OVERVIEW OF ETHYL FORMATE – 85 YEARS AS A FUMIGANT

Robert F. Ryan[1] and C. P. Francis De Lima[2]

[1]VAPORFAZE, PO Box 4, Sans Souci NSW 2219 Australia; robert.ryan.consultant@gmail.com
[2]Principal Research Entomologist, Department of Agriculture, South Perth WA; francis.delima@agric.wa.gov.au

Summary

Among the earliest published information on the use of ethyl formate (EF) was its effectiveness against insects in dried fruits, published in 1925. This was followed up in 1933 with a method for mixing CO_2 with EF to limit flammability. Since 1980 the successful use of EF to fumigate insects infesting stored cereals has been reported in India and Australia. The relatively recent registration of commercial formulations of EF has made it more widely available for use in agriculture. Over the past 12 years ethyl formate has been found effective in controlling a variety of insects in citrus, grapes, strawberries, bananas and sweet corn in addition to stored cereals, pulses and fodder crops. While the initial EF commercial treatment of sultanas has continued over the years, new EF applications have been limited because of high treatment costs with cereal grains and phytotoxic issues with fresh produce. Innovations are required to reduce cereal grain application costs to take advantage of the niche fumigation application of phosphine resistant [*Cryptolestes sp.*] insects in stored grain. While EF treatment cost is not an issue with high value fresh produce, significant R&D is required to determine the "window" which allows treatment efficacy while avoiding any phytotoxicity.

Keywords: ethyl formate, fumigant

INTRODUCTION

The successful use of ethyl formate (EF) was reported in studies to control insect pests in dried fruits and in stored wheat (Neifert *et al*. 1925,Cotton and Roark 1928, Roark and Cotton 1929, Simmons and Fisher, 1954). Shepard *et al*. (1937) found EF more toxic than carbon disulphide to *Tribolium confusum* Duv. and *Sitophilus granarius* L; Vincent *et al*. (1972) found that EF compared favorably to phosphine against insects infesting dates and other dried fruits. Muthu et al. (1984) conducted large-scale tests on cereals, pulses, spices, dried fruits, nuts and dried tubers and recommended EF was a safe general fumigant for stored food. EF was recognized as an effective fumigant for control of insects in several commodities: cereals and pulses (Pruthi and Singh 1945,, CFTRI 1979), clothing (Busvine and Vasuvat 1966, David 1943) and fresh fruit, vegetables and flowers (Aharoni and Stewart 1980, Stewart and Aharoni 1983, Stewart and Mon 1984, Wang 1982). EF was not found to adversely affect the quality or flavor of treated commodities. EF was also found to have fungicidal properties in cereals (Raghunathan *et al* 1974, Deo and Gupta 1986) without affecting viability or germination of the seeds. To minimize potential flammability in air, Jones (1933) established the specific non-flammable mixture range of EF in CO_2 as 1:6 by volume to avoid dangerous explosions. An added benefit of CO_2 is that it accelerates the penetration of insecticides into insect spiracles (Hazelhoff 1928). Cotton and Young (1929) reported that CO_2 increased the toxicity of ethylene dichloride, ethylene oxide, carbon disulfide, and methyl chloroacetate to the confused flour beetle (*T. confusum*) and the rice weevil (*Sitophilus oryzae* L.). CSIRO reported on the rapid action of EF (Damcevski & Annis, 1998); methods to determine natural & residual levels of EF in a range of commodities (Desmarchelier et al, 1999) plus at the Australian Post harvest Technical Conference, Canberra, 2000 (APTC, 2000) CSIRO reported that a EF dose of 80g/m^3 is efficacious for most stored product species but marginal for immature *S. oryzae* (Annis, 2000). Post 2000 there has been increasing growth in EtF application which was given a boost by the commercial availability of the patented Vapormate® – a pre-mix of EF /CO_2 (Ryan & Bishop, 2003)

DRIED FRUIT

Muthu *et al*. (1984) and found that EF had excellent potential as a replacement for methyl bromide in the treatment of durable commodities, noting that the insects pests infesting dried fruits are generally the same as those found in cereal commodities. Hilton and Banks (1996) found that the rate of EF sorption in dried sultanas was independent of concentration but greatly increased with filling ratio and moisture content. Effective control for *Oryzaephilus surinamesis* (L.) *Oryzaephilus Mercator* (Fauvel), *Plodia interpunctella* (Hubner) and *Carpophilus hemipterus* (L.) was obtained in an 8-h fumigation at 541 g.h.m^{-3}. Infestations of *Carpophilus spp*, in dates for which fumigation using methyl bromide is the standard treatment in Israel were controlled using 420g/m^3 Vapormate® (2.3% EF + 19% CO_2) for 12 hours exposure (Finkelman *et al*. 2010).

