ECO$_2$FUME$^2$: GLOBAL STATUS UPDATE

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ABSTRACT

The use of this cylinder source of phosphine (PH$_3$) fumigant has gained government approvals and industry acceptance as the fumigant of choice for a variety of applications around the world. ECO$_2$FUME$^2$ has many advantages over traditional PH$_3$ fumigation, including ease of application, precise PH$_3$ concentration control, and reduced risk use. In addition, ECO$_2$FUME is non-flammable, generates no waste, and is environmentally friendly. This paper provides an up-to-date review of the existing and pending country approvals, and the global activities on progress to expand the use of this important source of PH$_3$ fumigant gas. Among the many activities that are reviewed are the SIROFLO$^5$ and SIROCIRC$^5$ techniques developed in Australia, the experimental fumigation of empty ship holds in Canada, and on-site blending of PH$_3$ in carbon dioxide techniques used in Australia and China.

INTRODUCTION

ECO$_2$FUME fumigant gas is a liquefied mixture of 2% wt. PH$_3$ (2.6% vol.) with carbon dioxide (CO$_2$). This mixture has been patented by BOC Gases of Australia. Commercial use of ECO$_2$FUME began in 1988 in Australia after years of development work by CSIRO that resulted in the patented SIROFLO$^5$ application technique. The advantages of using ECO$_2$FUME fumigant gas are numerous.

This mixture of PH$_3$ with CO$_2$ ensures it is non-flammable in all proportions with air. This eliminates all safety concerns with dispensing rates or dilution rates. Traditional solid formulations can generate PH$_3$ concentration above the lower flammability limit for PH$_3$ thereby creating a hazard.

In addition to the elimination of the flammability hazard the use of ECO$_2$FUME does not require the applicator to enter the fumigation space. These ready-to-use cylinders can be dispensed from outside of silos or structures being fumigated. This
eliminates the need for entry into confined spaces to apply fumigant or to retrieve spent solid waste.

Disposal of solid waste products is becoming more difficult every day. ECO₂FUME fumigant gas eliminates the concern associated with deactivating spent solid phosphide formulation and the disposal of the waste product. Left over product in the ECO₂FUME cylinders can be saved for the next application or returned to the supplier.

ECO₂FUME fumigant gas does not rely on the reaction of a solid formulation with moisture to generate PH₃. By dispensing a gas formulation the desired PH₃ concentration can be precisely established and then controlled for the duration of the fumigation period.

The controlled application of fumigant gas results in less fumigant introduced in stored-products. Traditional solid formulations rely on the generation of high initial PH₃ concentrations followed by a slow deterioration to ensure that the PH₃ concentration x time product (Ct) will result in an effective fumigation. With ECO₂FUME fumigant gas, the concentration can be easily controlled and adjusted by the applicator to maintain an efficacious concentration.

Unlike alternatives such as Methyl Bromide (MB), ECO₂FUME fumigant gas will not harm the ozone layer.

AUSTRALIA

BOC Gases in Australia patented and produced the ECO₂FUME blend (previously known as Phosfume®) and developed the specialized dispensing equipment for use in the SIROFLO application.

Cytec Industries Inc. has been producing PH₃ gas and PH₃ derivatives at its Niagara Falls, Ontario, Canada facility since 1969. Cytec began supplying VAPORPH₃(OS)³ phosphine (97% PH₃) to BOC Gases in 1994 for the production of ECO₂FUME fumigant gas. On August 20, 1999 Cytec Industries Inc. purchased the global phosphine fumigant business from BOC Gases. This included all patents, trademarks, registrations and pending registrations. Cytec has contracted with BOC Gases Australia to continue to toll manufacture ECO₂FUME fumigant gas for the Australian market. Cytec also constructed another ECO₂FUME blending plant at its Niagara Falls, Ontario, Canada phosphine production facility to supply the North American market.

Cytec has secured agreements with CSIRO Australia for the use of SIROFLO and SIROCIRC® application technology with ECO₂FUME.

