A REVIEW OF IN-TRANSIT SHIPBOARD FUMIGATION OF GRAIN - METHODOLOGY, EFFICACY AND SAFETY [1].

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Abstract

The use of pesticides in ships has long been a recognized necessity. Ship's crews of all maritime nations have always used pesticides in one form or another to protect themselves, their food supplies and their cargoes from pests. Currently, most maritime nations have regulations of their own regarding pesticide use in ships or they utilize the guidelines suggested in the United Nation's, Intergovernmental Maritime Organization's, Maritime Safety Committee's Circular 298 entitled: "Recommendations on the safe use of pesticides in ships".

In this presentation the role of fumigants is emphasized in ships at anchorage and in-transit. The latter usage, in-transit fumigation, constitutes a major portion of this presentation, including the research basis for the current fumigant of choice, current application methodology and safety procedures.

Introduction

Ships' crews have always made use of insect repellents for their personal protection and comfort and insecticidal aerosols and residual sprays as treatments for the control of cockroaches and other insect pests inhabitating their living and working quarters. Likewise, most everyone is familiar with the use of grain and oilseed protectants, such as malathion, which are occasionally used on grain as it is loaded aboard vessels to prevent the spread of any incipient insect infestations. The use of grain protectants is described by Storey et al. (1979). Protection of commodities on board vessels using insect-resistant treated bags and tricalcium phosphate fortified blended cereal foods also have been investigated and widely used (Highland 1975, Highland 1977, Highland et al. 1970).

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1. Mention of a commercial or propietary product does not constitute an endorsement of this product by the USDA.

The use of fumigants in ships is not new. They have been used to disinfest empty ship holds for quarantine purposes for more than 50 years. The use of fumigants to disinfest cargo in ship holds also has been a long standing quarantine-type treatment procedure. However, this latter use has been on break bulk cargoes and not been used on bulk cargoes such as grain. For the reader interested in the historical background on this use of fumigants in ships several general publications are noted with asterisks in the bibliography of this paper.

The use of fumigants on board vessels loaded with grain began in the United States in 1949, when the US Department of Agriculture (USDA) and the US grain trade began ship storage of wheat on an experimental basis. In that year the lower holds of several liberty ships were filled with wheat to within four feet of the tween deck. This four foot space allowed for inspection and treatment of the stored wheat. Each Liberty ship was loaded with approximately 225,000 bu. into their five holds. All wheat stored in 1949 and 1950 in Liberty ships was loaded out in 1950-51.

This type of storage had many problems which related primarily to quality maintenance. However, with increasing quantities of wheat going into storage, it was apparently acceptable. In 1953, fifty Liberty ships of the Hudson River Reserve fleet were set aside for wheat storage. Later in 1953, fifty Liberty ships of the James River Reserve fleet were also included. Ultimately 210 ships made up this wheat storage fleet. Between March 1953 and June 1959 some ships were loaded and unloaded several times. The total amount of wheat stored in this fleet was more than 95 million bushels with an average storage time of 26 months. The longest storage time was nearly 6 years (Cotton 1961).

Insect control in this grain fleet involved the use of several pesticides and several different applications procedures. Water base surface sprays of 0.3% pyrethrins and 3% piperonyl butoxide and 3% methoxychlor sprays were used. In 1953, early in the storage program, a liquid fumigant of 3 parts ethylene dichloride (EDC) and 1 part carbon tetrachloride (CT) was applied to the wheat surface at the rate of 5 gallons per 1000 bushels (Cotton 1961). In 1954, tests were conducted using methyl bromide (MB) at the rate of 2 lbs per 1000 ft^3 (Phillips and Bulger 1954, Phillips 1955). This use required the modification on the ship's in-place aeration system for recirculation of the fumigant. Methyl bromide proved efficacious and cost effective, but repeated fumigations resulted in excessive residues. In 1958 all cargoes were fumigated in the storage hold upon arrival with a liquid mixture of 60% (CT), 35% (EDC) and 5% ethylene dibromide (EDB) applied at 3 gal per 1000 bu. The aeration (recirculation) system was used for a few minutes at 24 and 48 hours to bring the fumigant vapors back to the surface.

Other researchers have reported on the effective use of fumigants in controlling insects in loaded ships. Pingale et al. 1972, reported on the effective use of EDB, an EDB/MB combination and hydrogen

phosphide (phosphine) on grain. Storey et al. (1980) reported on the use of hydrogen phosphide in transit on containers of hay. Snitko (1977) Sharp and Banks (1979), reported on containers of wheat treated in transit with atmospheres of carbon dioxide.

