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VAPORMATE™: non-flammable ethyl formate/liquid carbon dioxide fumigant mixture

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Abstract. BOC Envirosol application technology uses liquid carbon dioxide (CO_2) as a solvent/propellant to dispense chemicals as aerosol particles (~5 μm). In addition to eliminating flammability, the synergistic effects of CO_2 enhance the efficacy of the formulated insecticide chemicals. The liquid CO_2 mixture is packaged in industrial gas cylinders fitted with a liquid withdrawal tube.

Non-flammable VAPORMATE™ (BOC patent application PCT/AU03/00087) contains 16.7% by weight ethyl formate dissolved in liquid carbon dioxide solvent/propellant (11% by volume ethyl formate in gaseous CO_2 when vaporised). The historical dried fruit fumigant Eranol contains 98% by weight ethyl formate as the active constituent.

The efficacy of VAPORMATE™ has been investigated by CSIRO, Australia as a grain fumigant ("is safe, efficacious and rapid"), the New Zealand Institute for Crop & Food Research Limited for fruit and vegetable treatment, and University of California, Davis, United States of America for quarantine treatment of imported grapes. Other commercial advantages of VAPORMATE™ include: short exposure time (3–6 hours); potential 'organic' status; is user friendly; can be used in storages that are not sealed to an acceptable level of gas-tightness; and no pesticide residual concerns as it is rapidly hydrolysed to the natural levels of formic acid and ethanol found in foodstuffs.

Pesticide registration application has been lodged with the Australian Pesticides and Veterinary Medicines Authority, the New Zealand Food Safety Authority, and the Fertilizer and Pesticide Authority of the Philippines.

Background

Ethyl formate (EtF) is a historical fumigant of dried fruit. Eranol (98% EtF) is currently registered as a pesticide in Australia through Orica Australia.

Non-flammable VAPORMATE™ (PCT/AU03/00087) contains 16.7% by weight ethyl formate and is based on BOC Envirosol technology which uses liquid carbon dioxide (CO_2) as a solvent/propellant to dispense chemicals as aerosol particles (size ~5 μm). 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 before discharge into the space to improve efficacy and distribution. In addition to eliminating flammability, the synergistic effects of CO_2 enhance the efficacy of the ethyl formate.

VAPORMATE™ efficacy

BOC Limited has been fortunate to take advantage of and to support research being conducted with ethyl formate and the VAPORMATE™ mixture in Australia, New Zealand and the United States of America (USA).

CSIRO Stored Grain Research Laboratory (SGRL) is the leading group and has conducted extensive research on ethyl formate and VAPORMATE™ over the last 5 years with a focus on cereal grain fumigation. A selection of CSIRO publications on ethyl formate efficacy is given in the bibliography. In addition, the following papers are also included in this volume: Haritos et al. (pp. 193–194), Damcevski et al. (pp. 199–204) and Mahon et al. (pp. 205–209).

Much of this research has been funded by the Grains Research and Development Corporation (GRDC). GRDC is a statutory corporation established in 1990 as a partnership between Australia's grain growers and the Commonwealth Government. The GRDC's mandate covers 25 leviable crops—temperate and tropical cereals, oilseeds and pulses. The research investments made by GRDC come from a 1% levy on growers' receipts after each harvest, plus a Commonwealth contribution of up to 0.5% of the gross value of production.

The New Zealand Institute for Crop & Food Research Limited (C&F) has conducted a number of projects on fresh produce, including bananas (two-spotted mite and mealybugs), apples (light-brown apple moth larvae), flowers—calla lilies (western flour thrips and greenhouse thrips), onions (thrips), lettuce (aphids), sweet potato (*Opogona* and tropical armyworm), honey bees (varroa mite) and tissue culture (mites). The issues with fresh produce include both efficacy and phytotoxicity, as

damaged produce is downgraded in value. The C&F banana project will be extended to the Philippines as the bananas are exported from there by DOLE Asia.

In the USA, the University of California, Davis has been funded to conduct research on the fumigation of fresh fruits and vegetables. Discriminating doses have been determined for aphids and western flower thrips (0.2–1% EtF, 1 hour); Pacific spider mite adults (3–4% EtF, 1 h); grape mealybug crawlers and adults (3–4% EtF, 1 h); omnivorous leafroller pupae (4% EtF, 2 h); Pacific spider mite eggs (1.9% EtF, 1 h); thrips eggs (2.4% EtF, 1 h); and grape mealybug eggs (4.7% EtF, 1 h). Concurrently, ethyl formate phytotoxic tolerance levels of some commodities were established and include: table grapes and Bartlett pears (2.4% EtF); strawberry fruit (1.6% EtF); cherries (1.8% EtF); and nuts, including walnuts, almonds and pistachios were not sensitive to ethyl formate.

Flammability

Ethyl formate is a volatile (boiling point = 51°C) and flammable liquid. Dispensing ethyl formate into a large space could result in a destructive explosion.

BOC Limited contracted TestSafe Australia (formerly the Londonderry Safety Centre & Department of Mines) which is expert in the determination of explosive limit testing of gases, flammable vapours and dusts. TestSafe Australia determined the flammability limits of ethyl formate in carbon dioxide. The objective was to find the maximum amount of ethyl formate that can be mixed with carbon dioxide while still maintaining safe operations below the lower explosive limit (LEL) for all proportions in air. The experiment resulted in a conservative 12.5% by volume or ~19% by weight ethyl formate in carbon dioxide. Based on these limits and allowing an additional margin for error, the preferred BOC Limited VAPORMATE™ mixture is 11% by volume or 16.7% by weight, i.e. a 6:1 dilution of ethyl formate with liquid carbon dioxide.

Pesticide registration

VAPORMATE™ has passed preliminary screening by Australian and New Zealand pesticide registration authorities—the Australian Pesticides and Veterinary Medicines Authority and the New Zealand Food Safety Authority, respectively. An experimental use permit (EUP) application has been submitted in the Philippines Food and Pesticide Authority. The recommended VAPORMATE™ dosages provided to the authorities are:

- **cereal grains and oilseeds** = 420 g/m^3, 6 h exposure for adult stages of *Sitophilus oryzae, Rhyzopertha dominica, Tribolium castaneum*, psocids (various species)
- **table grapes and horticultural produce** = 420 g/m^3, 3 h exposure for Pacific spider mite, western flower thrips, omnivorous leafroller, aphids, mealybugs, black widow spiders
- **fresh produce (e.g. bananas), stored products, equipment** = 420 g/m^3, 3 h exposure for quarantine pests.

  Note: the treatment dose of 420 g/m^3 is equivalent to 2.4% EtF and 26% CO_2; treatment temperature must be >15°C, and the withholding period is 7 days for cereal grains.

Acknowledgment

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