CEREAL GRAINS

Allen and Desmarchelier (2000) conducted insect bioassay studies in desiccators at 25°C, using a dose of 70g/m^3 of EF with high (75%) and low (35%) humidity and with / without added 7% CO_2 for exposures of 30 minutes. The found that high humidity and addition of 7% CO_2 gave 100% mortality with *Liposcelis entomophila* (Enderlein) (psocids), *O. surinamensis* (sawtoothed grain beetle), *Rhyzopertha dominica* (F.) (lesser grain borer), *S. oryzae* (rice weevil) and *Tribolium. castaneum* (Herbst.) (red flour beetle). No control was achieved of *Trogoderma variabile* (Ballion) (warehouse beetle) at this exposure time. Damcevski and Annis 2000 tested 90g/m^3 EF for 24 hours at 16, 24 and 29°C and found no survivors of *R. dominica* or *T. castaneum* adult or immature stages at 29, 24 and 16°C. However, while no *S. oryzae* adults survived, there were survivors of immature stages at all temperatures. After incubation for 14-21 days there was one adult at the 29°C and 305 adults from 16°C exposure compared to >2000 in the control. Wright et al. (2002) and Ren and Mahon (2003) evaluated EF as a liquid to find an alternative to dichlorvos and phosphine for wheat, sorghum and split faba bean in unsealed farm bins, finding that while residues in sorghum at 10°C persisted significantly longer than at 20°C all residues fell to natural levels without aeration, consistent with results from previous trial with ethyl formate on wheat.

Mahon *et al*. (2003) used a mixture of 26g/m^3 EF + 128g/m^3 CO_2 in a 260m^3 semi-sealed seed store 30% loaded with seeds of barley, wheat and barley with an applied dose of 40kg Vapormate® (BOC Gases Ltd.). Mixed aged *Callosobruchus phaseoli* (Gyllenhal), *T. castaneum, R. dominica, S. oryzae, Oryzaephillus spp., Cryptolestes spp.* and psocids were all controlled. EF residues declined to natural levels and the treatment had no adverse effect on germination of the treated seeds. During fumigation the EF concentrations in the adjacent untreated stores and 1-3m from the front door of the fumigated store ranged from 5 to 25ppm, far lower than the TLV (100ppm). Haritos *et al*. (2006) evaluated EF as an alternative fumigant to methyl bromide (ozone-depleting) and phosphine (insect resistance) for stored grain. They found that combining 5 to 20% CO_2 with EF doses significantly enhanced efficacy against the rice weevil (*S. oryzae* L), the lesser grain borer (*R. dominica* F) and the flour beetle (*T. castaneum*). Mortality in 3h exposures of mixed stage cultures were 99.8% for *T. castaneum* and 95.1% for *S. oryzae* with applied EF doses of 111 and 185 mg.h litre^{-1} respectively. They concluded that the combination of CO_2 with EF enhances the distribution and efficacy of the fumigant against stored grain insects. Fifty tonne silos (Haritos 2005 and Haritos et al. 2003) were chosen for efficacy studies in field trials. Insects were selected based on the frequency found in storages, economic damage caused and known tolerance to insecticidal treatments. Phosphine resistant field strains of *R. dominica*, *T. castaneum* and *S. oryzae*, in mixed stage cultures (eggs, larvae, pupae and adults), were exposed to EF+ CO_2 and showed virtually 100% mortality across four trials at a range of temperatures (28 - 30°C) and moisture contents (10.7 -11.7%). Based on these studies, the recommended rate for the complete control of all stages of the lesser grain borer, *R. dominica*; flour beetle, *T. castaneum* and Psocids (various species) was recommended as 70g/m^3 EF for 24 hour exposure. In large scale trials (Allen and Desmarchelier 2000) to disinfest empty silos of psocids *Liposcelis spp* at Grain Export Terminals in Newcastle, NSW and Fisherman's Island, Queensland, EF was applied to the "partially-sealed" silos grain sampling system by on-site mixing and vaporizing the EF liquid in a stream of CO_2. This treatment gave 100% mortality of *Liposcelis spp* and no residues of EF could be detected in grain travelling through the sampling path in equipment following treatment.

