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Commercial performance and global development status of ProFume® gas fumigant

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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 as an alternative to methyl bromide. ProFume can be used in non-residential structures, 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's an odorless, colorless inorganic gas, and as such, does not form unpleasant odors. In addition, due to its favorable vapor pressure characteristics, ProFume penetrates commodities better and reaches target pests faster for optimum control.

ProFume received its first global registration in Switzerland for use in flour mills in 2003. In January 2004, the US EPA granted a registration for ProFume as a post harvest fumigant for use in dried fruits and tree nuts and cereal grain storage, milling and processing. Additional ProFume registration was granted in July 2005 that included expanded food tolerances and use pattern. Canadian registration was obtained in 2006. Within the European Union, ProFume registration has been granted in Italy, United Kingdom, Germany, France and Belgium. Registration in Australia is anticipated soon. Registration activities for Asia, Latin America and the Middle East are underway. Commercial launch in all the European countries and in the United States have been very successful. Globally, over 200 commercial fumigations have been completed with high level of customer satisfaction. Development and commercial launch success in many countries prove that ProFume is technically and economically viable alternative to Methyl Bromide.

Introduction

Post-harvest insect pests that infest food commodities in mills, warehouses, food storage facilities and food handling establishments cause substantial economic and quality losses. Since, post-harvest insect pests can be found anywhere within the food storage and handling establishment, localized treatment or physical methods may not control pests adequately. Fumigation is therefore a preferred method of pest control. Methyl bromide has been the fumigant of choice, but this product, identified as an ozone depleting chemical, 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

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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 other countries approached Dow AgroSciences to consider developing Sulfuryl fluoride for food commodity use. As a result, Dow AgroSciences formed a partnership with leading stored product researchers, fumigators and food industries around the world and developed ProFume as a successful post-harvest fumigant.

History

Dow AgroSciences has registered and marketed sulfuryl fluoride as Vikane® gas fumigant 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 introduced in the early 90s in Germany to eliminate wood destroying beetles e.g. *Anobium punctatum* and *Ptilinus pectinicornis* from structures. In Sweden SF is used in shipping containers and for the disinfestations of homes and wooden artifacts. With the adoption of the Montreal Protocol, the phase out of methyl bromide in developing countries started, and the search for replacements began.

Physical and chemical properties

Sulfuryl fluoride is an inorganic, non-flammable, odorless and colorless gas. Because of the 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 non corrosive, an important characteristic for any fumigant, especially in settings 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, as temperatures over 400 °C will cause decomposition products. Because of its low sorption characteristics, it 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 in less than three hours (Bell et al., 2002). Table 1 summarizes the most important chemical and physical properties of sulfuryl fluoride.

Table 1. Main physical and chemical characteristics of sulfuryl fluoride.

Structural formula	|| F-S-F || O
Empirical Formula	SO2F2
Color	None
Odor	None
Molecular Weight	102.07
Vapor pressure	1611,4 kPa at 20 °C
Boiling Point	–55.2 °C at 760 mm Hg
Stability	Stable to temperatures normally encountered in fumigations.
Reactivity	non-reactive as a gas
Sorption to commodity and materials	Low
Desorption	Quick

Toxicity

Sulfuryl fluoride is an odorless, colorless gas and at low concentrations, non-irritating to mucous membranes and gives no warning of its presence. ProFume is toxic and must be handled carefully in regard to the potential hazards it presents. Therefore, sulfuryl fluoride presently is, and will continue to be, labeled for use only by trained, professional fumigators. Professional fumigators are trained in proper fumigation techniques.

Oral ingestion of sulfuryl fluoride is unlikely because of its physical properties and is not toxic dermally. The main route of exposure is through inhalation. Like other fumigants, sulfuryl fluoride can cause adverse effects after acute exposure, depending on the exposure concentration and duration. The AOEL (Acceptable Operator Exposure Limit) for Europe is 3 ppm. Respiratory protection (positive pressure Self Contained Breathing Apparatus (SCBA) is required when entering a fumigation site that exceeds this level of concentration or is unknown.

Dow AgroSciences enforces a strict product stewardship policy to augment the training and certification required by government authorities. In common with other fumigants, SF has hazards that require full understanding and correct execution of application and safety measures to ensure effective pest control with minimal risk to fumigators and the public. A summary of acute toxicology data is provided Table 2.

Ecotoxicology and environmental fate

Ecotoxicology studies (Table 3) have been conducted for labeling and classification purposes. Since ProFume is a gas and applied in closed spaces, the risk of exposure for terrestrial and aquatic wildlife species is considered negligible.

SF 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 (Bailey, 1992, Chambers and Millard, 1995). SF is broken down mainly through hydrolysis to release fluoride and fluorosulphate ions (Bailey, 1992).

Table 2. Main acute toxicity data of sulfuryl fluoride.

Study Type	Animal	Sex	Results
Acute Oral	Rat and Guinea Pig	n/a	LD50 100 mg/kg
Acute Dermal	Rat, F-344	Male and Female	LC50 > 9599 ppm
Acute Inhalation	Rat, F-344	Male and Female	4-Hr LC50 1122 ppm males
			4-Hr LC50 991 ppm females
Acute Inhalation	Rat, F-344	Male and Female	1-Hr LC50 3730 ppm males
			1-Hr LC50 3021 ppm females
Acute Inhalation	Mice, B6C3F1	Male and Female	4-Hr LC50 400-600 ppm
Acute Inhalation	Mice, CD1	Male and Female	4-Hr LC50 400-600 ppm

Table 3. Main ecotoxicological data of sulfuryl fluoride.

