12 minutes to apply, three hours to fumigate and two hours to air out with no withholding period.

Pesticide Authority Approval:

VAPORMATE has recently been approved by registration authorities in Australia & New Zealand. VAPORMATE is attracting global interest as a niche alternative for methyl bromide which has been 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 publications demonstrated that ethyl formate breaks down on the commodity after fumigation and the breakdown products (ethanol and formic acid) are natural occurring components of foodstuffs has resulted in a "No Withholding" registration status for VAPORMATE.

Current Registered Label:

Situation	Insects	Application rate g/m^3	Critical Comments
Cereal grains and oilseeds in sealed storage	Adult stages of: Rice weevil [*Sitophilus oryzae*]; Lesser grain borer [*Rhyzopertha dominica*]; Flour beetle [*Tribolium castaneum*]; Book lice [Psocids - various species]	420 g/m^3(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^3) 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 100ppm) and Co_2 (less than 5000 ppm) before out loading or re-entry.
Grain storage premises and equipment	Adult stages of: Rice weevil [*Sitophilus oryzae*]; Lesser grain borer [*Rhyzopertha dominica*]; Flour beetle [*Tribolium castaneum*]; Book lice [Psocids - various species]	420 g/m^3 (6 hours exposure)	
Horticulture produce (post harvest only) – fruit, vegetables, flowers in sealed storage.	Pacific spider mite *(Tetranychus pacificus*),western flower thrips (*Frankliniella occidentalis*), omnivorous leaf roller (*Platynota stultana*), , aphids (eg: *Macrosiphum euphorbiae*), mealy bugs (Pseudococcus longispinus),	420 g/m^3 (4 hours exposure)	

Proposed new VAPORMATE label rates:
Complete control of all stages of lesser grain borer [*Rhyzopertha dominica*], flour beetle [*Tribolium castaneum*], Psocids - table will include storage moths [*Esphestia spp*., *Plodia spp*.] *Trogoderma variabile*, *Orysoephilus spp*., *Collosobruchus spp*., *Bructus pisorum:* in cereal grain and oilseeds:

Dose: 660g/m3 held for 4hours or ***420g/m3 held for 24 hours***.

Complete control of all stages of Rice weevil (Sitophilus oryzae) in cereal grains and oilseeds:
Dose: 940g/m3 held for 72 hours.

Note:
Insect resistance to the most common fumigant currently available, phosphine, show no cross resistance to VAPORMATE.

Effect on Barley Germination

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

While the maximum dose on the registered VAPORMATE label is:
420g/m^3 [~2% v/v ethyl formate & ~19% v/v carbon dioxide],
the preliminary barley germination test were conducted at five times (5x) this dose. 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 & 72 hours. Treated barley was sent to Barrett Burston for germination testing.
Germination test are given in table below.

% Germination Energy (GE) Test Results – BBM Barley Laboratory
[100 seeds in each Petri dish; Arapiles barley – 2004 season; Tested Feb 2006]

Sample	24 hr 4 ml	24 hr 8 ml	48 hr 4 ml	48 hr 8 ml	72 hr 4 ml	72 hr 8 ml
No treatment	59	98	94	100	100	100
Purged with 11% EtF in CO_2, 24 hrs exposure	74	96	90	100	96	100
Purged with 11% EtF in CO_2, 72hrs exposure	86	90	97	95	100	96

Conclusions: "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." [Personal Communication, Ralph Nischwitz, 2006]

References:

Ryan, R.F., Shervington, E.A. and Catchpoole, D.J (1978) Aust.Pat. 494,198.
Personal Communication, Ralph Nischwitz, (2006) % Germination Energy (GE) Test Results – BBM Barley Laboratory, 23 February.