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Commercializing a New Fumigant: the ProFume® Success Story

Ellen Thoms[1], John Busacca[2] and Suresh Prabhakaran[2]

Abstract: ProFume gas fumigant (99.8% sulfuryl fluoride) is a broad spectrum, non-ozone depleting fumigant developed and manufactured by Dow AgroSciences LLC for the control of rodent, insect and other invertebrate pests. This fumigant was developed in response to post-harvest industry requests for an alternative to methyl bromide. ProFume has been developed for use in food handling establishments (eg., pet food facilities, bakeries, food production facilities, mills, warehouses, etc.), stationary transportation vehicles (railcars, shipping containers, trucks, etc.), temporary and permanent fumigation chambers, and storage structures. ProFume is relatively non-reactive as a gas and does not cause off-flavors. It is an odorless, colorless inorganic gas, and as such, does not form unpleasant odors. In addition, due to its higher vapor pressure and lower sorption characteristics, ProFume® compared to methyl bromide penetrates commodities more effectively reaching target pests faster for optimum control. Globally, over 1 000 commercial fumigations have been completed with high level of customer satisfaction. Development and successful commercial use in many countries prove that ProFume is a technically and economically viable alternative to methyl bromide and can also be used to fumigate insects resistant to phosphine.

Introduction

Post-harvest insect pests that infest food commodities in mills, warehouses, food storage and processing facilities can cause substantial economic and quality losses. Localized treatment, sanitation, and other physical methods may not adequately control these pests if infestations are widespread or in inaccessible areas. In these situations, fumigation has been the preferred method of pest control. Methyl bromide, previously the fumigant of choice, has been identified as an ozone depleting chemical and is being phased out under an international agreement known as the Montreal Protocol. It is to be completely phased out in developed nations by 2005 (with some critical use exemptions) and by 2015 in developing countries.

With the adoption of the Montreal Protocol, the phase out of methyl bromide in developing countries started and the search for replacements began. About this time, several progressive food industries in the United States and Europe approached Dow AgroSciences to consider developing sulfuryl fluoride for food commodity use. As a result, Dow AgroSciences formed partnerships with leading stored product researchers, fumigators and food industries around the world and developed ProFume® gas fumigant as a successful post-harvest fumigant.

Sulfuryl fluoride is fully oxidized and does not interact with or contribute to local ozone formation. It contains no chlorine or bromine and does not contribute to stratospheric ozone depletion[1,2]. Sulfuryl fluoride is broken down mainly through hydrolysis to release fluoride and fluorosulphate ions[1]. In 2002, Dow AgroSciences was awarded the Stratospheric Ozone Protection Award by the U. S. A. Environmental Protection Agency (EPA) for the development of ProFume gas fumigant. This award recognizes global, extraordinary achievements in international leadership and innovation in preserving the Earth's protective stratospheric ozone layer. Nominated winners have demonstrated a commitment to environmental stewardship through their precedent-setting innovation and leadership. In 2007, Dow AgroSciences was named a winner of the United Nations Montreal Protocol Innovators Award at the meeting commemorating the 20th anniversary of the Montreal Protocol. At that meeting, Dow AgroSciences was also named a winner of the EPA's "Best of the Best" Ozone Protection Award which honors an elite group of companies, organizations and individuals who have demonstrated long-term excellence in efforts to protect the stratospheric ozone layer.

History

Dow AgroSciences has registered and marketed sulfuryl fluoride as Vikane gas fumigant

1. *Dow AgroSciences LLC*, 7257 *NW 4th Blvd* #20, *Gainesville*, *FL* 32607, *USA*
2. *Dow AgroSciences LLC*, 9330 *Zionsville Road*, *Indianapolis*, *IN* 46268 *USA*

since 1961. It has been successfully used to fumigate more than one million structures including homes, museums, cathedrals, historical landmarks, rare book libraries, and scientific and medical research laboratories to eradicate termites and wood boring beetles. In Europe it was first introduced in the early 1990s in Germany to eliminate wood destroying beetles, such as *Anobium punctatum* and *Ptilinus pectinicornis*, from structures. In Sweden, sulfuryl fluoride is used in shipping containers and for the disinfestations of homes and wooden artifacts.