Study Description	Species and Strain	Value
Acute toxicity	Rainbow Trout 96h	LC50 0.89 mg/L
Acute toxicity	Daphnia magna48h	EC50 0.62 mg/L
Algal growth inhibition	Selanastrum capricornutum72h	EC50 0.58 mg/L

Dow AgroSciences was awarded the 2002 Stratospheric Ozone Protection Award by the U.S 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.

Mode of action in insects and other arthropods

Once sulfuryl fluoride enters an insect or other arthropod through the spiracles in postembryonic life stages, or diffusion through the egg shell, the compound is broken down to the insecticidally active fluoride anion. The fluoride anion disrupts the glycolysis and fatty acid cycles, depriving the insect of necessary cellular energy.

Insecticidal activity results from fluoride inhibition of enzyme systems utilizing magnesium within the glycolysis cycle (Meikle et al., 1963). After inhibition of the glycolysis and fatty acid cycles, insects attempt to utilize protein and amino acids to maintain a viable energy level, however, these alternative energy producing processes are insufficient to maintain a proper metabolic rate for survival.

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.

Efficacy and commercial performance

Efficacy research have been carried out 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; the Dried Fruit Association (DFA) of California, Central Science Laboratory in the UK, Federal Biological Research Center for Agriculture and Forestry in Germany, the University of Milan in Italy and Laboratoire National des Denrées Stockées in France to define the dosages required to control all the life stages of target pests under a range of fumigation conditions. These studies (Drinkall et al., 2002, Ducom et al., 2002, Reichmuth et al., 2002, Thoms and Scheffrahn, 1994) have confirmed the effectiveness of sulfuryl fluoride on all life stages of a wide range of post harvest insect pests (Table 4), including the important pest species of the coleoptera and lepidoptera orders.

Efficacy of ProFume was also confirmed in actual field fumigations conducted in the US and Europe. In addion to the field efficacy studies, population rebound studies were undertaken in Europe and the US to demonstrate effectiveness of ProFume in controlling stored product pest populations. The objectives of these studies were to compare the impact of ProFume and methyl bromide fumigations upon populations of the red flour beetle (T*ribolium 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 indicated clearly that ProFume had good efficacy and compare very favorably with the efficacy of methyl bromide.

Globally, over 300 commercial scale fumigations have been performed with a very high degree of satisfaction. A survey of ProFume fumigant users in the US 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. Whereas, miller satisfaction ratings (at 60 days post-fumigation) averaged 4.5 out of 5.

Table 4. Partial list of post harvest insect pests controlled by Sulfuryl fluoride.

Common Name	Scientific Name
Indian Meal Moth	*Plodia interpunctella*
Red Flour Beetle	*Tribolium castaneum*
Confused Flour Beetle	*Tribolium confusum*
Warehouse Beetle	*Trogoderma variabile*
Mediterranean Flour Moth	*Ephestia kuehniella*
Sawtoothed Grain Beetle	*Oryzaephilus surinamensis*
Turkish Flat Grain Beetle	*Cryptolestes turcicus*
Yellow Mealworm	*Tenebrio molitor*
Lesser Grain Borer	*Rhyzopertha dominica*
Granary Weevil	*Sitophilus granarius*
Rice Weevil	*Sitophilus oryzae*
Codling Moth	*Cydia pomonella*
Navel Orangeworm	*Amyelois transitella*
Drugstore beetle	*Stegobium paniceum*
Cigarette Beetle	*Lasioderma serricorne*
Merchant Beetle	*Oryzaephilus mercator*
Hide Beetle	*Dermestes maculates*
Dried Fruit Beetle	*Carpophilus hemipterus*
Flat Grain Beetle	*Cryptolestes pusillus*
Rusty Grain Beetle	*Cryptolestes ferrugineus*
Almond Moth	*Ephestia cautella*
Cowpea Weevil	*Callosobruchus maculatus*
Bean Weevil	*Acanthoscelides obtectus*

Commodities fumigated with sulfuryl fluoride

ProFume is registered in the US for use in non-residential structures, 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. Maximum residue limits (MRL) have been established for commodities such as, wheat, sorghum, corn, rice, barley and oats; dried fruits such as raisins, prunes, figs, apples, apricots, bananas, and dates; tree nuts including walnuts, almonds, hazelnuts, pecans, and all other tree nuts. MRL's have also been established for other commodities and processed foods such as, coffee, cocoa, beans, spices, cheese, ham, etc.

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 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. National Association of British and Irish Millers (NABIM) also evaluated these studies and is satisfied by the results. Recently Chocolate Manufacturer Association (CMA) conducted sensory

evaluation using ProFume fumigated cocoa and concluded that the results are satisfactory.

Global registration status

ProFume received its first global registration in Switzerland for use in flour mills in 2003. In January 2004, the US EPA granted a registration for ProFume as a post harvest fumigant for use in dried fruits and tree nuts and cereal grain storage, milling and processing. Additional ProFume registration was granted in July 2005 that included expanded food tolerances and use pattern. Canadian registration was obtained in 2006. Within the European Union, ProFume registration has been granted in Italy, United Kingdom, Ireland, Germany, France and Belgium. Registration in Australia is anticipated soon. Registration activities for Asia, Latin America and the Middle East are underway. Recently CODEX Alimentarius Commission approved for sulfuryl fluoride for international trade.

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 in-depth treatment. Methyl bromide being phased out, little solutions remained and Sulfuryl fluoride, recognized as an excellent wood fumigant for over 40 years has been developed by Dow AgroSciences to fill this gap. Studies conducted both in Europe and US 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.

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