It has only been recently that maritime and other governmental regulators and the various grain trade interests recognized the need and value of pesticide use on grain cargoes. The need was first recognized in the 1960's by the international maritime community through the United Nation's Inter-governmental Maritime Consultative Organization (IMCO). This organization has now dropped the word Consultative from its name and is referred to as IMO. In 1971, this organization's Sub-Committee on the Carriage of Dangerous Goods issued Maritime Safety Committee Circular (MSC/Cir.) 108 entitled: "Recommendations on the Safe Use of Pesticides in Ships". However, this circular did not include guidelines for the use of in-transit shipboard fumigation.

Background:

In the 1970's large increases in the volume of United States export grain resulted in occasional problems of insect infestation occurring at the port, on the vessel, or upon receipt by the foreign buyer. One possible solution to this problem was in-transit shipboard fumigation. However, to appreciate the value of in-transit shipboard fumigation one must understand the US grain trade industry's methods of handling export grain.

The marketing of grain in the United States has some unique features compared with those of other major grain-producing nations. For example:

1. it is relatively free of governmental regulation,

2. it is primarily in the hands of the grain industry,

3. governmental control is limited in most instances to certification of quality and weight, and

4. ownership is very diverse prior to marshalling grain in sufficient quantities to meet export sales contracts.

The diversity of ownership and of knowledge to adequately store grain can result in a variety of preventive insect control practices ranging from none to the very best. Grain is often stored on the farm in relatively small quantities. As a result, when it becomes necessary toassemble large quantities to meet one or more sales contracts the grain rapidly becomes admixed as it moves from the multitude of storage sites and collection points to a U. S. export elevator. During this period, to find an opportunity to adequately search out or detect lots of grain which may harbor insect infestations is often impossible from

the standpoint of logistics. Even when an opportunity does exist and an infestation is discovered, the requirements of sufficient time and proper facilities may not be available to effect an acceptable insect control procedure.

Grain exported from the U.S. is visually inspected by th USDA's Federal Grain Inspection Service (FGIS) for the presence of live adult insects injurious to grain. If sufficient numbers of live insects are found, the lot of grain in question is assigned the special grade "weevily". Prior to 1976, it the grain was determined to be "weevily" the exporter had the following options:

1) Receive an inspection certificate indicating that the grain is "weevily";

2) Remove the portion of grain determined to be "weevily" from the vessel. Inspection personnel were required to conduct a subsequent inspection of the grain remaining in the hold to ensure no infestation remained;

3) Fumigate the grain in the hold after which inspection personnel examine the grain to ensure that the insects had been killed.

In most U.S. grain-exporting terminals, facilities exist only to load ships. To remove grain containing an insect infestation from a ship often will require moving a floating unloading facility and a barge to the site. This significantly increases the grain handling costs of loading and can delay the loading of other ships awaiting the berth. The option of fumigating the infested lot of grain on board the ship also requires that loading into the hold be stopped. Loading can recommence only after the inspector has certified that the insects have been killed. This option too can cause considerable delays, particularly if the other holds on the ship are filled or out of position for loading. However, the major objections to this latter option are the safety hazard caused by the requirement that the inspector enter the hold to determine if the fumigation treatment has been effective; and the fact that only the infested lot of grain is fumigated and consideration is not given to the total volume of the ship's hold.

Experimentation:

In 1976, scientists from the Stored-Product Insects Research and Development Laboratory, Agricultural Research Service (ARS), USDA, Savannah, GA, recommended to USDA, FGIS that they revise their procedures to allow continued loading when an insect infestation is detected. This change would be based on the condition that the entire hold would be fumigated and sealed after it was filled. The recommendation was limited to the holds of bulk dry cargo vessels that were certified by a licensed fumigator as acceptable for such treatments. In this recommendation, it also was implied that FGIS, ARS, the U.S. grain industry, and other interested parties would

cooperate in a research program to determine the efficacy and safety at sea of this procedure and to continue research to expand the regulation to other types of vessels and fumigants.

The research program has involved and will continue to involve only fumigants that are known to be efficacious as a result of extensive research and practical use and are also acceptable for use in land storage situations. Therefore, the primary objectives have been to investigate methods of applications and formulations of fumigants that will achieve uniform distribution of the gas so the potential effectiveness of a fumigant is achieved in a safe manner.

