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GASEOUS PHOSPHINE — A REVITALISED FUMIGANT

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ABSTRACT

Phosphine (PH_3)-generating formulations, commercially available for some fifty years, have made significant contributions to grain protection. A patented non-flammable PH_3 formulation, PHOSFUME™, both overcomes the hazard of flammability associated with quick release of gaseous PH_3 from metallic phosphide formulations and offers controlled dosing of PH_3. The PH_3 formulation is a liquefied gas mixture of PH_3 and carbon dioxide which satisfies a wide range of concentration and exposure time (Ct) options by being dispensed through innovative equipment. PHOSFUME™ has been adopted by the Australian bulk grain authorities, who have successfully treated in excess of 15 million t of grain using both traditional fumigation procedures in sealed storage and flow-through fumigation (SIROFLO®) in non-gastight structures. International interest is intense. A number of countries are actively planning to adopt this fumigation technique, which would enable them to expand the use of traditional PH_3 fumigation applications.

Because of its ability to instantly deliver high concentrations of PH_3, an investigation has been initiated to test the practicality of the use of PH_3 as a replacement for the ozone-depleting methyl bromide in disinfestation treatment. The investigation aimed at identifying and eliminating contaminants formed by PH_3 reacting with atmospheric oxygen. It uncovered new aspects of phosphorus chemistry and led to the development of the recently patented multi-component non-flammable compressed gas formulation which reduces costs for both the production and dispensing of the liquefied gas mixture. This investigation supports the use of gaseous PH_3 as a revitalised fumigant.

INTRODUCTION

Although the use of residual pesticides has resulted in a high standard of insect disinfestation, international consumers now demand that stored products be both insect- and residue-free. This is resulting in the replacement of liquid insecticide grain protectants by fumigant gases. Gaseous phosphine (PH_3), with its proven track record, low cost and residue levels of less than 1 ppb (Winks *et al.*, 1995), is an ideal fumigant, except that it is highly flammable. BOC Gases has patented a non-flammable PH_3 mixture, PHOSFUME/

ECO_2Fume. PHOSFUME™ is marketed as an alternative to traditional problematic insect control methods. Grain protectants pose a residue problem. Metallic phosphide tablets pose problems of operator exposure and safe disposal. And methyl bromide is an ozone depletor.

The safe, accurate and controlled metering of the universal grain fumigant, PH_3, has revolutionised stored-product disinfestation. PH_3 fumigation is a proven cost-effective alternative to residual pesticides. PH_3 is, however, an extremely flammable gas, and existing commercial metallic phosphide formulations do not eliminate this hazard. PHOSFUME™ is patented (US Patent No: 4,889,708) and its fumigant non-flammable gas mixture of 2% w/w PH_3 in carbon dioxide (CO_2), marketed by the international BOC Group, is easily, accurately and safely dispensed into all types of grain storage by using gastight pipelines.

BOC Gases has supplied some 600 t of PHOSFUME™ to date. It has been used to fumigate in excess of 20 million t of grain. The cost of a 21-d fumigation with PHOSFUME™ (0.3 g PH_3/t) is 15 US¢/t. A major use of PHOSFUME™ is in conjunction with SIROFLO® in unsealed storages. The PHOSFUME™/SIROFLO® combination can be applied directly to grain in any storage type, and it obviates the need for "turning" the grain for spraying with insecticide. The cost of turning is dependent upon storage type and the capacity of the machinery, but it can be as high as US$3.50/t. A hidden cost is the need for empty storage to receive the grain.

TRADITIONAL PHOSPHINE GENERATING PRODUCTS

PH_3 generated *in situ* from metallic phosphide formulations has made a significant contribution to grain hygiene for over 60 years; the original patent was issued in 1934.

PH_3 is an extremely flammable gas with explosive limits of 1.6–100% in air, and existing commercial formulations generate gas mixtures with a PH_3 composition which is usually in excess of 50% PH_3. The phosphide formulations are designed for slow release of the PH_3 gas which is generated by reaction with atmospheric moisture. This slow release allows the PH_3 gas to diffuse into the commodity being fumigated, minimising the risk of an explosive mixture.