STRAWBERRY FRUIT

Ethyl formate was used in concentrations from 0.8 to 2.4% (24 - 72g/m^3) to control western flower thrips *Frankliniella occidentalis* (Pergande), and two-spotted spider mites *Tetranychus urticae* (Koch) in strawberry fruit (Simpson et al. 2004). EF effectively controlled western flower thrips but not two-spotted spider mite. None of the dosages applied affected affect strawberry fruit quality. However combined treatment of EF + 10% CO_2 increased mite mortality significantly but did not result in complete control in the 1 hour exposure times tested.

BANANAS

Ethyl formate was successfully used in the disinfestation of bananas exported from the Philippines (Krishna *et al.* 2005). After several trials 80g/m^3 of EF + CO_2 (Vapormate®) equivalent to 2.6% EF and 24% CO_2 was found to control mites, mealybugs and soft scale. In laboratory and field trials, these pests were eliminated when EF was applied into the plastic liner covering banana hands prior to chilling.

GRAPES

Arthropods commonly infest table grapes in California. Simpson *et al*. (2007) successfully used EF in combination with CO_2 to control of all life stages of Western flower thrips, *F. occidentalis*, Grape mealybug, *Pseudococcus maritimus* (Ehrhorn), Pacific spider mite, *Tetranychus pacificus* (McGregor) and the omnivorous leafroller, *Platynota stultana* (Washington). The EF doses used ranged from 0.07% - 3.48%, and the addition of 10% CO_2 achieved LC_{99} in 1-2 hours exposure periods for all insects except spider mites. De Lima (2010a) used mixtures of EF + CO_2 for the control of light brown apple moth, *Epiphyas postvittana* (Walker) in freshly harvested table grapes for export during the cool down process directly after harvest as well as during pre-chilling in the cold room to cover the major events in the table grape cool chain process. De Lima used a range of conditions: CO_2 from 12 - 20%, temperatures from 10°C – 20°C, exposure times of 3-4 hours and EF concentrations of 30-52g/m^3 to achieve probit 9 level of control. De Lima (2010b) developed a quarantine treatment data package for registration of new label rates for use of Vapormate® in table grapes against light brown apple moth *E. postvittana* , redback spiders *Latrodectus hasselti* (Thorell), long-tailed mealybugs *Pseudococcus longispinus* (Targioni-Tozzetti), two spotted spider mite *T. urticae* (plague thrips *Thrips imaginis* (Bagnall) and western flower thrips (*F. occidentalis*). Tests were carried out at 5, 10, 15, 20 and 25°C in the laboratory using pure technical grade product, and using commercial product Vapormate® (BOC Gases Ltd) in 20ft / 6m (28 m3) and 40ft/12m (68m^3) ISO refrigerated shipping containers and in commercial licensed fumigation chambers. Successful quarantine treatments (Probit 9 = 99.9968% efficacy) were achieved during the chilling process using doses from 16 to 52g/m^3 based on pest species, treatment temperature and exposure time. The studies showed that fumigation of Red Globe, Thompson Seedless and Crimson Seedless with EF+ CO_2 did not adversely affect fruit quality.

