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VAPORMATE™ [NON-FLAMMABLE ETF/CO₂ FUMIGANT]: UPDATE

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ABSTRACT

The non-flammable VAPORMATE contains 16.7 wt% ethyl formate [EtF diluted 6x] in liquid carbon dioxide [CO₂]. EtF a volatile highly flammable liquid is a historical fumigant of dried fruit [also a GRAS registered food additive]. In addition to eliminating flammability, the CO₂ in the VAPORMATE formulation has a synergistic effect which enhances the efficacy of the ethyl formate. This product is based on BOC Envirosol technology which uses liquid CO₂ as a solvent-propellant to dispense chemicals as aerosol particles [particle size ~5 microns]. The volatile ethyl formate aerosol particles rapidly vaporizes in the ambient air and aerosol “fog” is converted into a vapor. For application in packed fumigation spaces, such as grain silos and shipping containers, the VAPORMATE is preferably vaporized and discharged as a gaseous vapor to improve efficacy and distribution.

Extensive research on ethyl formate has been conducted by CSIRO, Australia who were funded by the Grain Research and Development Corporation (GRDC). 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). Previous 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.

TestSafe Australia [Londonderry Safety Centre, Australia] conducted flammability testing and determined a maximum composition that will remain inert in all proportions of air [VAPORMATE formulation is conservative being less than 75% of this maximum composition].

VAPORMATE has less OH&S issues than existing fumigants eg ethyl formate is 300x less toxic than phosphine. It is expected that VAPORMATE will be granted pesticide registration status in Australia and New Zealand before Year End 2004.

FLAMMABILITY

TestSafe Australia (WorkCover, Londonderry Safety Centre) was commissioned to find the maximum amount of ethyl formate that can be mixed with carbon dioxide whilst still maintaining safe operations below the Lower Explosive Limit [LEL] for all proportions in air. This was determined to be 15 vol%, however a conservative 12.5vol% or ~19wt% was recommended (Ryan and Pearson, 2002). BOC allowed an additional margin for error and formulated VAPORMATE as a 16.7wt% EtF / CO₂ i.e. a 6:1 dilution of EtF with liquid carbon dioxide (equivalent to 11vol% EtF in gaseous CO₂ when vaporised).

FORMULATION

The non-flammable VAPORMATE (Patent Application: PCT/AU03/00087) contains 16.7wt% ethyl formate and is based on BOC Envirosol technology which uses liquid carbon dioxide (CO₂) as a solvent-propellant to dispense chemicals as aerosol particles (size ~5 μ).

The small volatile ethyl formate aerosol particles vaporise in ambient air and the “fog” is converted to a vapour. However for packed fumigation spaces the VAPORMATE is vaporised prior to discharge into the space to improve efficacy and distribution.

EFFICACY

In addition to eliminating flammability, the synergistic effects of CO₂ enhance the efficacy of the ethyl formate. The effect of carbon dioxide on ethyl formate toxicity is variable depending on species and life stage eg the mortality in *Tribolium castaneum* due to ethyl formate increased from 3 to 99% in the presence of the fumigant and 5% carbon dioxide (Victoria Haritos, CSIRO).

VAPORMATE as a product would not exist without the innovation and research efforts of CSIRO Division of Entomology, Stored Grain Research Laboratory [SGRL]. CSIRO has published widely on the efficacy of ethyl formate / VAPORMATETM (see examples of published paper in the Reference). CSIRO state “EtF works quickly, making it potentially useful for rapid disinfestation”.

CSIRO report:

- very high levels of control (>99%) of all stages of tolerant stored grain insects at exposure times of 3 h except the rice weevil which achieves only moderate level of control (82-89%).
- a single application of 70 g m⁻³ ethyl formate (420 gm⁻³ of formulation) is sufficient to obtain high level control (>99%) of all stages of *T. castaneum* and *Rhizopertha dominica* when grain is held for 24 h. *Sitophilus oryzae* is moderately controlled (84%) at this combination of concentration and exposure time
- very high levels of control of *S. oryzae* can be achieved with a single treatment at 156 g m⁻³ EF (940 g m⁻³ formulation) held for 72 h.

