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Sterigas™ and Cosmic™: update on proposed new fumigants

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Abstract

Sterigas (EthanediNitrile, EDN = C_2N_2) is a new environmentally-safe fumigant with initial focus on control of pathogens, weeds and insects in soil; control of timber pests in export logs and timber and the devitalisation of imported grains (sterilisation of grain and weed seeds plus elimination of any pathogens). At low doses Sterigas is effective against common stored product pests and is an alternative methyl bromide alternative. Cosmic (Carbonyl sulphide, COS) initial focus is a grain fumigant for use in phosphine resistance strategy. CSIRO (Commonwealth Scientific and Industrial Research Organisation - an Australian Government R&D organisation) and the international industrial gas company BOC Limited signed an agreement (2 September 2004) to globally market the new CSIRO patented Sterigas and Cosmic fumigants. CSIRO is supplying BOC with efficacy and related data for to assist in the global registration of these new pesticides (pesticide registration application was submitted for Sterigas and Cosmic to the Australian Pesticide and Veterinary Medicines Authority, June 2005).

Sterigas Draft Label Applications

Devitalise grains and weed seeds + sterilise pathogens: - 115 g/m^3 for 5 d exposure

Timber and logs for export - 50 g/m^3, 6 h exposure

Strawberries runners and fruit growing - 500 kg/ha for 24 h.

Cosmic Draft Label Applications

All life stages of stored grain insects - 32 g/m^3 for 24 h

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

Introduction

Sterigas (EDN) and Cosmic (COS) are BOC trade names for new fumigants identified, patented and researched by CSIRO Division of Entomology. BOC Limited has an exclusive global licence to market both these new fumigants and has made application for pesticide registration in Australia (June 2005).

Methyl bromide, the world's most widely used fumigant, has been classified by the Montreal Protocol as an Ozone Depleting Product (ODP) and a phased reduction is in place. With the exception of Quarantine and Pre-Shipment (QPS), the Montreal Protocol dictates the use of methyl bromide for fumigation in developed countries must have been phased out by January 2005. The total consumption of methyl bromide in 2000 was estimated at 75,203 tonnes (source: TEAP Report, April 2001) and approximately 80 % was used for soil and timber fumigation treatment.

Sterigas™ 1000 Fumigant (Active Constituent: 1,000 g/kg Ethanedinitrile)

Ethane DiNitrile (EDN):

Ethane DiNitrile (EDN = C_2N_2 = cyanogen)

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is a potential replacement for methyl bromide. CSIRO currently hold patents for use of EDN as a fumigant in the major worldwide markets. These patents are valid until 2014. BOC has signed an exclusive global license agreement with CSIRO's Division of Entomology for EDN. Initial focus for application of EDN is as a soil, timber fumigant and grain sterilant. Once registration is obtained further markets may be able to be exploited, examples include: Stored product fumigation of grains, fruits, nuts and spices; Fruit sterilisation for export; Quarantine and Pre-Shipment (QPS)

Comparative Laboratory test toxicity examples (LC_{95} mg/h/L) highlight the superior efficacy of EDN.

Soil insect (whitefringed weevil) - 50 mg/h/L (C_2N_2); 135 mg/h/L(CH_3Br)

Nematode - 40 mg/h/L (C_2N_2); 100 mg/h/L (CH_3Br)

Fungus (Rhizoctonia) - 8 mg/h/L (C_2N_2); 55 mg/h/L(CH_3Br)

Timber studies on the toxicity to five species of timber or wood related Coleoptera and Isoptera were reported by Dowsett and Ren. Exposure for 6 hours to EDN at 21-25 ^oC, the adult stage of *Rhyzopertha dominica* was completely killed at 1.4 g/m^3 (0.06 %), all the larval stages of *Anoplophora glabripennis* were completely killed at 11 g/m^3 (0.5 %) and workers of *Coptotermes acinaciformis, Cryptotermes brevis* and *Mastotermes darwiniensis* were completely killed at 1.61 g/m^3 (0.07 %), 3.0 g/m^3 (0.14 %) and 2.3 g/m^3 (0.11 %) respectively. In general, EDN showed high toxicity to all immature and adult stages tested and in this respect is more toxic than methyl bromide and sulfuryl fluoride (1ppm = 2.16 mg/m^3).