CITRUS

Complete control of bean thrips in Navel oranges was obtained by using EF in a simulation of a commercial fumigation with a 20ft marine container using a concentration of 1% EF and exposing 6,000 bean thrips for 1 hour to give 100% mortality (Mitcham 2011). Waxed citrus exposed to to 2% EF dose was found in good condition even after 5 weeks of cold storage and simulated retail handling. De Lima (2011a) conducted laboratory and large scale trials to develop quarantine treatment data packages for registration of new label rates for citrus using Vapormate®. EF+ CO_2 mixtures were tested against Fuller's rose weevil *Asynonychus cervinus* (Boheman), light brown apple moth *E. postvittana*, longtail mealybug *P. longispinus*, and citrus mealybug *Planococcus citri* (Risso). Successful quarantine treatments were achieved using doses between 10 and 55g/m^3 ethyl formate + >10% CO_2 (60 – 330g/m^3 Vapormate®) based on pest species, treatment temperature and exposure time in Navel oranges, Rio grapefruit and Imperial mandarins.

SWEET CORN

To obtain fumigation treatments that do not damage produce, while providing control in the shortest possible period over a range of temperatures that fit within the cool chain process, De Lima (2011b) developed new label rates for Vapormate® against several insect pests in sweet corn. The insects successfully controlled were: cotton bollworm or corn earworm, *Helicoverpa armigera* (Hubner) (cotton bollworm), *Helicoverpa. punctigera* (Wallengren)native budworm) or, two spotted spider mite *T. urticae*, plague thrips *T. imaginis*, western flower thrips *F. occidentalis*, green peach aphid *Myzus persicae* (Sulzer) and corn aphid *Rhopalosiphum maidis* (Fitch). Effective doses for 4 hour fumigation treatments were 30, 40 and 44 g/m^3 ethyl formate + >10% CO_2 (180 – 264g/m^3 Vapormate®) at >21, >15 and >10°C respectively.

BALED HAY

Insects infesting hay fodder exported to Japan were disinfested using laboratory and field research into EF+ CO_2 mixtures (De Lima 2006). In fumigating 67m^3 shipping containers filled with approximately 30 tonnes of compressed hay bales Vapormate® (BOC Gases Ltd) was applied at the rate of 720 g/m^3 (26% CO_2 + EF120 g/m^3) for 24 h in the winter temperature range of 8 to 19°C. All stages of *Sitophilus* spp. and *T. castaneum* (>12,000 of each spp.) placed in vials in the hay bulk were killed. The final free gas concentration (58g/m^3 EF +8% CO_2) was sufficient to provide longer-term protection from re-infestation in transit.

SYNERGY OF CO_2 AND ETHYL FORMATE

The effect of CO_2 on EF efficacy was reported by Haritos *et al*. (2006) wherein EF at 12.5g/m^3 and no added CO_2 resulted in 3, 82 and 91% mortality from 200 adult *T. castaneum*, *S. oryzae* and *R. dominica* respectively; but when combined with 5% CO_2 the mortality for each species increased to 99.5, 100 and 100% respectively. Adding 10 and 20% CO_2 to EF resulted in 100% mortality of all species, indicating that there was no antagonism at high CO_2 concentrations. No insect mortality was observed from exposure to 5, 10 and 20% CO_2 in the absence of EF. Potentiation of EF by CO_2 was found by De

Lima (2006) to vary with species, with up to 27% increase in mortality for aphids, thrips *T. castaneum*, and light brown apple moth in the presence of >10 <15% CO_2; while up to 22% increase in mortality was observed for red back spiders, two spotted spider mite, Fullers rose weevil *Sitophilus* spp. and *Helicoverpa* spp. in the presence of >15% CO_2. No mortality occurred in insects in 4 hour exposures to 20% CO_2. Mealybugs were found to be so susceptible to EF gas alone that 6g/m^3 EF without added CO_2 was sufficient to give 100% mortality within an exposure period of 30 minutes at 10°C. In large scale trials using Vapormate® (De Lima 2006, 2010b, 2011a, 2011b) the accumulation of CO_2 in the free air space of the refrigerated 20 or 40 ft shipping container was always greater than 10% and often over 20% CO_2. Depending on quantity of product applied the EF to CO_2 ratio in air was >1:8.4.