Physical Properties of Sulfuryl Fluoride

Sulfuryl fluoride has many physical properties that make it suitable for commodity fumigation. Sulfuryl fluoride is an inorganic, non-flammable, odorless and colorless gas. Because of its low boiling point and high vapor pressure, sulfuryl fluoride readily vaporizes under normal fumigation conditions, thus allowing rapid dispersion after gas introduction. Sulfuryl fluoride is noncorrosive, an important characteristic for a fumigant used in environments where sensitive equipment and electronic devices are employed. It does not react with materials to form unpleasant odors. However, heaters and open flames must be extinguished, because temperatures over 400℃ will cause decomposition products. Because of its low sorption characteristics, sulfuryl fluoride rapidly aerates from structures and commodities. Penetration in material and commodities is also fast. A study has shown that 60% of initial sulfuryl fluoride concentration could be reached at a depth of 30 cm of wheat flour in less than three hours[3].

Sulfuryl fluoride residues are transient in fumigated commodities. Sulfuryl fluoride rapidly dissipates following proper aeration procedures. The common residue following fumigation is fluoride. An extensive program of food quality studies have been conducted on a variety of dried fruits and tree nuts in cooperation with the Dried Fruit and Tree Nut Association (DFA) of California and other commodity groups. Similar studies on cereal grains, flour, and other key commodities have been conducted with food science experts. These research studies confirmed lack of adverse quality effects on cereal grains, dried fruits and tree nuts. The National Association of British and Irish Millers (NABIM) also evaluated these studies and is satisfied by the results.

Efficacy of ProFume

Efficacy research has been conducted in the laboratory and in the field to define dosages and treatment practices to optimize the control of key post-harvest insect pests. Laboratory efficacy studies have been conducted in cooperation with the USDA-ARS in Fresno, California; DFA of California, Central Science Laboratory (CSL) in the UK, Julius Kuehn Institute (formerly the Federal Biological Research Center for Agriculture and Forestry) in Germany, the University of Milan in Italy, and Laboratoire National des Denr es Stock es in France to define the dosages required to control all the life stages of target pests under a range of fumigation conditions. These studies[4-7] have confirmed the effectiveness of sulfuryl fluoride on all life stages of a wide range of post harvest insect pests including the important pest species of Coleoptera and Lepidoptera. These data have been used to develop the dosage calculations for the ProFume Fumiguide™, described below.

In addition to extensive laboratory and field efficacy trials with ProFume gas fumigant, population rebound studies have been undertaken in Europe[8,9] and the USA[10,11] to demonstrate effectiveness of ProFume in controlling stored product pest populations. The objective of these studies was to compare the impact of ProFume and methyl bromide fumigations upon populations of the red flour beetle (*Tribolium castaneum*), the confused flour beetle (*Tribolium confusum*), the Mediterranean flour moth (*Ephestia kuehniella*) and the Indian meal moth (*Plodia interpunctella*). Calculated percentage reduction in insects trapped per day during the post-fumigation monitoring period clearly indicated that ProFume has good efficacy and compares very favorably with the efficacy of methyl bromide. Variations in the long – term level of control following fumigation were attributed more to the level of hygiene and sanitation in the structure than to the product used, methyl bromide or sulfuryl fluoride[8].

ProFume® Fumiguide™

ProFume has been developed with an emphasis on Precision Fumigation™, defined as optimizing fumigant use to maximize efficiency and minimize risk. An important tool in Precision Fumigation is the ProFume Fumiguide, proprietary software developed by Dow AgroSciences. The Fumiguide integrates factors such as target pest, temperature, half loss time (HLT) and exposure period to accurately determine the fumigant dose and accumulated concentration x time (CT) CT dosage required for the space or commodity. When monitoring data are entered into the Fumiguide, the program will calculate

the actual HLT and accumulated CT dosage, predict the CT dosage outcome for the planned exposure period, and update instructions on exposure time (on target, shorten or lengthen) and fumigant concentration ("on target" or "add more").

The Fumiguide software continues to be enhanced. The most recent edition was released in January, 2008. It includes new pests, additional temperature calculations for selected key pests, one step report generation, and commodity sorption adjustments. The Fumiguide has been programmed to meet the needs of a global fumigation market; its calculations can be converted to English or metric units and the program is available in multiple languages.

The Fumiguide has been an invaluable aid in enabling fumigators to adapt ProFume fumigations to meet the needs of their customers. Fumigators can easily run multiple fumigation scenarios for a site to determine which combination of factors best meets the customer needs. The ability to accurately determine the fumigation dose when changing fumigant exposure time, temperature, or confinement is a great asset which has not been available for methyl bromide or phosphine. In addition, the Fumiguide provides a written record of each job, including the fumigation plan (pest, temperature, volume, etc.), monitoring data, and achieved CT dosage. The reports can be customized to meet customer requests and regulatory requirements.