Materials and Methods:

Preparation for conducting an in-transit shipboard fumigation experiment begins before the ship is loaded. First the holds are inspected in the company of a designated ship's officer and then into each empty hold there is placed a "trunk line" consisting of a braided hollow core rope into which nylon tubing lines and bioassay cages containing insects and infested grain are inserted. The trunk line extends from the center across the bottom and up the side of the hold and terminates in a manhole on deck. This arrangement establishes several sampling positions for monitoring fumigant concentrations and placement of the bioassays. After the holds are filled gas sampling positions are established on the surface of the grain. Then ropes containing caged insects and infested grain and gas-sampling tubes are probed into the grain near the center of the hold to establish assay positions within the grain mass. Gas-sampling lines from these positions also terminate in the manhole on deck.

The insects used in the bioassays are the adult and immature stages (ranging from 1-day-old eggs to 3-wk-old larvae) of the maize weevil or granary weevil, Sitophilus spp.; the lesser grain borer, Rhyzopertha dominica (F.), and the confused flour beetle, Tribolium confusum Jacquelin duVal.

During the loading of the grain, official grade samples are collected by FGIS inspectors for each 1360-1633 tons (50,000 to 60,000 bu). A representative portion of these grade samples (ca. 2 kg) are collected and taken to the Savannah laboratory for incubation and examination for emergence of any internal (hidden) insect infestation. Similar samplings are made also during the off loading of the grain. The interested reader is referred to Leesch et al. 1978, Redlinger et al. 1979, Gillenwater et al. 1981, Redlinger et al. 1982, and Zettler et al. 1982, for specific details of the research used to develop the recommended procedures of in-transit shipboard fumigation of grain.

Application of Fumigants: In all tests, the dosage of the fumigant applied has been in accordance with the manufacturer's label or the Environmental Protection Agency's experimental use permit. For 80-20, the dosage was 0.27/m^3 (2-1/2 U.S. gal/1000 bu); and for hydrogen phosphide several dosages have been used including 1.17 g/m^3 (33

g/1000 ft^3), 1.77 g/m^3 (50 g/1000 ft^3), and 3.18 g/m^3 (90 g/1000 ft^3). The formulation of 80-20 used contained 81.54% CCl_4, 16.16% CS_2, 1.54% SO_2, and 0.76% inert ingredient. The hydrogen phosphide formulations (aluminum phosphide) used were the 3-g tablet (Phostoxin (R)), the 0.6 g pellet (Phostoxin (R)), and the 34-g sachet of granules (Detia EX-B gas (R)).

The 80-20 liquid fumigant was applied as evenly as possible over the entire surface area of the grain. The formulations of aluminum phosphide have been applied by several methods. The Detia EX-B gas sachets in bag blankets were laid on the surface of the grain. Tablets have been broadcast on the grain surface and stepped or walked into the surface by the applicator or probed into the surface to depths of ca. 1 m (2-4 ft.) and 4-5 m (13-16 ft.); in one instance, a layering application was accomplished by broadcasting tablets onto the grain when the hold was filled to depths of 1/3, 2/3, and 9/10. In another experiment, pellets mixed with grain were poured into perforated drain field pipes, that were installed in the ships' holds before loading in an effort to achieve faster and more uniform distribution of the fumigant gas.

As soon as possible after the fumigants were applied, the hatch covers were closed. In every case except one, the hatches remained closed as recommended until the ship arrived at the port of destination.

Fumigant Gas Readings (and Safety Considerations): During transit, concentrations of the fumigant gases have been monitored on a routine schedule by collecting samples from 8 to 12 positions in each test hold and at as many as 26 selected sites throughout the living and working areas. Gas samples were taken at approximately 6-hour intervals during the first 48-hour and then at 12-hour intervals during the remaining time in transit. Concentrations of gas were determined with Drager(R) or Auer(R) gas detector tubes and/or by use of a Miran(R) IR (infrared) gas analyzer.

Monitoring for fumigant gases, both on the ship and in the receiving elevator facilities, was conducted throughout the unloading period. On the ship, gas samples were taken from the bottom of the fumigated holds, from the surface of the grain where men work, and from the crew's work areas. In the grain elevator, gas samples were taken from near the grain surface on the conveyor belt and from the air spaces in the belt house and the scale house.

Concentrations of the fumigants have never been detected in any of the ship's living quarters. Concentrations have been detected in some test vessels in the keel duct, paint lockers and engine room. Never have these concentrations created a health or safety hazard or any cause for alarm. The only working areas where hydrogen phosphide has been detected have been on the decks downwind and immediately adjacent to the open hatches at the time of application and also when the hatches were opened for unloading. At these times the gas concentrations persisted for only a matter of minutes. In the case of

80-20, concentrations of both CCl_4 and CS_2, at levels that frequently exceeded the TLV, have been detected on the surface of the grain and in the belt house when grain was being discharged. However, these gases have not been detected in the scale house.

