REPORT OF STUDY ON SPOT FUMIGATION WITH 70-30 MIXTURE OF ETHYLENE DIBROMIDE (EDB) AND METHYL BROMIDE (MeBr) AT THE BURRUS MILLING AND ELEVATOR COMPANY AT FORT WORTH, TEXAS ON JUNE 26, 1954

By V. K. Rowe
Biochemical Research Department
The Dow Chemical Company
Midland, Michigan

July 28, 1954

PURPOSE

The purpose of this study was to evaluate the health hazards associated with the use of the subject material as a spot fumigant for equipment common to flour mills and similar establishments. Information regarding methods of handling, equipment used in application, method of application, and vapor (fumigant) concentrations encountered in these operations is essential to a sound evaluation.

DESCRIPTION OF MILL AND EQUIPMENT TREATED

The subject mill was a 7 story concrete structure in good condition. There were many windows and these were in good repair. Actual measurements of the dimension were not made but it was estimated that the section where the fumigation was done was about 75' long, 40' wide, and that the ceilings were about 13' high. The blending section was adjacent to the flour mill and was perhaps 1/3 as large in terms of floor space.

The equipment which was treated consisted essentially of the following:

7th Floor

34 cyclones	102 injections
80 spouts to sifters on 6th floor	80 injections
40 spouts to lower floors	40 injections
108 elevators	108 injections
2 sifters	8 injections
2 dust conveyors	12 injections
1 flour conveyor	14 injections
Approximate total injections on 7th floor	364 injections

6th Floor

40 sifters (10 chutes below each).....	400 injections
1 large sifter (20 chutes).....	20 injections
2 dust conveyors.....	8 injections
Approximate total injections on 6th floor.....	428 injections

Blending Section - 6th and 7th Floors

Equipment consisted of various conveyors, elevators, spouts, sifters, and bins requiring a total of something over 200 injections.

PREPARATION OF FUMIGANT MIXTURE

The fumigant mixture was prepared by weighing 93 pounds of EDB into a pressure vessel improvised from an air force oxygen tank. The MeBr (40 pounds) was then added by bubbling it into the tank from a regular MeBr Cylinder. This whole operation was slow and was characterized by spills, leaks, and no doubt the waste of an appreciable amount of MeBr. This difficulty was brought about because proper conditions and equipment for handling the materials were not available.

APPLICATION OF THE FUMIGANT

Application of the fumigant was made to the equipment listed previously. By applying the material to the top floors, sufficient diffusion occurs downward through the equipment to effect insect control throughout the equipment on the lower floors. Application, in general, was made by injecting approximately 2, 3, or 4 ounces of the fumigant into the various chutes, elevators,

conveyors, etc., located on the top two floors. Each such piece of equipment has a hole in it about 1/4" in diameter through which the injection can be made.

The equipment used to apply the fumigant consisted of a short copper tube (perhaps 3/16" in diameter and 6" long) which could be shoved into the holes in the equipment mentioned above. This tube was connected to a "squeeze type" valve which in turn was connected to the pressurized cylinder of fumigant by means of perhaps 100 feet of polyethylene tubing (about 1/2" in diameter, O.D.). The cylinder was pressurized by connecting it to the compressed air line in the mill. According to the men doing the work, depression of the valve for 1 second allowed the delivery of approximately 1 ounce of fumigant. Dosage was judged on this basis.

Application of the fumigant was made by 2 crews, one working in the blending section and the other on floors 6 and 7 of the flour mill. This was done rapidly, as actual application did not require more than 1 to 1 1/2 hours. Except for the difficulty in preparing the fumigant mixture, the whole job was done with dispatch.

RESULTS

Sampling with the midget impinger pump was done in the breathing zones of the men applying the fumigant. General atmospheric samples were taken either with the electric pump in a central area just off the floor or with the midget impinger pump while walking about the floor.

The samples were all taken by passing measured volumes of contaminated air over activated silica gel which absorbs th fumigant. In the laboratory, the silica gel was subjected to heat to drive off the fumigant which in turn was burned to carbon dioxide (CO_2), hydrobromic acid (HBr), and Br_2 (bromine). The HBr and Br_2 were absorbed in an appropriate solution and the amount of Br determined by titration (Volhard) with standardized silver nitrate. Thus by determining the mg. of Br/sample and the sample volume, it is possible to calculate the concentration of gas in the air sampled.

This method does not allow the differentiation of EDB and MeBr so that results must be expressed as EDB, as MeBr, or as some fixed mixture of the two. In this particular situation it seemed that the atmospheric contaminant would be largely MeBr and furthermore if the results were expressed as ppm of MeBr, the highest possible figures would be obtained which represents the worst possible condition. For these reasons, it seemed desirable to express the data obtained as ppm of MeBr and draw conclusions based on these figures.

The analytical results are summarized in Table 1. If one is interested in converting the values given (ppm of MeBr) to concentrations of EDB, this can be done (approximately) by merely halving the figures given.