Global Registration Status of ProFume

ProFume® gas fumigant received its first global registration in Switzerland for use in flour mills in 2003. Since then, ProFume has been registered in an additional 13 countries (Table 1). Registration activities have been started in Spain (flour mills), Greece, (flour mills, dried fruit, tree nuts), Turkey (dried fruit, tree nuts), and Thailand. The European Union t – MRLs (Annex III of 396/2005/EC) are anticipated in September, 2008 to set the MRLs for sulfuryl fluoride and fluoride in various commodities. Registration feasibility assessments for ProFume are underway in Asia, Latin America, Africa and the Middle East. .

Commercial Acceptance of ProFume®

Over 1 000 commercial fumigations have been completed using ProFume with high levels of customer satisfaction. These fumigations were conducted in many different geographies at different times of the year in a wide range of environmental conditions. The pest control ratings and satisfaction levels expressed by users of ProFume gas fumigant clearly demonstrate its technical and economical viability.

Table 1. Global registration status of ProFume as of June 2008

Year	Geography	Registration
2003	Switzerland	Flour mills
2004	USA	Dried fruit, tree nuts, cereal grain storage, milling, and processing
2004	Italy	Emptied flour mills/pasta factories; food processing facilities
2004	UK	Emptied flour mills
2004	Germany	Flour mills, dried fruit and tree nuts
2005	Puerto Rico	Dried fruit, tree nuts, cereal grain storage, milling, and processing
2005	USA	Expanded food tolerances and use patterns
2005	Belgium	Emptied flour mills
2006	Canada	Emptied flour mills and food processing facilities
2006	France	Emptied flour mills
2006	CODEX Alimentarius Commission approved MRLs for sulfuryl fluoride for international trade	
2007	European Union Annex I listing of Directive 98/8/EC (Biocide) of the active ingredient sulfuryl fluoride	
2007	Ireland	Emptied flour mills
2007	Spain	Food processing facilities
2007	Trinidad and Tobago	Dried fruit, tree nuts, cereal grain storage, milling, and processing
2007	Mexico	Cereals and beans
2007	Australia	Dried fruit, tree nuts, cereal grain storage, seed, hay
2007	Mauritius	Cereal grains, flour mills and processing
2008	European Union	Harmonized MRL (maximum residue level) of sulfuryl fluoride (Directive 396/2005/EC)

In North America, Dow AgroSciences has verified using Fumiguide data that at least 455 individual structures at more than 182 locations in 25 states, two Canadian Territories, and Puerto Rico have been fumigated using ProFume. About 32% of the structures have been fumigated 2 – 7 times with ProFume over successive

years, indicating customer satisfaction and adoption. Rice mills representing 50% of the USA rice processing have converted to fumigating with ProFume.

A survey of ProFume® gas fumigant users in the USA revealed that 96% of the survey respondents would use ProFume again and 4% remained undecided. ProFume fumigator satisfaction ratings averaged 4.4 out of 5 and miller satisfaction ratings (at 60 days post-fumigation) averaged 4.5 out of 5.

In Europe, Dow AgroSciences has documented at least 361 commercial structural fumigations with ProFume from 2003 – 2007 (Table 2). The total number of fumigation conducted in 2007 doubled compared to those conducted in 2006, indicating commercial acceptance.

Table 2. Commercial Structural Fumigations Conducted with ProFume in Europe, 2003 – 2007.

Country	2003	2004	2005	2006	2007	Total
Belgium	0	0	0	0	8	8
France	0	0	0	0	30	30
Germany	0	3	16	30	60	109
Italy	0	2	30	40	80	152
Spain	0	0	0	0	1	1
Switzerland	1	7	8	15	15	46
UK	0	1	4	3	7	15
Total	1	13	58	88	201	361

Additional ProFume fumigations have been conducted in Australia, Trinidad, Mexico, and Mauritius. A ProFume fumigation conducted on Dec. 31 – Jan 2, 2008 of a flour mill in Mauritius was funded from the Multilateral Fund (Montreal) and implemented through GTZ (Windhoek) under the direction of the Mauritius Ministry of Environment. Representatives from Insects Limited, Inc., Dow AgroSciences, Hardy Henry Services, and Rentokil International assisted. The mill was fumigated in the past with phosphine as a methyl bromide alternative; however, even with careful sealing of the electronic panels and equipment, these components suffered serious damage during phosphine fumigations. For the ProFume fumigation, the mill had a mean HLT of 12.9 and a mean accumulated CT dosage of 855 mg · h/L. The target pests were successfully controlled with no damage to electrical equipment.