PRE-MIX & ON-SITE MIXING OF ETHYL FORMATE AND CO_2

The solvent-propellant properties of liquid CO_2 was the basis of a patent (Ryan *et al*. 1978) where active liquid constituents are dissolved in liquid CO_2 at high pressure (50 bar) and contained in an industrial high pressure gas cylinder fitted with a "dip" tube to enable withdrawal of the liquid mixture. Pre-mixing EF and CO_2 as liquids produces a non-flammable, self-propelled and ready to use mixture. On-site mixing, a common practice with liquid insecticides, also has benefits with fumigants. On-site mixing with CO_2 has advantages of choice selection of the active constituent and flexibility in the selection of the ratio of EF to CO_2 required to optimise efficacy. Carbon dioxide has a synergistic effect with other fumigants and reduces flammability. The general consensus on the optimal amount of CO_2 to improve efficacy is in the range of 5% - 20% (Ryan and Shore 2010). In the early development of fumigant application methods, Jones (1933) noted the benefits of CO_2 to overcome flammability of potential fumigants including ethylene oxide (12.2% CO_2), ethyl formate (14.4% CO_2) and propylene oxide (8.3% CO_2). The results of on-site mixing and vaporizing EF liquid into a stream of CO_2 in trials at Grain Export Terminals at Newcastle, NSW and Fisherman's Island, QLD were reported by Allen and Desmarchelier (2000). These trials achieved 100% mortality of *Liposcelis spp* (psocids: the target species) and left no residues on grain travelling through the equipment following treatment.

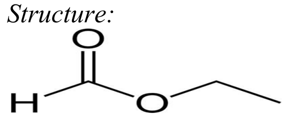
GENERAL USE INFORMATION

(Merck Index 1989).

Summary of Important Chemical and Physical Properties

Ethyl formate is an ester formed when ethanol (an alcohol) reacts with formic acid (a carboxylic acid). Ethyl formate has the characteristic smell of rum and is partly responsible for the flavor of raspberries. It is "Generally Recognized As Safe" [GRAS] by the U.S. Food and Drug Administration.

Structure:



[Formula: $C_3H_6O_2$]

Synonyms: Ethyl methanoate; formic acid ethyl ester; ethyl formic ester; formic ether.

Identifiers: CAS No.: 109-94-4; RTECS No.: LQ8400000; DOT UN: 1190 26

DOT label: Flammable Liquid (it is highly flammable and poses a dangerous fire and explosion risk).

Molecular weight: 74.1; Boiling point (at 760 mm Hg): 54.3^{o}C; Specific gravity (water = 1): 0.92 at 20^{o}C

Vapor density: 2.6; Vapor pressure at 20^{o}C: 194 mm Hg; Solubility: Soluble in water with some hydrolysis; miscible with alcohol, benzene, and ether; Reactivity: Unstable in heat or flame; readily hydrolyzes to the acid and the alcohol; Incompatibilities: reacts with nitrates, strong oxidizers, strong alkalis and strong acids; No Hazardous decomposition products reported; Flammability: assigned a flammability rating of 3 (severe fire hazard); Flash point: minus, -20^{o}C (closed cup); Auto ignition temperature: 455^{o}C; Flammable limits in air: 2.8% to 16.0%.

Occupational Safety and Health Guidelines

According to the U.S Occupational Safety and Health Administration (OSHA), ethyl formate can irritate eyes, skin, mucous membranes, and the respiratory system of humans and other animals; it is also a central nervous system depressant. In industry, it is used as a solvent for cellulose nitrate, cellulose acetate, oils, and greases. It can be used as a substitute for acetone. The current exposure limit for ethyl formate is 100 ppm [300 mg/m^3: OSHA PEL; NIOSH REL; ACGIH TLV]. There are also issues of risks to eyes, nasal irritation and narcosis in animals at high concentrations.

Natural Occurrence of Ethyl Formate

EF and formic acid are present naturally in a variety of plant and animal products, such food grains, fruits, vegetables, beer, wine and spirits, tuna, meat, mussels, cheese and bread (Desmarchelier 1999). In newly harvested wheat, barley, oats and canola natural levels of EF in stored crop varied from 0.5 to 2 mg/kg with commodity, temperature, moisture and period of storage ranging. The EF present in grains at harvest, increased during the first 4-5 months of storage, and then began to decline, particularly for grain temperatures higher than 20^oC and moisture content higher than 9.5% (Ren and Desmarchelier 2000). EF is used commercially in the manufacture of artificial rum, as a flavor for lemonade and essences, as a fungicide and as an organic solvent (Merck Index 1989).