Non-Flammable Formulation

EDN is a very flammable liquefied gas with a flammability range of 6-32 % by volume. While the flammable Sterigas 1000 Fumigant (Active Constituent 1000 g/kg Ethanedinitrile) can be accommodated in the agricultural environment, there is a preference for non-flammable formulations in many industrial applications. To cater for this a non-flammable mixture of EDN in liquid carbon dioxide has been developed. This mixture has been conservatively set at 20 wt% EDN in CO_2 - hence the product: Sterigas 200 Non-Flammable Fumigant (Active Constituent 200 g/kg Ethanedinitrile).

Devitalisation of grain: overview

The Meat and Livestock Association (MLA) membership are active in commercial feed lots where cattle are fed grain. The grain used in feedlots amount to 2.5 million tonne pa and during droughts there is a need to import grain. The requirements for importing are strict especially when grain needs to be transported into the countryside where the feedlots are located. The requirement is the devitalisation of grain & weed seeds and elimination of pathogens. MLA funded the R&D required to prove that this task can be performed using EDN. CSIRO Division of Entomology conducted this research and determined that devitalisation of grain & weed seeds and elimination of pathogens require a Ct of 13,800 g h/m^3 or 115 g/m^3 in the grain store for 5 days.

EDN commercial issues

There are a number of commercial issues including – Manufacture and Supply:

Need to secure a supply of EDN as there is no known global tonnage plant manufacturer. BOC is currently negotiating a commercial deal with a large chemical manufacturer for the supply of tonnage quantities of EDN. Cost of the product is still uncertain. While there is a large cyanide manufacturing industry in Australia (in excess of 40,000 tpa of sodium cyanide manufactured in Gladstone, Qld), BOC has yet to find a local commitment to manufacture in Australia

There is some sensitivity in handling cyanides which resulted in adopting the IUPAC official name of Ethanedinitrile, EDN for cyanogen (C_2N_2).

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Sterigas 1000 *Fumigant*

ACTIVE CONSTITUENT: 1,000 g/kg ETHANEDINITRILE
PRODUCT ONLY AVAILABLE TO AUTHORISED OR LICENSED FUMIGATORS

For the control of pathogens, weeds and insects in soil, timber pest in timber & wood products and devitalisation of imported grains. (Soil fumigation for pre-plant strawberries to control pathogens, weeds and insects in soil intended for cultivation of strawberry runners / strawberry fruit, Fumigation of timber & logs and for export; Devitalisation of imported grains).

DIRECTION FOR USE

Situation	Pest	Application rate	Critical Comments
Strawberries runners and fruit growing	Pathogens, weeds and insects	500 kg/ha for 24 hours.	Apply pre-planting by suitably calibrated soil injection equipment. Ensure covers are airtight. Keep covered for 24 hours. After 24 hours, remove covers and allow to ventilate for 14 days.
Timber and logs for export	Insect pests and pathogens	50 g/m^3, 6 hours exposure.	Fumigate in sealed fumigation chamber or under sealed tarpaulins using good fumigation practice in accordance with State regulations. Commodity temperatures should be greater than 15 °C
Imported grains	Weed seeds and pathogens	13,800 g h/m^3	Maintain airtight seal to achieve the dose/ time. The required dose/time can be achieved by maintaining a concentration of 115 g/m^3 in the grain store for 5 days. Fumigated grain will be killed along with other seeds, pathogens and insects in the grain.

Not to be used for any purpose, or in any manner, contrary to this label unless authorised under appropriate legislation.

Cosmic™ 1000 Fumigant (Active Constituent: 1,000 g/kg Carbonyl Sulfide)

Carbonyl sulfide (COS):

Carbonyl sulfide (COS) is a new fumigant identified and developed by CSIRO Entomology for durable commodities (Desmarchelier, 1994). Its chemistry, toxicity (Haritos, 2000) and environmental fate (Ren, 1997) have been reviewed. Many natural sources of COS have been identified, including oceans, soils, volcanoes and marshes (Ren, 1997). It is also present in range of raw and processed foodstuffs, including cereals and oilseeds. The natural levels of COS in grains and oilseeds were found to be ~0.05 mg/kg (Ren, 1997);

Commercial-scale trials

In an earlier commercial-scale (50-500 t) trials on wheat, barley, oats and canola (Desmarchelier et al., 1998) it was shown that COS as a fumigant has excellent physical, chemical and biological fumigant functions. COS kills all life stages of all test insects (*S. oryzae, R. dominica, T. castaneum, T. variabile, O. surinamensis, C. ferrugineus, E. cautella* and psocids) in all developmental stages with concentration x time product (Ct) of 1650-1950 mg h/L at grain temperatures of 10-35 °C. After aeration COS left residues indistinguishable from levels in control samples (unfumigated) of wheat, barley, oats and canola. COS had no effect on the quality, such as quality of bread, noodles or sponge cakes made from the fumigated wheat; germination; seed colour and oil colour. In comparison with phosphine and methyl bromide, COS easily penetrated and diffused through the grain bulk. During application, fumigation and aeration, the levels of COS were < 10 ppm (TLV).

