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Carbon Dioxide——the Veteran and Versatile Fumigant

Robert F. Ryan *

Abstract: Reported ninety years ago to be the "most effective" fumigant compared to carbon disulphide(CS_2) and hydrogen cyanide (HCN), carbon dioxide still finds niche applications, e. g. "organic" grain protectant. In addition to its use in Controlled Atmospheres (>35%, 15days), carbon dioxide has been used to improve efficacy, pesticide distribution and the elimination of flammability in pesticide mixtures.

High pressure formulations in industrial gas cylinders use the unique solvent-propellant properties of liquid carbon dioxide to achieve mixtures of various fumigant chemicals. An early example of this formulation is the non-flammable mixture of 10% ethylene oxide in CO_2. More recent formulations include 2% phosphine [CYTEC product ECO_2 FUME] and 16.7% ethyl formate [LINDE Group-VAPORMATE].

In addition to its use in formulation of fumigant chemicals, the solvent-fpropellant property of carbon dioxide has been used to dispense aerosol mixture of contact insecticides. The "industrial aerosol formulation" marketed in a number of countries and typically using quick-knockdown and non-residue insecticides (e. g. natural pyrethrins, dichlorvos) are excellent for "fogging" applications.

Commercial carbon dioxide is recycled from by-product process streams (petroleum refineries, breweries, fertiliser manufacture). The carbon dioxide purified, liquefied and marketed by industrial gas companies is equivalent to less than 0.05% of the total carbon dioxide emissions to the atmosphere.

Key words: fumigation, fumigants, carbon dioxide, organic, aerosols, methyl bromide alternative, stored product pests

Introduction

The examples given below are examples of the variety of uses of carbon dioxide in pest control, using its solvent, propellant, toxic and synergistic properties.

Carbon Dioxide + Insecticides

An outbreak of encephalitis (inflammation of the brain transmitted by mosquitoes) initiated the development of an insecticide dispensing system to treat large areas. The development investigated liquid propellants that could be used in industrial gas cylinders (the high pressure rating of these cylinders extended the potential candidate propellants). The propellants included a range of liquefied gases that have the dual role of solvent and propellant (co-solvents can be added to assist in any solubility issues).

The pressure pack ("aerosol") can was invented by the Norwegian, Eric Rotheim, in 1924. He used dimethyl ether (DME) as the propellant of a ski wax aerosol. There was no wide acceptance of the aerosol can until World War II, when aerosol insecticides were used to help protect soldiers fighting in insect-infested jungles in the Pacific (40 000 000 aerosol units were distributed by the US Government). The potential for this unique packaging system was quickly recognised and, in 1947, the first consumer aerosol can appeared on the market. Chlorinated fluorocarbons (CFCs) were developed in 1930 by the Frigidaire Division of General Motors to replace toxic and corrosive ammonia and sulphur dioxide then in commercial use as refrigerants. After World War II, CFCs became the basic propellant for the new aerosol industry. Implications of ozone depletion by CFCs caused concern in the aerosol industry and led to developments of alternative propellants. Australian industry statistics show in 1970 more than 90% of all aerosols contained fluorocarbons but, by 1987, more than 80% of aerosols were CFC – free.

Fluorocarbons, hydrocarbons, nitrous oxide (NO_2) and carbon dioxide (CO_2) were among the candidate liquefied gases investigated as suitable solvent-propellants. Fluorocarbons had ozone depletion issues, hydrocarbons (propane, butane, isobutane) are flammable and nitrous oxide had the potential to decompose forming an

5 *Endeavour Street, Sans Souci, NSW* 2219, *Australia.* [* *ary53730@ bigpond. net. au*]

Note: vol% and wt% are identical as EtO and CO_2 have similar molecular weights oxidant which would react violently with combustible ingredients. Only low pressure gaseous nitrous oxide (used in whipped cream) and carbon dioxide (surface spray products) can be used as propellants, because their equilibrium vapour pressure is four times (4x) the pressure rating of pressure pack aerosol cans (pressure rating of cans is less than12 bar). The industrial gas cylinder chosen for the bulk aerosol dispenser have pressure rating > 200 bar.