Registered Product

Registration of EF with the Australian Pesticide & Veterinary Medicines Authority (APVMA):

1. *VAPORMATE®* (APVMA Approval No. 56186 – BOC Gases: 16.7% EF in 83.3% CO_2 w/w)
2. *ERANOL®* (APVMA Approval No. 51232 – ORICA: 98% EF w/w).
3. *eMate®* (APVMA Approval No. 64944 – VAPORFAZE: 98% EF w/w).

Note: ERANOL® and eMate® can be mixed on-site with CO_2 to dispense EF as a non-flammable gaseous mixture. In addition to eliminating flammability, the synergistic CO_2 enhances efficacy.

GENERAL CONCLUSIONS

Ethyl formate is a safe and effective alternative to methyl bromide for quarantine treatment of farm produce. Although EF is a natural product, it is toxic to insects and in its pure form it requires to be handled with care. It is much safer for human use than methyl bromide . In Australia EF registration as a 98% pure product and as a mixture with CO_2 enables it to be used with more versatility for commercial applications in grain storage and in horticulture.

REFERENCES

Aharoni, Y. and Stewart, J.K. (1980). Thrips mortality and strawberry quality after vacuum fumigation with acetaldehyde or ethyl formate. *Journal of American Society of Horticulture*. **105**: 926-929.

Allen, S.E. and Desmarchelier, J.M. (2000). Ethyl formate as a fast fumigant for disinfestations of sampling equipment at grain export terminals. In: Wright, E.J. H.J. Banks,H.J. and Highley, E (eds), *Proceedings of the Australian Postharvest Technical Conference 2000*,, CSIRO Entomology, Canberra , ACT, Australia,

Annis, P.C. (2000). Ethyl formate – where are we up to? In: Wright, E.J, Banks, H.J and Highley, E. (eds), *Proceedings of the Australian Postharvest Technical Conference 2000*, CSIRO Entomology, Canberra , ACT, Australia.

Busvine, J.R. and Vasuvat, C. (1966). A simple fumigation method for disinfecting clothing or bedding containing body lice. *Journal of Hygiene*. **64**: 45-51.

CFTRI (Central Food Technological Research Institute). (1979). Consolidated report on the evaluation of ethyl and methyl formate as stored product fumigants, Mysore, India.

Cotton, R.T. and Roark, R.C. (1928). Fumigation of stored products with certain alkyl and alkylene formates. *Industrial and Engineering Chemistry* **20**: 380.

Cotton, R.T. and Young, H.D. (1929). The use of carbon dioxide to increase the insecticidal efficacy of fumigants. *Proceedings of the Entomological Society of Washington.,* **31**: 97.

Damceveski, K.A. and Annis, P.C. (1998). Two old fumigants for the new millennium. In: Zalucki, MP., Drew, R.A.I. and White, G.G. (eds) , *Pest Management – future challenges*. *Proceeding of the 6th Australasian Applied Entomological Research Conference*, Brisbane, Australia. Univ. of Q, **2**: 307.

Damcevski, K.A. and Annis, P.C. (2000). The Response of three stored product insect species to ethyl formate vapour at different temperatures. In: Wright, E.J., Banks, H.J and Highley, E (eds.), *Proceedings of the Australian Postharvest Technical Conference 2000*CSIRO Entomology, Canberra , ACT, Australia.

David, W.A. 1(943). Delousing of clothing by fumigation. *British Medical Journal* **4307**: 108

De Lima, C. P. F. (2006). Effect of ethyl formate & propylene oxide on *Sitophilus oryzae* (L.) and *Tribolium castaneum* (Herbst) at 10°C and 20°C. *Proceedings of the Australian Postharvest Technical Conference*, CSIRO SGRL, Perth, July 2006.

De Lima, F. (2010a.). Ethyl formate + CO_2 Fumigation of Table Grapes for Light Brown Apple Moth. 2010 *Annual International Research Conference on Methyl Bromide Alternatives and Emission Reductions*, Orlando, Florida USA.pp?

