RECYCLED CARBON DIOXIDE – THE VETERAN & VERSATILE PESTICIDE

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Abstract: There is a long history of using carbon dioxide (CO_2) in the control of stored grain insects. The ancient practice of burying grain and benefiting from the insecticidal effect of the respired CO_2 has advanced to other pesticide applications.

- ✓ Anon (1917) reported CO_2 the "most effective" fumigant V's CS_2 & HCN.
- ✓ In addition to Controlled Atmospheres use (>35% CO_2 for 15 days exposure), CO_2 improves the efficacy / distribution & eliminates flammability of pesticides.
- ✓ Jones (1932) published details of reducing flammability of EO, PO & EtF in CO_2 - commercial non-flammable CO_2 mixtures of these gases are now marketed.
- ✓ The solvent-propellant property of CO_2 has been used to dispense aerosol mixture [fogging applications] of contact insecticides e.g. natural pyrethrins & dichlorvos.
- ✓ Commercially CO_2 is recycled from by-product process streams e.g. petroleum refineries, breweries, fertiliser manufacture & is <0.05% of total CO_2 emissions.

Carbon dioxide the "Organic" Fumigant:

There has always been the need to control insects in food stuffs to prevent food losses and to satisfy marketing requirements. Carbon dioxide controlled atmosphere fumigation has an important role in the production of grain where residue-free, in situ treatment is needed and CO_2 continues to finds niche applications e.g. "organic" grain fumigant. Global food customers are hardening attitude 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. Fumigants have been used worldwide for many years; however to be effective must be carried out in gastight storage. A review [Annis, 1986] 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 >70% CO_2 in air, declining to 35% in 15 days.

The acceptable level of sealing is that which gives a pressure half-life decay of greater than 5 minutes (relaxed to 3 minutes in <300 tonne storages) when the structure is full.

Carbon Dioxide + Fumigant

The Jones (1932) paper *"Reducing Inflammability of Fumigants with Carbon Dioxide"*, published in 1932, details the maximum vol% of potential fumigant in CO_2 necessary to eliminate flammability for: carbon disulfide (4%), ethylene oxide (12%), methyl formate (30%), ethyl formate (14%), propylene oxide (8%) and ethyl acetate (14%). This data continues to

assist in the search for new fumigants to replace the ozone depleting methyl bromide. Some of the above fumigant-CO_2 mixtures (ethylene oxide, propylene oxide & ethyl formate) have been marketed commercially as high pressure liquid CO_2 mixtures in industrial gas cylinders. The unique solvent-propellant property of liquid CO_2 achieves non-flammable fumigant mixtures with improved efficacy and uniform distribution. The >50 year old formulation of 10% ethylene oxide in liquid CO_2 has been followed by recent formulations of 2% phosphine [CYTEC's ECO_2FUME^{TM}] and 16.7% ethyl formate [LINDE Group - VAPORMATE™] in liquid CO_2. The proposed new fumigant, Ethane DiNitrile (EDN = cyanogen = C_2N_2) is non-flammable at 20% EDN in CO_2 [Ryan et al, 2006].

Carbon dioxide + Insecticides:

The solvent-propellant properties of liquid carbon dioxide were the basis for the internationally patented [Ryan et al, 1978] BOC Australia's ENVIROSOL™ product range. The ENVIROSOL system relied on liquid CO_2 at high pressure (50bar) 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, 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 time release systems.

Conclusion:

The unique property of carbon dioxide to dispense insecticide chemicals ("giant" industrial aerosols) is an addition to its approved "organic" fumigant status. Current developments continue to find application for carbon dioxide in fumigant gas mixtures with benefits of improved efficacy, uniform distribution and the elimination of flammability.

References:

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