The solvent-propellant properties of liquid carbon dioxide were the basis for the internationally patented[1] BOC Australia ENVIROSOL product range. The ENVIROSOL system relied on liquid CO_2 at high pressure (50 bar) to act as a solvent and propellant to dispense liquid insecticide as an aerosol fog (non-flammable, ultra-fine particle sizes, sized for commercial and industrial needs and ease of automation). The active constituent dissolved in the liquid CO_2 is contained in an industrial high pressure gas cylinder fitted with a "dip" tube to enable the liquid mixture to be withdrawn and dispensed as an aerosol spray. The small droplets size range (2 – 20 microns-over 2 billion droplets are created from a gram of chemical) of the particles formed results in the insecticide being suspended for over two hours. A small quantity of insecticide applied as a liquid CO_2 aerosol can quickly fill a large space (spray travels > 30m) and no insect can escape the treatment. The product can be dispensed manually using portable equipment or automatically using programmable timed release systems.

ENVIROSOL products have revolutionised pest control. They include PESTIGAS (0. 4% synergised natural pyrethrum in liquid CO_2 a quick knockdown, non-residual and low mammalian toxicity insecticide) and INSECTIGAS (5% dichlorvos in liquid CO_2 a rapid action non-residual insect control agent used by professional pest controllers).

The older style treatments of wetting surfaces with large volumes of insecticide/water mixtures or fogging with oil-based carrier are inefficient, messy, hazardous and time consuming. The ENVIROSOL system treats the total space with low concentration (3ppm levels) of insecticide, minimises occupational health and safety hazards of handling chemicals. The process is clean, fast and biologically efficient.

This technology has been extended into animal health products (automatic spraying of sheep for lice control); the joint CSIRO project on ECO_2 FUME/SIROFLO treatment of bulk grain; the new, low toxic fumigant, VAPORMATE; the project with partner CSIRO on potential new fumigants-Ethane Dinitrile (EDN) and Carbonyl Sulphide (COS).

Carbon dioxide + Sterilant

The use of carbon dioxide + ethylene oxide [EtO] mixtures have been in use for over fifty years as both sterilant and fumigant. Detailed EtO flammability studies [2] showed that, for non-flammability in air, the initial mixture mustbe less than 12% EtO in CO_2. The international dangerous goods-approved non-flammable mixture is a conservative 9% EtO in CO_2.

While a range of mixtures have been marketed over the years, the major demarcation is between flammable and non-flammable EtO products. However carbon dioxide is usually the gas of choice for pre-purging and post-purging EtO vacuum chambers used for both medical device sterilisation and quarantine fumigation. The unique penetrative properties of EtO make it the ideal quarantine fumigant required to overcome barriers such as paints and plastic wrappings. A recent publication[3] describes EtO quarantine fumigation dosages, pre-purging and post-purging actions and *Ct*-product details for effectiveness.

The new fumigant, Ethane Dinitrile (EDN = cyanogen = C_2N_2) also has sterilant properties. In addition to the pure material, a non-flammable 20% EDN in carbon dioxide formulation has been developed [4].

Carbon Dioxide + Phosphine

The patented non-flammable mixture of 2% w/w phosphine in liquid carbon dioxide [PHOSFUME = ECO_2 FUME] usage became widespread because of its superior biological efficacy, accurately controllable dosage and operator safety. Supply of ECO_2 FUME also supported the CSIRO development of SIROFLO which revolutionised fumigation of grain stored-products in "leaky" storages.