- contrary to expectations, lowering the grain temperature to 15°C did not effect efficacy of VAPORMATE™ as an application of 62 g m⁻³ EF (370 g m⁻³ formulation) at 15°C achieved very similar mortality to an application of 63 or 75 EF g m⁻³ at 25°C.
- In the presence of a light infestation of *S. oryzae*, the lower rate of application 70 g m⁻³ (420 g m⁻³ VAPORMATE™ formulation) held for 24 h would be sufficient to greatly reduce the insect load in the grain. At heavy infestations of *S. oryzae*, the higher rate of 156 g m⁻³ (940 g m⁻³ formulation) should be used for high level control.

REGISTRATION AS A PESTICIDE

It is expected that VAPORMATE will be granted pesticide registration status in Australia and New Zealand before the end of 2004.

The draft label under consideration is shown in:

- **Appendix 1:** Current Draft APVMA label – poison schedule and product name
- **Appendix 2:** Current Draft APVMA label – directions for use.

The proposed future modified label to be submitted is shown in:

- **Appendix 3:** Proposed revised future label – directions for use.

MARKETS

The initial markets are seen to be on-farm silo fumigation; treatment of fresh produce before export and quarantine treatment of imported fresh produce and equipment. Ongoing trials are being conducted to extend the existing range of fresh produce (eg flowers, sweet corn) and initial test indicate a niche application in Public Health Pest Control (cockroaches in kitchen cupboards etc).

APPLICATIONS

The sorption and penetration of ethyl formate has been extensively studied at CSIRO Entomology. As the result of this study ‘forced flow fumigation’ was developed to apply VAPORMATE™, in which the fumigant is introduced into a sealed silo by tubing attached directly from the cylinder and vaporiser and introduced into an enclosed stream of air generated by an aeration fan, and at required rate to achieve homogenous concentration and penetration. Aeration systems are commonly installed on farm silos to cool the grain and suppress insect populations. This is shown in:

- **Appendix 4:** Application of VAPORMATE™ into sealed silo (CSIRO, SGRL):

REFERENCES

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Appendix 1: Current Draft APVMA label – poison schedule and product name.

POISON

KEEP OUT OF THE REACH OF CHILDREN
READ SAFETY DIRECTIONS BEFORE USE

VAPORMATE

ACTIVE CONSTITUENT: 166.7g/kg ETHYL FORMATE

VAPORMATE is a non-flammable liquid ethyl formate and carbon dioxide fumigant gas mixture for the control of insect pests in dried stored product and fresh produce. For use by Professional and registered fumigators as specified in Directions for Use table.

Net Weight: 31 kg

BOC Limited A.B.N. 95 000 029 729
10 Julius Avenue, North Ryde NSW 2113

Approval No: 56186/

Appendix 2: Current Draft APVMA label – directions for use.

DIRECTIONS FOR USE

RESTRAINTS

Treatment Temperature: Produce temperature must be > 15°C

VAPORMATE Dosage

Situation	Insects	Application rate	Critical Comments
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 ³ , 24 hours exposure	<p>Only apply VAPORMATE with BOC LIMITED approved equipment.</p> <p>Only apply VAPORMATE into a gastight closed system for the exposure time period.</p> <p>VAPORMATE will control stored product and related pests (see dosage table below) and is best vaporised into a gastight enclosure to allow the volatile ethyl formate active ingredient to penetrate deep into the commodity being treated for the recommended exposure period. The storage volume (m³) needs to be calculated so correct VAPORMATE dose can be accurately dispensed..</p> <p>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 (<100ppm) before out loading or re-entry.</p>

Grain storage premises and equipment especially for use in export grain.	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 ³ , 6 hours exposure	
Horticulture produce – fruit, vegetables, flowers etc.	Pacific spider mite (<i>Tetranychus pacificus</i>), western flower thrips (<i>Frankliniella occidentalis</i>), omnivorous leafroller (<i>Platynota stultana</i>), , aphids (eg: <i>Macrosiphum euphorbiae</i>), mealybugs (Pseudococcus longispinus), black widow spiders (<i>Latrodectus spp.</i>).	420 g/m ³ , 4 hours exposure	

NOT TO BE USED FOR ANY PURPOSE OR IN ANY MANNER
CONTRARY TO THIS LABEL UNLESS AUTHORISED UNDER
APPROPRIATE LEGISLATION

Withholding period: Not required when used as directed [the fumigation chamber must be thoroughly ventilated until ethyl formate vapour is < 100ppm before out loading or re-entry].