Ren et al. (2005) report on a larger COSMIC trial on 2,500 tonne of wheat fumigated with COS at 24 g/m^3 at Nevertire NSW. The COSMIC was applied as a liquid formulation into the top of the silo and released 2 m below the grain surface. The application of 85 kg of liquid COS was completed within 30 minutes.

During the two days exposure period, the COS concentration in the bin remained relatively high (~29 g/m^3). The concentration by time product (Ct) achieved was 1,900 g h m^{-3}, which was sufficient to kill all life stages of mixed age cultures of *Sitophilus oryzae , Rhyzopertha dominica, Tribolium castaneum, Trogoderma variabile, Oryzaephilus surinamensis, Cryptolestes ferrugineus* and *Ephestia kuehniella* larvae.

After 2 days exposure, the silo was aired overnight assisted by the aeration fan resulting in the COS in-bin concentration falling below 4 ppm. Residues declined to below the Australian Experimental Maximum Residue Limit of 0.2 mg/kg after overnight aeration. During out loading, 50 samples of 100 g of wheat were taken. COS was not detected in any samples at concentrations above the detection limit (0.05 mg/kg).

The workspace and environmental levels of COS were monitored during application, fumigation, aeration and outloading. The levels of COS and H_2S were less than the detection limit of 0.1 ppm.

The treatment with carbonyl sulfide had no affect on the wheat germination and seed colour compared to untreated controls. Oil quality tests showed that carbonyl sulfide had no effect on total lipid (made from treated wheat) content or the lipid colour.

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Cosmic Fumigant

ACTIVE CONSTITUENT: 1,000 g/kg CARBONYL SULFIDE

A flammable gas for control of pests in grain as specified in the Directions for Use. For use only by professional, licensed fumigators

DIRECTIONS FOR USE

Restraints

DO NOT release gas unless all potential sources of sparks or ignition have been isolated or extinguished.

DO NOT allow gas to build up to concentrations greater than 6.6 %

DO NOT apply if grain bulk temperature is less than 15 °C.

Situation	Pest	Exposure	Temp. (°C)	Rate g/m³	Critical Comments
Stored Grains Wheat Barley Oats Triticale Rye	*Sitophilus oryzae* Adults only	4 days	> 15	15	Increase rates for quicker fumigations and/or when grain temperatures are low. These rates and timings will only kill adults present at the time of fumigation. Eggs and other stages may not be controlled.
		2 days		20	
		1 day		30	
			30	25	
		12 hours	15	50	
			20	45	
			25	40	
			30	32	
	Sitophilus oryzae All Stages (including eggs)	10 days	> 15	10	Use higher rates for quicker fumigations or if temperatures are low. Effective control of eggs will not be achieved by fumigations shorter than 2 days. 2 day fumigations will be effective on eggs only if grain temperature is 20 °C or greater.
		7 days	> 15	20	
			20	15	
		4 days	>15	55	
			20	25	
			25	20	
		2 days	20	60	
			25	40	

Not to be used for any purpose, or in any manner, contrary to this label unless authorised by appropriate legislation.

Withholding period: 3 days

BOC Capabilities

BOC is a global manufacturer with specialised expertise in technical, marketing and commercial aspects of industrial gas. Area of knowledge include gas cylinder and bulk transport and storage competencies, experience in handling toxic gases, emergency response capabilities and handling of dangerous goods, BOC has the capability to fill, transport, distribute and market this flammable liquid gas and the ability to extend the technology and manufacture a value added non-flammable mixture. As a marketer of industrial gas products BOC limited has had involvement with fumigant gases (eg ethylene oxide: FUMIGAS 1000 and FUMIGAS Non-Flammable; methyl bromide: AGRIGAS M and AGRIGAS MC; phosphine; ECO_2FUME and $VAPORPH_3OS$; insecticides: INSECTIGAS and PESTIGAS and the new non-flammable ethyl formate fumigant VAPORMATE).

Registration

BOC has a long-term involvement with pesticide registration having registered eight unique products in Australia (also have registered products in UK, New Zealand, South Africa, China, Cyprus, Egypt).

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