Residue Analysis: Residues of 80-20 are exempt from tolerance in the U.S., and in most cases, residues of CCl_4 were found to be less than 100 ppm. Hydrogen phosphide residues were well below the tolerance of 0.1 ppm, except in four instances. In these instances, it was highly probable that the sample collected contained some residual dust from a spent tablet of the aluminum phosphide formulation.

Residues of hydrogen phosphide were determined by using the method of Rosebrook (1972). The weighed sample is refluxed with water in a closed system with nitrogen gas flowing through at 100-150 ml/min. The nitrogen-hydrogen phosphide mixture is scrubbed through saturated lead acetate, 10% sulfuric acid and 10% sodium hydroxide. The hydrogen phosphide is collected and measured with low-level Drager detector tubes. Parts per million of hydrogen phosphide is calculated by multiplying the tube reading by 1.39 and dividing by the sample weight (gm).

Residues of CCl_4 were determined by extracting samples with acetone after grinding and diluting aliquots with cyclohexane. Two-microliter samples of the cyclohexane dilutions were then injected into a gas-liquid chromatograph (Hewlett Packard(R) series 5750) equipped with an electron capture detector. The chromatographic column used was a 4-m, 3-mm o.d. stainless steel column packed with 10% Carbowax(R) 1540 on Gas Chrom Q(R) (80/100 mesh). The chromatographic conditions were as follows: column temperature, 50°C; nitrogen carrier, 8 cc/min; detector voltage, 80 v; injection port temperature, 130°C; detector temperature, 240°C; an purge flow, 90 cc/min.

Summary

The research program has, in fact, been the recipient of considerable interest and of participation by all segments of government and industry since its inception. The following directives have been issued by the USDA, FGIS as a result of this research:

GR INSTRUCTION 918-6, Aux. 19; "Shiphold Fumigation"; September 26, 1976.

GR INSTRUCTION 918-6, Aux. 19, Revision 1; "Shiphold Fumigation"; June 22, 1977. Auxillary 19 (Revision 1) went into more detail regarding the procedure and the limitations of using this technique particularly in calling to attention the structures that would limit penetration of the fumigant. The only approved fumigant under Auxillary 19 and Revision 1 were liquid fumigants containing approximately 80% CCl_4 and 20% CS_2.

GR INSTRUCTION 918-6, Aux. 19, Revision 2; "Shiphold Fumigation"; September 12, 1977. Auxillary 19 (Revision 2) provided for the use of aluminum phosphide formulations of the fumigant hydrogen phosphide.

FGIS INSTRUCTION 919-1; "In-Transit Fumigation of Grain Loaded Aboard Tanker-Type Vessels"; April 21, 1982. The instruction delineated the procedure to safely and effectively fumigate grain in transit aboard tanker-type vessels.

In addition to the above USDA regulations the data generated by this research program were utilized in the U.S. securing the incorporation in an IMO revision of MSC/Circular 108 "Recommendations on the Safe Use of Pesticides in Ships". This revision is IMO MSC/Circular 298.

In conducting this research, USDA, FGIS and Foreign Agricultural Service (FAS) have been invaluable cooperators since the inception of this program. In the conduct of individual experiments the cooperators have been many and varied from experiment to experiment. Some of the cooperators are as follows: Cargill Inc., Continental Grain Company, Central Soya Inc., Louis Dreyfus Corporation, Cook Industries Inc., Pestcon Systems Inc. (formerly Phostoxin Sales Inc.), Research Products Co. Inc., Degesch America Inc., National Cargo Bureau, U.S. Coast Guard, Charrier, Fettig and Donalty Inc., South Inc., Aeron Marine Shipping Co. Inc. Ultramar Shipping Inc., Point Shipping Inc., Rolimpex-National Foreign Trade Enterprise (Poland), Exportkhleb-National Foreign Trade Enterprise (USSR), Vitasa Steamship Co. (Yugoslavia), Atlantska Plovidba Co. (Yugoslavia), the Egyptian Agricultural Research Organization, Korean Silo Company, All Union Soviet Grain and Grain Products Institute (USSR), Spett le Silos Cerealicola Ferruzzi (Italy), and the USDA - Animal Plant Health Inspection Service (APHIS).

While there remains considerable research to be conducted on in-transit shipboard fumigation of grain cargoes, data secured to date have shown that this method is practical and safe for use on bulk dry cargo vessels and tanker-type vessels. In most every instance, hydrogen phosphide has given acceptable levels of insect control. In some of the tests with 80-20 less than satisfactory control has been achieved against insects on or near the grain surface. Research is continuing to develop better methods of fumigant application to achieve more rapid and even gas distribution throughout the grain and to extend the procedure to other types of vessels.

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