Prior to SIROFLO development, the traditional liquid insecticide "grain protectants", applied as chemical sprays, were one of the very few insect control options for leaky storages. SIROFLO, the flow-through fumigation application, achieves insect-free and residue-free status in existing non-gastight storages. SIROFLO delivers a low continuous dosage of PH_3 over a period of 28 days-shorter exposure times are possible with increased PH_3 levels[5]. The phosphine dosage initially less than 50ppm has been increased over time to triple this level as insect's phosphine tolerance has increased. The advantage of the SIROFLO treatment is the ability to treat any grain storage irrespective of air tightness as demonstrated in Cyprus[6].

Installation of relative simple PVC pipework allows recirculation of gases, converting SIROFLO to SIROCIRC, enabling fumigation of multiple grain storages of varying sizes with cylinders of ECO_2FUME [7]. For large storages, e.g. 1.3 million tonnes grain storage at Dalian, China, the on-site mixing of ECO_2FUME using bulk carbon dioxide supply and VAPORPH$_3$OS (100% gaseous PH_3) is a more practical option[8].

A separate patent was also granted for the on – site mixing of VAPORPH$_3$ OS and air where it is critical to ensure that the initial dilution to 1% PH_3 in air was done externally i.e. prior to addition to the grain storage (important to avoid any possibility of flammable gas within the storage).

While cylinderised formulations are a relatively expensive form of PH_3 supply, it is possible to use ECO_2FUME in a SIROFLO installation to achieve the economical fumigation of "leaky" storage ina way not possible with solid formulations. Also ECO_2FUME can be used in fumigate sealed storage where time is critical or where "top-up" of PH_3 levels is needed using conventional solid PH_3 formulations. The instant delivery of PH_3 using ECO_2FUME allows reduced exposure time which makes possible selective methyl bromide replacement applications.

Studies on the oxidation reaction of mixtures of PH_3 and CO_2[9] identified the formation of a polymeric solid, $(-CO_2-P_2H_4-)_n$. This solid, on prolonged exposure to air, forms a paste mixture which also contains phosphonic, phosphinic and phosphoric acids. This equipment-clogging material can be avoided by purging air remaining in delivery systems for ECO_2 FUME after use with carbon dioxide to less than 100 ppm O_2.

Carbon Dioxide + Ethyl Formate

The development of alternative fumigants is important because of threats to the widely used fumigants, methyl bromide and phosphine. Specifically, methyl bromide is an ozone depletor 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 (EtF) is a fumigant that satisfies these requirements. Historically used as fumigant of dried fruit and packaged food, EtF is naturally occurring, found in many foods, e.g. green apples, cabbages.

VAPORMATE is a LINDE Group registered formulation of EtF in CO_2. When CO_2 is mixed with EtF, it not only eliminates flammability, but also acts synergistically to enhance the efficacy of the ethyl formate. The naturally occurring EtF has GRAS (Generally Regarded As Safe) status as a food additive. EtF is diluted six times (6x) in liquid CO_2 to formulate the non-flammable VAPORMATE (16.7% w/w ethyl formate in liquid CO_2, equivalent to 11% v/v ethyl formate in gaseous CO_2). VAPORMATE is a post harvest fumigant that controls insects in stored grains[10], fresh produce and food processing equipment. VAPORMATE is dispensed as a "fog" (particle size –5microns) or warm (40℃) gas mixture to assist uniform distribution and optimise efficacy.

VAPORMATE ["No Withholding Period" status] applications include:

· Niche alternative for methyl bromide (e.g. grain, dried fruit, nuts);

· Rapid treatment system: e.g. 50 – tonne silo of grain: 12 minutes to apply, three hours to fumigate and two hours to air out, with no withholding period.

· Disinfestation of food processing equipment containing food residues.

· Modified Atmosphere Package [MAP] treatment for packaged food.

VAPORMATE dispensing innovations include:

· Product sprayed as a liquid via metering orifice nozzles to treat food processing equipment. The resultant "fog" permeates the space quickly, propelled by the high cylinder pressure [50 bar]. VAPORMATE installation can be piped to convenient locations throughout the food plant.