The basis for conversion of mg. of Br to ppm of MeBr or EDB is described below:

Calculations:

Mol. wt. Br.	= 79.916	Mol. wt. Br.	= 79.916
Mol. wt. C	= 12.	Mol. wt. Br.	= 79.916
Mol. wt. 3-H.	= 3.002	Mol. wt. 2-C	= 24.
		Mol. wt. 4-H.	= 4.003
Mol. wt. MeBr	= 94.918	Mol. wt. EDB	= 187.835

94.92 g. MeBr = 22.4 l.(liters) at 760 and 0°C.

Since operating conditions were estimated to be about 750 mm.Hg. and 95°F (35°C.)

$22.41. \times \frac{760}{750} \times \frac{308}{273} = 25.6$ l. = Mol. volume at operating conditions

So 25,600 cc MeBr gas = 94.92 g. = 94,920 mg.

1 cc MeBr = $\frac{94,920}{25,600} = 3.71$ mg.

Then 1 ppm MeBr = 1 cc of gas or 3.71 mg./1,000,000 cc of air,

or 0.00371 mg. MeBr/l. = 1 ppm at 760 mm.Hg. and 35°C.

and 1 mg./l. MeBr = $\frac{1}{0.00371}$ = 269 ppm

Since results are in terms of Mg. of Br. and

1 mg. of Br. = 1.185 mg. of MeBr

then 1 mg./l. of Br. = 1.185 x 269 = 319 ppm MeBr

Similarily, 1 mg./l. of Br. = $319 \times \frac{94.918}{187.835}$ = 162 ppm EDB

Therefore, $\frac{\text{mg.Br./sample}}{\text{Sample Vol (l)}}$ or $\begin{matrix}(319) \\ (162)\end{matrix}$ = ppm of MeBr
= ppm of EDB

A summary of the results of the analyses is given in the following tabulation.

TABLE 1

Floor No.	Concentration of Fumigant Found Calculated as ppm of Methyl Bromide				
	At Breathing Zone of Operator While Applying Fumigant	General Atmosphere			
		During Application Windows Open	After Application Windows Closed		
	(June 26, 1954)	(June 26, 1954)	(June 26)	(June 27)	(June 28)
7	31.9 61.9	----	73.2	12.9	----
6	87.3* 17.1 42.1 51.6	23.0 18.0 17.0	83.0	24.6	14.6 8.9
6 (Blending Section)	----	----	141	16.4	----
5	----	----	1610 515	32.8	----
4	----	----	517 528	23.4	----
3	----	----	437 309	12.4	----
2	----	----	219 121	15.1	5.5
2 Inside a Boot	----	----	----	1830	----

* Sample taken during mixing of fumigant - spills occurred.

DISCUSSION

The results of analyses show:

(1) Even though there was good cross ventilation during the mixing of the EDB and the MeBr, the spillage that occurred resulted in a concentration of 44 ppm calculated as EDB or 87 ppm calculated as MeBr. Aside from the hazard of excessive vapor exposure, the procedure provided excellent opportunity for severe skin contact.

(2) Vapor concentrations in the breathing zone of the operator during application were found to be quite low considering the operation. They averaged about 40 ppm with a range of 17 to 62 ppm.

(3) Vapor concentrations in the general atmosphere of the sixth floor where the fumigant was being applied were not excessive. They averaged about 19 ppm. The presence of excellent cross ventilation was no doubt responsible for these low values.

(4) When the windows were closed after all the fumigant was applied, the vapor concentration in the general atmosphere rose appreciably, particularly on the lower floors, to levels which constitute a serious hazard to life upon exposures of 30 minutes or more. This is no doubt a reflection of the diffusion downward through the chutes and other connecting channels of the heavy fumigant vapors. It also reflects the ability of the fumigant (probably to a large extent the

methyl bromide) to escape from the equipment into the general atmosphere. A large portion of this escape is no doubt through the socks connecting moving equipment such as sifters with stationary equipment.

(5) On the first and second day following the application of the fumigant (20-21 hours later) the concentration of the fumigant in the general atmosphere was not excessive. This indicates that in this mill sufficient ventilation was present, even though the windows and doors were closed, to allow the escape in 20 hours of a large portion of the fumigant. Atmospheric conditions were not unusual during this period. There was, however, a gentle prevailing breeze during most of the period.

(6) Even though the contamination of the general atmosphere was not excessive on the day following the application, checks with the halide leak detector showed that high vapor concentrations of fumigant still existed inside the equipment throughout the mill. It is suspected that this was largely ethylene dibromide since the odor of EDB was very pronounced and it is believed that a large part of the methyl bromide had already escaped. One air sample was taken from a chute just above a boot on floor 2 and found to contain 1830 ppm of MeBr or 930 ppm of EDB.

CONCLUSIONS

(1) The mixing of the EDB and the MeBr as it was done in this instance was a hazardous operation and should be discouraged.

(2) The actual application of the 70-30 mixture of EDB and MeBr was accomplished without the occurrence of acutely dangerous concentrations of fumigant in the breathing zone of the operator. It should be pointed out, however, that the application of a fumigant such as this should never be attempted without the use of proper respiratory protection (full face gas mask with fresh black canister).