Occupational health and safety concerns about metallic phosphide formulations exist in two areas: the inhalation risk, associated with the formulation's generating PH_3 immediately on exposure to air, and the safe disposal of the "spent" residual powder, which contains ~2% unreacted phosphide.

GASEOUS PHOSPHINE

The predominant component of the smell of acetylene is PH_3. Historically, industrial gas companies have produced PH_3 as an impurity (~400 ppm) in acetylene, with some 100 t of PH_3 generated annually. It is possible to fumigate with industrial, PH_3-containing acetylene even at concentrations below the explosive limit of 2.5% acetylene.

In more recent years, electronic-grade PH_3 (99.9999% pure), together with silane,

diborane, arsine, stibine, etc., has been used in the manufacture of silicon wafers/integrated circuits.

While the necessary purity of fumigation-grade PH_3 is not as high as that of electronic-grade, some impurities are critical. Purification of the PH_3 gas, unlike that of metallic phosphide formulations, ensures that such pyrophoric contaminants as diphosphine (P_2H_4) and white phosphorus (P_4) are removed from the PH_3 gas prior to its being mixed with inert gas. In early investigations (Gallagher *et al.*, 1991), an analytical procedure based on extraction and ^{31}P NMR analysis techniques was developed. The exposure of PH_3 to atmospheric oxygen and moisture can result in the formation of an inert orange-yellow polymer plus phosphorus acids (Gallagher *et al.*, 1995). The reactivity of PH_3 disguises its reported natural abundance. It is the cause of the reported ignitions of marsh gas which result in the "will-o-the-wisp" flickering lights observed in marshlands at night (Toy, 1976); it evolves from sewage treatment (Devai *et al.*, 1988); and it has been detected in animals and humans at significant levels (Gassmann and Glindermann, 1993).

About twenty years ago (Ryan, 1976), BOC Gases approached the Gosford Postharvest Laboratories (a joint CSIRO/NSW Department of Agriculture research laboratory) to request consideration of gaseous PH_3 mixtures for fumigating fruit for the control of fruit flies. This project was resurrected in 1983 when BOC Gases supported the CSIRO Division of Entomology flow-through fumigation research project which culminated in the SIROFLO® process.

FLAMMABILITY

Extensive flammability testing has been conducted by BOC Gases and by WorkCover Australia (Londonderry Occupational Safety Centre). The systems studied included PH_3–CO_2, PH_3–N_2 and PH_3–CO_2–N_2. This research resulted in two patent applications (Ryan and Latif, 1989; Ryan and Nguyen, 1995 (provisional application)), one for a non-flammable liquid mixture of PH_3 and CO_2 (2 w/w% PH_3/CO_2) and one for a non-flammable gaseous mixture of PH_3, CO_2 and N_2 (2.4 v/v% PH_3–60% CO_2–N_2).

This research showed that the PH_3/N_2 system could not contain more than 2.0% v/v PH_3 in N_2. It would thus be necessary to replace one cylinder of the existing 2.6% v/v PH_3 in liquid CO_2 mixture (PHOSFUME™) with approximately three cylinders of the 2.0% v/v PH_3 in N_2 mixture; i.e. a ~300% increase in the number of cylinders would be required. The PH_3/60% CO_2/40% N_2 system could contain 2.5% v/v PH_3, and with a cylinder filled to 163 bar it would be necessary to replace two cylinders of the existing 2.6% v/v PH_3 in liquid CO_2 mixture (PHOSFUME™) with approximately three cylinders of this mixture; i.e. a ~50% increase in the number of cylinders would be required.

HAZARD RANGE

The estimate of the hazard range for non-flammable PH_3 mixtures of 200 ppm, based on the NIOSH/OSHA IDLH (Immediately Dangerous to Life or Health) concentrations, a

range within which a worker could not escape without symptoms of impairment or irreversible effects, was 20 m or less from the release point under all foreseeable circumstances (Hill, 1988).