De Lima, C. P. F. (2010b). Fumigation of table grapes for export. Final project report TG04003. Horticulture Australia Limited. 2010. 52p.

De Lima, C. P. F. (2011a). Fumigation of citrus for access to China. Final project report CT07046. Horticulture Australia Limited. 2011. 33p.

De Lima, C. P. F. (2011b). Disinfestation of sweet corn for export using phosphine and controlled atmospheres. Final project report VG01014. Horticulture Australia Limited. 2011. 32p.

Deo, P.P. and Gupta, J.S. (1986). Further studies on prevention of storage moulds of grain by application of chemicals. *Pesticide* **20**: 43-46

Desmarchelier, J.M. (1999). Ethyl formate and formic acid: occurrence and environmental fate. *Postharvest News and Information* **10**: 7N-12N.

Desmarchelier, J.M., Johnston, F.M. and Vu, L.T. (1999). Ethyl formate, formic acid and ethanol in air, wheat, barley & sultanas: analysis of natural levels & fumigant residues. *Pesticide Science* **55**: 815-824.

Finkelman, S., Lender, E., Navarro, S., Navarro, H. and Ashbell, G. (2010). New prospects for ethyl formate as a fumigant for the date industry, 10th *International Working Conference on Stored Product Protection*, Estoril, Portugal 27 June – 2 July.

Haritos, V.S. (2005). A new fumigant for stored grain. *Australian Grain* July-August: 21-24.

Haritos, V.S. Damcevski, K.A. and Dojchinov, G. (2003). Toxicological and regulatory information supporting the registration of VAPORMATE as a grain fumigant for farm storages, In: Wright, E.J., Webb M.C. and Highley, E. (eds.) Stored grain in Australia 2003. *Proceedings of the Australian Postharvest Technical Conference*, CSIRO SGRL, Canberra, 25-27 June.

Haritos, V.S., Damcevski, K.A. and Dojchinov, G. (2006). Improved efficacy of ethyl formate against stored grain insects by combination with carbon dioxide in a "dynamic" application. *Pest Management Science* **62**:325-333.

Hazelhoff, E.H. (1928). Carbon dioxide a chemical accelerating the penetration of respiratory insecticides into the tracheal system by keeping open the tracheal valves. *Journal of Economic Entomology*, **21:**790.

Hilton, S.J. and Banks, H.J. (1996). Ethyl formate as a fumigant of sultanas: sorption and efficacy against six pest species. In: Donahaye, E.J., Navarro, S., Varnava, A. (eds.) *Proceedings of the International conference on Controlled Atmosphere and fumigation in Stored Products*, Nicosia, Cyprus, 21-26 April 1996. Printco Ltd, Cyprus, pp. 409-422.

Jones, R.M. (1933). Reducing Inflammability of Fumigants with Carbon Dioxide. *Industrial and Engineering Chemistry* **25**: 394-396.

Krishna, H., Ryan, R.F., Munez, A., Hirst, G., Yoshihara, H. and Barton, S. (2005). VAPORMATE: Disinfestation of Philippine Export Bananas, *2005 Annual International Research Conference on Methyl Bromide Alternatives and Emissions Reduction*, San Diego California USA, 31 Oct - 3 Nov., pp. 119-121.

Mahon, D., Ren, Y.L. and Burrill, P.R. (2003). Seed store disinfestations with VAPORMATE [EF + CO_2]. In: Wright, E.J., Webb M.C. and Highley, E. (eds.), Stored grain in Australia (2003). *Proceedings of the Australian Postharvest Technical Conference*, CSIRO SGRL, Canberra, 25-27 June.

Merck Index, (1989). *An Encyclopedia of Chemicals, Drugs and Biologicals*, Merck and Co., Rahway, NJ, USA 600pp.

Mitcham, E.J. (2011). Preliminary report on VAPORMATE fumigation controls bean thrips in navel oranges. http://research.citrusrdf.org/reports/2011/02/11/bean_thrips_quarterly-report-FL_Citrus_2010.pdf

Muthu, M., Rajenderan, S., Krishnamurthy, T.S., Narasimhan, K.S., Rangaswamy, J.R. Jayaram, M. and Majumder, S.K. (1984). Ethyl formate as a safe general fumigant. In: Ripp, B.E. (ed), *Proc. Int. Conf. on Practical Aspects of Controlled Atmosphere and Fumigation in Grain Storages*, Perth, Australia, 11-12 April 1983, 369-293.