· Product vaporised as a warm gas using a hot water vaporiser and dispensed using aeration fans in grain storages (product is dispensed during one air change) or venturi devices to dilute the gaseous mixture with atmospheric air to optimise use.

VAPORMATE development had input from the (Australian) Grain Research and Development Corporation (financial support), CSIRO

Entomology (innovation from researchers) and BOC Limited (product development).

The approved dosage on the registered VAPORMATE label is 420 g/m^3 (i. e. equivalent to 2.3% v/v ethyl formate and 21% v/v carbon dioxide). CSIRO reports the VAPORMATE forced flow fumigation of stored grain is safe, efficacious and rapid (high level of mortality of tolerant insects was achieved in 3 hours).

Carbon Dioxide as the "Organic" Fumigant

There has always been the need to control insects in foodstuffs to prevent food losses and to satisfy marketing requirements. Global food customers are hardening in attitudes to pesticide residues in grain, following consumer demands for minimal or no chemical residues in food. An alternative to the traditional practice of spraying grain with liquid insecticide grain protectants is fumigation using gases. With increasing restrictions being placed on the chemical treatment of grain, CO_2 atmospheres, which have been approved by "organic" certifying associations, will be used more extensively.

Carbon dioxide controlled atmosphere fumigation has an important role in the protection of grain where residue-free, in situ treatment is needed.

CO_2 fumigations have been used worldwide for many years, but, to be effective, must be applied in gastight storages. There is a long history of CO_2 fumigation in Australia with a reccommended dosage in 1917 of 0.72kg CO_2 per tonne of grain in an airtight silo[11] being themost effective' fumigant then available, when compared with carbon disulfide (CS_2) and hydrogen cyanide (HCN). Another publication, in 1921[12], recommended a dose of 1.4 kg/tonne for maize in galvanised iron tanks. Oosthuizen et al, in 1942[13], in South Africa, tested the use of CO_2 against *Callosobruchus chinensis* (cowpea weevil). In France, CO_2 as soliddry ice' has been used[14] to treat wheat and gaseous CO_2[15] was used to treat wheat stored for two years. In USA, systems were developed for CO_2 fumigation of peanuts[16] and maize[17]. In the decades following the late 1980s, CSIRO Division of Entomology, Australia published extensively on the use of CO_2 as a fumigant and Controlled Atmospheres treatment in general.

Recirculation is known to be beneficial in the fumigation of bulk grain and its treatment with CO_2. CSIRO[18] recommended one air change/day in tall structures, 15m or higher, to prevent low concentrations developing in the upper part of the structure. A review[19] of the extensive laboratory studies of the lethal effects of controlled atmosphere data resulted in the following schedules for commercial controlled atmosphere treatments:

* **Oxygen deficient atmosphere**

0% –1% oxygen for longer than 20 days

* **Constant CO_2 composition**

80% 16 days if *Trogoderma granarium* is present

8.5 days for all other species

60% 11 days for all species except *Trogoderma granarium*

40% 17 days for all species except *Trogoderma granarium*

* **Declining CO_2 concentrations**

Initial concentration above 70% CO_2 in air, declining to 35% in 15 days or longer.

General details of how to convert existing storage to a gas tightness level suitable for modified atmospheres have been documented[20]. The acceptable level of sealing is that which gives a pressure half-life decay of greater than 5 minutes (often relaxed to 3 minutes in less than 300 tonne storage) when the structure is full. The application of fumigation using carbon dioxide in concrete storage can result in carbonation reaction with alkaline constituents[21]. However no corrosion was observed in 50 year old stores, suggesting there is no risk associated with carbonation as long as storage atmosphere maintains a dry environment around the steel reinforcement.

Conclusions

The unique properties of carbon dioxide allow it to be used to dispense insecticide chemicals ("giant" industrial aerosols) in addition to its use as an approved "organic" fumigant. Current developments continue to find applications for carbon dioxide in fumigant gas mixtures with benefits of improved efficacy, uniform distribution and the elimination of flammability.

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