APPLICATIONS

Structures/flour mills

Fumigation Services & Supplies carried out fumigations using PH_3, CO_2 and heat to fumigate flour mills (Mueller, 1994). This technique, which requires quick release of PH_3 (~100 ppm), has achieved good results. Concerns about corrosion of electrical circuits, since PH_3 reacts with copper, could be overcome.

Grainco Queensland developed innovative techniques for the fumigation of wheat in sealed storages (Ryan, 1992). In concrete/steel vertical silos and bunker/pad storages, the Grainco technique ensured quick release of PH_3, achieved peak PH_3 concentration some four times that resulting from metallic phosphide formulations, ensured rapid distribution and resulted in entomologically effective concentrations. Fumigations at dosages as low as 0.3 g/m^3 PH_3 were successfully performed.

Recirculation fumigation

The Western Australian Cooperative Bulk Handling (WACBH) authority used PHOSFUME™ at their ~1.5 million-t capacity Kwinana Grain Terminal. WACBH injected PHOSFUME™ into the forced air recirculation system of their 2,200-t vertical storage. A capillary tube restrictor ensured that the PHOSFUME™ was dispensed at a uniform rate over the ~5 h required for the air blower to change one complete volume. The 2-d saving in time achieved by using PHOSFUME™ is critical at a seaboard terminal.

SIROFLO®

Fumigants have been used worldwide for many years, but to be effective they should be carried out in hermetically sealed (gastight) storages. The pressure standard for gastightness requires the decay of externally applied pressure from 500 Pa (50 mm water gauge) to 250 Pa (25 mm water gauge) in filled storages in not under 5 min (SCA Technical Report, 1980).

An exception to the requirement for appropriately sealed storage for gaseous grain fumigation is the CSIRO flow-through SIROFLO® fumigation technique. The CSIRO Division of Entomology patented SIROFLO®, the flow-through fumigation technique (Winks, 1986). It is a positive-pressure continuous-application technique designed for structures that are not gastight but can be effectively sealed in critical areas. It is based on the continuous introduction of PH_3 (~30 ppm) from a PH_3 source, such as cylinders of PHOSFUME™, into an air stream which provides positive pressure within the storage. This positive pressure and the continuous flow ensure SIROFLO®'s independence from either leaks or the influence of high wind, and together they maintain a minimum PH_3 concentration over the fumigation exposure period (~4 weeks).

Levels of PH_3 in the workspace environment are less than the TLV (0.3 ppm) because of the low levels specified by the SIROFLO® technique. In addition to providing improved safety, SIROFLO® controls PH_3-resistant strains which succumb to the gas provided that the exposure periods are long enough (Winks and Ryan, 1990).

In the 1995/96 grain season, it is expected that over 10 million t of grain will be treated with SIROFLO®. The capital cost of SIROFLO® has been found to range between US$1/t for vertical silos and US$3/t for horizontal storage. Fumigation costs for large storages vary from US$0.20 for vertical silos to US$0.80 for horizontal storage. Although the horizontal sheds have higher treatment costs, their capital cost is about half that of vertical silos; e.g. a 7,000-t horizontal storage costs US$300,000 (~US$40/t). A major cost of large vertical silos is the grain-handling equipment.

Continuous Dose

This technique using PHOSFUME™ was initially described in a UK report (Bell *et al.*, 1991) as a "continuous flow system". The difficulty of controlling gas flow, experienced in the UK study, can be overcome using LoDOSE™ regulators. The requirement for a low-cost fumigation method, with "nil electrics" equipment, makes this technique attractive for on-farm fumigation.

CONCLUSION

PHOSFUME™ provides a controlled PH_3 source that allows concentrations to be adjusted during a fumigation to compensate for unforeseen air ingress. This adds an order of sophistication to grain fumigation. Combined with the non-flammability and Occupational Health and Safety benefits, PHOSFUME™ yields significant advantages over alternatives. The new LoDOSE™ regulator provides the long-term continuous flow that is required for techniques such as SIROFLO®.

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