Case Studies

Cocoa

In the USA, fumigation of cocoa beans is now being conducted with ProFume® gas fumigant. This is the result of a collaborative research effort between Dow AgroSciences, cocoa fumigators, and the Chocolate Manufacturer's Association (CMA). Cocoa beans and fractions (cocoa butter, cake and liquor) fumigated at maximum CT dosage rate (1 500 mg · h/L) with ProFume had a marginal increase in F-residues that was much lower than the MRLs granted by the USA-EPA. The CMA conducted sensory evaluation using ProFume-fumigated cocoa and concluded that the results are satisfactory. ProFume is more economical than methyl bromide for this use pattern. This is due in part to the sorption of sulfuryl fluoride into cocoa beans is much lower than that of methyl bromide under identical conditions, as confirmed by research conducted by Phillips et al., Oklahoma State University (unpublished data). A commercial efficacy trial demonstrated that ProFume killed the target pests of cocoa beans at low temperatures. Pallets of bagged cocoa beans were stored in two refrigerated trucks for two days at 7.2℃, then one trailer was fumigated with ProFume for 20 h at an accumulated CT dosage of 750 mg · h/L. All insects in bioassays in the fumigated trailer died, including eggs of the Indian meal moth, compared to the moderate to high survival rates of insects in bioassays in the non-fumigated trailer. The demonstrated technical and economic viability of ProFume for cocoa bean fumigations resulted in the withdrawal of the methyl bromide critical use nomination for this use pattern.

Seeds

Dow AgroSciences conducted extensive research for three years evaluating seed of grass, wheat, corn, cotton, soybean, and canola in collaboration with three major seed companies. Comparative tests were conducted between phosphine and ProFume gas fumigant, under varying exposure periods and temperatures. The results concluded that fumigating all tested seed types at 750 mg · h/L did not negatively impact germination or interact with seed treatments, and compared well with phosphine regarding germ impact. As a result, major seed companies in the USA are now adopting ProFume for their seed fumigation. ProFume is used for insect and rodent control in climate controlled and non-climate controlled seed warehouses for production export, farm returns, and commercial seed storage. ProFume offers flexibility compared to phosphine in reducing the fumigant exposure time, an important attribute when seed warehouses are on tight time schedules to fumigate

seeds prior to international shipment. In addition, all areas of a seed production facility can be fumigated with ProFume, including those with valuable electronic equipment; i. e. sizing towers, packaging lines, etc. that would be susceptible to damage from phosphine fumigations. ProFume, when applied according to label directions, can be used to fumigate sensitive electrical equipment without damage.

Grain Fumigation of Phosphine Resistant Insects

Studies testing sulfuryl fluoride efficacy on strains of phosphine-resistant red flour beetle indicated no cross – resistance. Resistance issues with sulfuryl fluoride are not anticipated because of use patterns, unique mode of action, and lack of known cross – resistance to other fumigants. Phosphine resistant lesser grain borer, *Rhyzopertha dominica*, is wide spread globally and well documented[12,13]. In the USA, phosphine-resistant lesser grain borer occurs in California and grain fumigations, primarily for rice and some corn, in this geography have successfully converted from phosphine to ProFume gas fumigant. Fumigators will typically install a J fan at the base of the bin to recirculate air, and introduce ProFume in the top of the sealed bin. Using this method, ProFume has been recorded dispersing to the base of the bin within about three hours, even in bins up to 36 m in height. ProFume exposure times average 48 – 72 h, and fumigations are monitored to confirm sufficient dosage accumulation for successful control of phosphine-resistant lesser grain borer and confused and red flour beetles. Farmers appreciate the flexibility to rapidly fumigate and aerate grain immediately prior to shipment, the reliability of control, and the absence of particulate residues that were left in the bottom of the bins following fumigation with aluminum phosphide (Jim Garret, Fume Tech Inc., West Sacramento, California, personal communication).

Conclusion

All efforts of quality and productivity of growers could be ruined after harvest without proper desinfestation of stored product insects in commodities. Fumigants are the preferred solution for a fast and thorough treatment. With methyl bromide being phased out and resistance issues with phosphine increasing, ProFume offers a solution. Sulfuryl fluoride, recognized as an excellent wood fumigant for nearly 50 years, has been developed by Dow AgroSciences for commodity fumigation. Studies conducted both in Europe and the USA have shown this molecule fits the needs of agriculture and food industry for fast, and effective fumigation of commodities, food storage, mills and food processing plants without adverse effect on equipment, food quality and the environment when used according to label. Development and commercial launch success in many countries prove that ProFume is technically and economically viable alternative to methyl bromide, and to phosphine where resistance, damage, or time constraints are issues.

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