(3) Vapor concentrations dangerous to life within a short period of time existed in this mill for several hours after the fumigation. There is no question that a structure so treated should be locked and posted so that no one could enter unless duly authorized and protected. The general atmospheric contamination of the mill was sufficiently low 20 hours after fumigation as to present no appreciable toxic hazards.

(4) This study convinces the writer that a 70-30 mixture of EDB and MeBr, if properly packaged and supplied to mill, could be applied as a spot fumigant (as in this case) with no appreciable hazard to those making the application, providing, of course, that those persons involved are equipped with appropriate respiratory protection and that they taken proper precautions to prevent skin contact.

RECOMMENDATIONS PERTAINING TO THE SUBJECT FUMIGATION

(1) The use of a Prest-O-Lite Halide Leak Detector or its equivalent is recommended for the detection of acutely toxic vapor concentrations of MeBr, EDB, and other halogenated compounds. In this study, a Prest-O-Lite unit gave us assurance that vapor concentrations where we were working were not excessive and that the life of our gas mask canisters would be adequate. It also served to point out areas of high concentration. In general, as long as there is no more than a slight green fringe at the top of the flame, it is safe to assume that acutely dangerous concentrations are not present. Such a flame, does however, indicate the presence of a halogenated vapor in significant concentrations.

The use of a leak detector in a flour mill should always be with great caution because of the possible hazard of fire.

(2) If MeBr and EDB are to be mixed on the premises, it was strongly urged that cooling facilities be provided. If the materials could be handled at perhaps 30°F or lower, then the hazards would be markedly lessened and further, much material would be saved.

(3) Mixing of components should always be done out of doors or in well ventilated areas.

(4) Old air force oxygen tanks have been known to fail when used as pressure vessels. They should be checked for safety before use and periodically thereafter. This is particularly

important if welding has been done or other alterations have been made for such operations, no doubt, create stresses in the metal which are likely to weaken it.

(5) MeBr and EDB present hazards of serious injury to the skin particularly if contact is for prolonged periods. Even slightly contaminated clothing or shoes, in particular, should not be worn, but should be removed promptly and thoroughly cleaned before re-use. Prompt washing of contaminated skin or eyes is very important.

(6) Particular precautions must be taken when handling MeBr or compositions containing it to prevent inhalation of vapors. MeBr presents a serious hazard from inhalation for it is a gas at ordinary temperatures and cannot be detected by odor - hence inhalation of acutely toxic concentrations can easily occur.

(7) Precautions must also be taken to prevent inhalation of EDB but the precautions need not be so stringent as with MeBr. EDB is just as toxic as MeBr is, but it has a distinct odor in hazardous concentrations, and furthermore, it is a liquid at ordinary temperatures. Therefore, the likelihood of accidentally inhaling dangerous concentrations is far less than with MeBr. If inhaled, however, it can be just as deadly.

(8) Men applying these materials always should wear full face gas masks equipped with appropriate canisters (black for organic vapors).

(9) The necessity for posting the mill after fumigation is emphasized. This is particularly important during the first 24 hours after spot treatment.

bb

CONFIDENTIAL RECOMMENDATIONS PERTAINING TO PRODUCT DEVELOPMENT BY THE DOW CHEMICAL COMPANY

On the basis of the observations made and the data obtained, it is recommended that The Dow Chemical Company seriously consider the marketing of a spot fumigant under pressure so that application can be made by injection into equipment such as is found in mills and other similar establishments.

The advantages of such a product would be:

(1) Convenience (merely attach appropriate hose and injection tube and valve and begin).

(2) Safety (opportunity for spills and prolonged exposure unlikely).

(3) Rapidly applied (mill such as Burrus could be treated in 30 to 60 minutes).

(4) Economical (labor saving and no expensive equipment required).

Whether a 70-30 EDB and MeBr mixture as a similar mixture of different proportions is what we want to market should be based on effectiveness. Reports from Supt. Box at the Burrus Mill at Ft. Worth stated that such a mixture gave them 95 to 98% control whereas Dowfume EB-15 gave only 78-85% control and Acrilan 80-90% control.

Consideration certainly should be given to the marketing of Dowfume EB-15 and perhaps other products in pressurized containers. It would seem that such a venture would have the same advantages as those mentioned above and create a lot of sales appeal.

UNIT INDEX

Results, discussion, and recommendations from a toxicological viewpoint resulting from a study of a fumigation at the Burrus Milling and Elevator Company in Ft. Worth, Texas using a 70-30 mixture of ethylene dibromide-methyl bromide mixture are given.

INDEX HEADINGS

Ethylene dibromide - methyl bromide (70-30 mixture).

Ethane: 1,2-dibromo-

Methane; bromo-

DISTRIBUTION

Director of Research - R. H. Boundy
Central Research Index
Western Central Research File
Texas File A
Agricultural Chemical Research - J. E. Johnson
Agricultural Chemical Development - K. C. Barrons
Agricultural Chemicals Sales - W. W. Allen (1)
J. L. Maxwell (1)
Agricultural Chemicals Sales - M. W. Held, Houston (1)
W. F. Hardy, Houston
J. W. Britton
W. W. Sunderland
F. C. Amstutz
B. L. Fayerweather
G. E. Cantwell
H. R. Hoyle

bb