Neifert, I.E., Cook, F.C., Roark, R.C., Tonkin, W.H., Back, E.A and Cotton, R.T. (1925). Fumigation against grain weevils with various volatile organic compounds. *U.S. Department of Agriculture Bulletin* **1313**: 40.

Pruthi, H.S. and Singh, M. (1945). Stored grain pests and their control. *Imperial Council for Agricultural Research Miscellaneous Bulletin* No. 57.

Raghunathan, A.M., Muthu, M.S. and Majumder, S.K. (1974). Further studies on the control of internal fungi of sorghum by fumigation.. *Food Science Technology* **11**: 80-81

Roark, R.C. and Cotton, R.T. (1929). Tests of various aliphatic compounds as fumigants. *U.S. Department. Agriculture Technical Bulletin* **162**: 52.

Ren, Y.L. and Desmarchelier, J.M. (2000). Natural occurrence of ethyl formate and carbonyl sulfide in grains. *International Conference on Controlled Atmosphere and Fumigation in Stored Products*, Fresno California USA, October 29 – November 3.

Ren, Y. and Mahon, D. (2003). Field trials on ethyl formate for fumigation of on-farm storage. In: Wright, E.J. Webb, M.C. and Highley, E. (eds.), *Stored grain in Australia 2003. Proceedings of the Australian Postharvest Technical Conference*, CSIRO SGRL, Canberra, 25-27 June.

Ryan, R.F. and Bishop S.R. (2003). "Fumigant formulation" Australia Patent No. AU 2003201533 B2. Date of filing 28/1/2003 (Priority Data: PS 0158; 25/01/2002).

Ryan, R.F., Catchpoole, D. and Shervington, E. (1978). Pesticide Distribution System, Australian Patent 494,198:26 June.

Ryan, R.F and Shore, W.P. (2010). Pre-Mix and on-site mixing of fumigants. *10th International Working Conference on Stored Product Protection*, Estoril, Portugal 27 June – 2 July.

Shepard, H.H., Lindgren, D.L. and Thomas, E.I. (1937). The relative toxicity of insect fumigants. University of Minnesota. Agricultiural. Experiment. Station Technical. Bulletin. **120**: 23.

Simmons, P. and Fisher, C.K. (1945). Ethyl formate and isopropyl formate as fumigants for packages of dry fruits. *Journal of Economic. Entomology* **39**: 715.

Simpson, T., Bikoba, V. and Mitcham, E.J. (2004). Effects of ethyl formate on fruit quality and target pest mortality for harvested strawberries. *Postharvest Biology and Technology* **34**: 313-319.

Simpson, T., Bikoba, V., Tipping, C., Mitcham, E.J. (2007). Ethyl Formate as a Postharvest Fumigant for Selected Table Grapes, *Journal of Economic Entomology* **100:** 1084-1090.

Stewart, J.K. and Aharoni, Y. (1983). Vacuum fumigation with ethyl formate to control the green peach aphid in packaged head lettuce. *Journal of the American Society of Horticultural Science* **108** : 295-298.

Stewart, J.K. and Mon, T.R. (1984). Commercial-scale vacuum fumigation with ethyl formate for postharvest control of the green peach aphid (Homoptera: Aphididae) on film-wrapped lettuce. *Journal of Economic Entomology* **77**: 569-573.

Vincent, L.E. and Lindgren, D.L. (1972). Hydrogen phosphide and ethyl formate: Fumigation of insects infesting dates and other dried fruits. *Journal of Economic Entomology* **65**: 1667.

Wang, C. (1982). Chemical control of insects on chrysanthemum cutflowers. *Journal of Agricultural Research China* **31**: 339-346.

Wright, E.J., Ren, Y.L. and Mahon, D. (2002). Field trials on ethyl formate for on-farm storage fumigation. In: *Proceedings of 2002 Annual International Research Conference on Methyl Bromide alternatives and Emissions Reductions*, November 6-8, Orlando Florida, USA, pp. 55.