The CSIRO patented SIROFLO application technique involves the slow addition of ECO₂FUME into an air stream thereby controlling and maintaining a very low concentration (~ 30 ppm) of phosphine in a stored-product bulk. The egg and pupal life stages of target insects are less susceptible to these low doses; however, maintenance of these low doses for several days (14-28 d) allows these stages to develop into more vulnerable stages of the insect's life cycle (lava and adult). This is a very useful application technique for partially sealed storage.
This application technique was further refined over time and adapted for sealed storage. In this case a small recirculation line is installed from the headspace above the stored-product to the inlet side of a recirculation fan. The CSIRO patented technique is called SIROCIRC®. By circulating the air stream through the grain bulk the use of ECO₂FUME can be substantially reduced by 50 to 90%.

This technique has gained wide acceptance and many storages are being sealed to allow the implementation of this technology.

NEW ZEALAND
ECO₂FUME is registered for use in New Zealand. Initial trials have been conducted, however, we are still in the early stages of marketing this product in New Zealand, and we have recently appointed a new distributor, Alchemy Chemicals.

SOUTH AFRICA
Registration in South Africa was received in May, 1998. Although we have seen a lot of interest in using ECO₂FUME, no substantial progress has been made in developing its widespread use.

ARABIAN GULF
SIROCIRC® demonstration systems have been installed in both Bahrain and Qatar. Both of these countries have very small storage capacities but are dependent on foreign supply of grain to meet their requirements. The demonstration systems have worked well and both countries are considering expanding and installing permanent systems. Work is in progress to apply for registration in these countries and also in Egypt.

CYPRUS
Registration of ECO₂FUME fumigant gas for use in Cyprus was granted in 1996. The first demonstration system was installed in 1995 at the Larnaca grain storage facility for demonstration during the previous CAF Conference in 1996. This SIROFLO installation has been performing successfully ever since. The system has worked so well that the Cyprus Grain Commission has expanded the use of ECO₂FUME with additional SIROFLO installations on all of their steel silos at Larnaca and 8 silos located at its Paphos storage facility. In addition Cyprus Grain Commission is considering installing SIROCIRC systems on their concrete storage silos in Limassol.

SOUTHEAST ASIA
Several United Nations Industrial Development Organization (UNIDO) sponsored projects are in progress in Southeast Asia.
Indonesia has carried out initial stack fumigation trials on bagged rice with BULOG. This trial has been funded by UNIDO, and additional trials are planned.

Thailand has the go-ahead from UNIDO to conduct trials on MB alternatives. Dispensing equipment and ECO2FUME fumigant gas cylinders have been shipped. Installation and trials are planned before the end of the year. Thailand will be using on-site blending of VAPORPH3OS PH3 with bulk CO2.

Vietnam has recently received approval from UNIDO for trials using ECO2FUME with the Vietnam Fumigation Company coordinating the fumigation projects.

**CHINA**

Cytec expects to receive ECO2FUME and VAPORPH3OS product registrations in late 2000, and we are in the process of formalizing manufacturing and distribution capabilities to support the China market.

SIROCIRC technology use continues to expand into other countries such as China. As reported in April, 2000 issue of World Grain magazine, China is constructing the Xizai Grain Terminal, one of the world’s largest storage facilities located in Dalian. The 1st phase of the project involves the construction of 150 bins, each with 3,000 metric ton storage capacity. This phase of the project has been funded by the World Bank. The second part of the project is being funded by the Chinese government. This phase involves the construction of 20 super silos each with a storage capacity of 30,000 tonnes. Both phases of this storage facility are designed to use ECO2FUME fumigant gas. However this installation will utilize the on-site blending of ECO2FUME (2% wt PH3) from a combination of bulk on-site storage of liquid CO2 and 14 kg size cylinders of VAPORPH3OS phosphine (97% wt. PH3). This method greatly reduces the number of cylinders that need to be supplied to the location.