Appendix 3: Proposed revised future label – directions for use.

VAPORMATE™ dosage

Insects	Grain Type	Application rate:
Complete control of all stages of: Lesser grain borer (<i>Rhyzopertha dominica</i>), flour beetle (<i>Tribolium castaneum</i>),	Cereal grains and oilseeds	Single application of 660 g m ⁻³ held for 3 h
Complete control of all stages of: Lesser grain borer (<i>Rhyzopertha dominica</i>), flour beetle (<i>Tribolium castaneum</i>), Psocids (various species) [New species to be added]	Cereal grains and oilseeds	Single application of 420 g m ⁻³ held for 24 h
Complete control of all stages of Rice weevil (<i>Sitophilus oryzae</i>)	Cereal grains and oilseeds	Single application of 940 g m ⁻³ held for 72 h

Appendix 4: Application of VAPORMATE™ into sealed silo (CSIRO Entomology, SGRL):

VAPORMATE™ liquid mixture is vaporised before enters into stream of air, provided by an aeration fan as shown in Figure 1. Neat vaporised VAPORMATE™ has 11% ethyl formate in 89% (v/v) of carbon dioxide (or 328 mg/L of EF). This is approximately four times higher than required concentration for most applications, and it needs to be diluted in air. The ratio between VAPORMATE™ vapours and air delivered by fan will determine the application concentration.

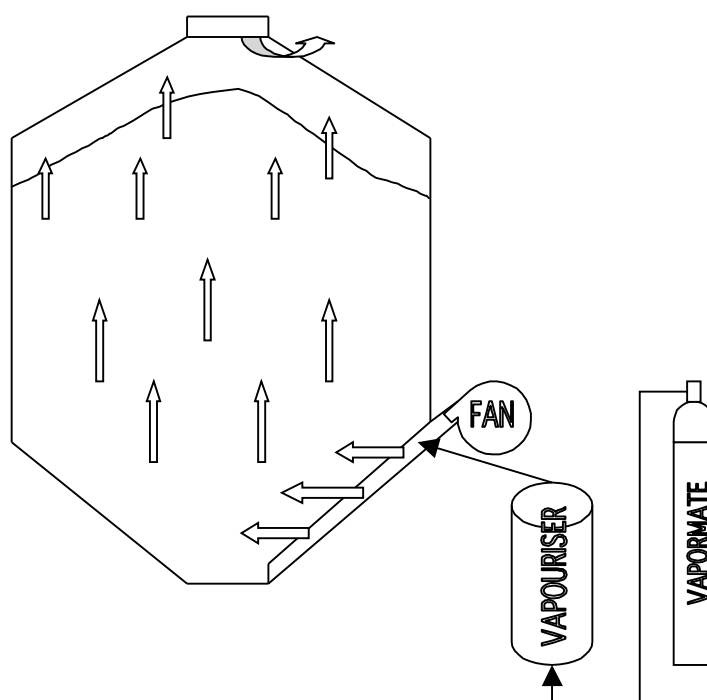


Fig. 1. Application of VAPORMATE to farm silo equipped with an aeration system.

The volume of VAPORMATE™ vapours and air mixture used for fumigations should be equal to the volume of an empty silo. As this will create positive pressure in the silo, the silo must be equipped with top lid for pressure relief. This is the only point where some VAPORMATE™ vapours could be released into atmosphere.

When fumigation is complete, aeration of the grain mass is required to reduce the intergranular concentration to below the TLV levels for ethyl formate and carbon dioxide before grain can be outloaded. The concentration of ethyl formate released after fumigation will be small, as most of it will be sorbed onto grain.