Design of the fumigation system at the Xizai Terminal was carried out by Grain Technology Systems of Australia and the blending equipment was supplied by GasApps of Australia.

**CANADA**

A few fumigations have been completed under experimental-use permits issued by the Pest Management Regulatory Authority (PMRA) in Canada. The most significant study was sponsored by Environment Canada and the Methyl Bromide Government/Industry Working Group, and involved the fumigation of 3 holds of a ship. This study was undertaken to demonstrate alternatives to MB. One of the holds was fumigated with MB and the recapture of MB was demonstrated at the end of the fumigation period. Another hold was fumigated to 1,000 ppm PH3 generated from the Horn Generator using Magnesium Phosphide. The third ship hold was fumigated to 500 ppm PH3 using ECO2FUME fumigant gas. Assisting in the ECO2FUME part of the fumigation was Fumigation Services Supply and Maheu & Maheu. All three demonstrations proved as effective alternatives to standard MB fumigations.
The experimental fumigation was conducted on June 5th, 1999 aboard the "Canadian Trader" moored in Toronto harbour. The hold used to demonstrate the ECO\textsubscript{2}FUME technology had a volume of 219,000 ft\textsuperscript{3}. A dose of 450 lb of ECO\textsubscript{2}FUME was applied over a 90 min period to reach a concentration of 500 ppm. As seen by the graph below the concentration of ECO\textsubscript{2}FUME was easily maintained over the 72 h fumigation duration.

![Graph showing concentration of PH\textsubscript{3} over time.]

**Fig. 1.** Phosphine fumigation in hold No. 4 of the "Canadian Trader" showing average PH\textsubscript{3} concentrations over time.

The method of application was very simple and inexpensive. One-quarter inch copper tubing was run from the cylinders into the ship hold. Liquefied ECO\textsubscript{2}FUME vapourized into the atmosphere inside the ship hold.

From this experimental fumigation we concluded that ECO\textsubscript{2}FUME is a viable alternative to MB. The required concentration of PH\textsubscript{3} can be quickly achieved and easily maintained over the entire fumigation period. During the fumigation no waste material was generated and therefore no disposal issues were encountered.

A copy of the ship hold report is available on the world wide web at:

http://www.ag.ca/policy/environment

Another fumigation performed under an experimental-use permit issued by the PMRA was fumigation of a "bird-seed blending and storage" facility. This fumigation was performed by Maheu & Maheu for Quebec city, Quebec, Canada. ECO\textsubscript{2}FUME was dispensed to achieve a concentration of 400 ppm in the area. Again this fumigation demonstrated how quickly the PH\textsubscript{3} concentration can be established and maintained.
UNITED STATES
ECO₂FUME fumigant gas received EPA 'Non-Food Use Approval' on December 20, 1999. This allowed the introduction of ECO₂FUME for the fumigation of many commodities including tobacco. ECO₂FUME received 'Food Use Approval' on August 28, 2000. Several demonstration fumigations have been performed including container, tarp and shed fumigations. The largest to date was the fumigation of a 1.2 million ft³ tobacco storage shed at R. J. Reynolds storage facility in North Carolina. The target concentration was 300 ppm with a minimum of 200 ppm. Twenty-three cylinders were applied over a 2 h period. Again simple dispensing equipment was used. Two-inch diameter copper lines were run from the cylinders to the shed interior. The cool nights and warm days resulted in convection currents within the shed that resulted in air escaping from the structure. Consequently there was a need to add additional ECO₂FUME. Four additional cylinders were added 20 h into the fumigation and 4 more 68 h into the fumigation. This addition of ECO₂FUME ensures that an efficacious concentration of PH₃ is maintained throughout the fumigation period.

SUMMARY
ECO₂FUME fumigant gas has many advantages over traditional fumigants. It can be used in a variety of applications and can be dispensed easily to control target insects. Cytec Industries Inc. intends to continue to register ECO₂FUME fumigant gas in countries around the world.