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AN INDUSTRYWIDE INDUSTRIAL HYGIENE STUDY OF ETHYLENE DIBROMIDE

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Worker exposure to ethylene-dibromide (106934) (EDB) was evaluated through industrial hygiene surveys at two manufacturing and two user facilities. Approximately 70 workers in 17 different job classifications were exposed to EDB at these facilities. Air monitoring included 75 personal samples and 22 area samples at different sites routinely entered or occupied by workers. In the manufacturing processes, the median personal EDB exposure for similar jobs was 10 to 500 parts per billion (ppb). In the antiknock blending operations, the exposures were 0.2 parts per million (ppm) at processing sites, 0.5 ppm at laboratory sites, 0.6 ppm at quality control sampling ports, and 0.04 ppm at control room sites. Concentrations at quality control sampling sites were 0.04 to 23.4 ppm for personal samples and 0.09 to 2.4 ppm at the tank car loading and unloading sites. The authors conclude that existing engineering controls at the four facilities were adequate to maintain EDB vapor concentrations below the current federal standard of 20ppm as an 8 hour TWA, but improvements to these control measures would be necessary to

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meet the NIOSH recommendation of an EDB ceiling limit of 1 milligram per cubic meter or 0.13ppm for a 15 minute period.

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ABSTRACT

An industrial hygiene survey was performed at two manufacturing and two user facilities of ethylene dibromide as a part of an industrywide study to evaluate worker exposure to ethylene dibromide. Seventeen different job classifications involving more than 69 workers were identified at these facilities where worker exposure to ethylene dibromide would occur. A total of 75 personal samples were taken for each of these job classifications for 8-hour TWA determinations and for determining the contribution of specific tasks to the worker's overall exposure to ethylene dibromide. Area samples were taken at 22 different sites identified as areas routinely entered or occupied by the sampled personnel.

The median 8-hour TWA determination in the manufacturing facilities ranged from 0.01-0.50 ppm and in the user facilities from 0.0002-0.054 ppm. Ethylene dibromide concentrations for comparable tasks ranged from <0.49-23.4 ppm (sampling time 1 min 18 sec - 18 min) for the manufacturers and from <0.28-3.75 ppm (sampling time 3 min 33 sec - 14 min 16 sec) for the user facilities. Ethylene dibromide concentrations at selected areas ranged from <0.00007-5.80 ppm for the manufacturing process areas and from <0.003-0.167 ppm for the user process areas.

The current federal standard for ethylene dibromide is 20 ppm as an 8-hour TWA concentration. Exposures to workers in all job categories

were found to be below this value. However, a current reassessment by NIOSH of the toxicity of ethylene dibromide has led to the NIOSH recommendation of 1 mg/cu m (0.13 ppm) as a ceiling limit determined by a sampling period of 15 minutes. Based on survey results, the two manufacturing facilities do not under present conditions meet the NIOSH ceiling limit and need to reevaluate existing engineering controls and work practices in order to develop an effective program of controls to reduce ethylene dibromide levels in the working environment. The user facilities have the potential to exceed the ceiling limit during the performance of certain specific tasks and an assessment of controls related to the performance of these tasks is necessary.

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INTRODUCTION

The Williams-Steiger "Occupational Safety and Health Act of 1970" was passed into law "to assure safe and healthful working conditions for working men and women..." This act established the National Institute for Occupational Safety and Health (NIOSH) in the Department of Health, Education, and Welfare and the Occupational Safety and Health Administration (OSHA) in the Department of Labor. The Act provides for research, informational programs, education, and training in the field of occupational safety and health and authorizes the enforcement of standards.

NIOSH has been given the authority and responsibility under the Act to conduct field research studies in industry, evaluate findings and report on these findings. Section 20(a)7 states that NIOSH shall conduct and publish industrywide studies of the effects of chronic or low-level exposure to industrial materials, processes, and stresses on the potential for illness, disease or loss of functional capacity in aging adults. Section 20(c) provides the authority to enter into contracts, agreements, or other arrangements with appropriate public agencies or private organizations for the purpose of conducting studies relating to responsibilities under the Act. For this purpose NIOSH established a contractual agreement with SRI International (formerly Stanford Research Institute) to perform an industrywide study of worker exposure to ethylene dibromide.

TOXICOLOGICAL EVALUATION
(Human and Animal)

Minimum concentrations of ethylene dibromide in air that have been reported to be detectable by odor range from 10 ppm[1] to 25 ppm.[2] The present federal TWA standard (29 CFR 1910.1000) and the ACGIH recommended TLV[3] are both 20 ppm, and are based primarily on the work of Rowe et al;[4] Olmstead[5], and McCollister et al.[6] Evidently, these values were set at 20 ppm for ethylene dibromide because of its irritant effect on the eyes and skin as well as its inherent reported toxic effects through inhalation of the vapor at concentrations greater than 25 ppm.

Ethylene dibromide is moderately toxic by ingestion as can be seen from the oral LD 50's of 55 mg/kg for rabbits, 110 mg/kg for guinea pigs, 46 mg/kg for rats, and 250 mg/kg for mice.[4] The lowest published toxic oral dose for humans is approximately 140-200 mg/kg.[5] Accompanying symptoms of the lethal dose were vomiting, diarrhea, CNS disorders, anuria, anorexia, abdominal pain, weak and rapid pulse, sinus tachycardia, heart murmurs, and microscopic damage to the liver and kidneys. Ethylene dibromide is also toxic by dermal contact, the dermal LD 50 for rabbits being about 300 mg/kg.[4]

Published inhalation LD 50's range from 390 ppm for a 3-hour exposure to guinea pigs to 689 ppm for a 1-hour exposure to the rat and 300 ppm for a 3-hour exposure to the rat.[4] Repeated exposures to rats, rabbits, guinea pigs, and monkeys at 50 ppm for 7-hours/day, 5 days/week for 4-6 months produced signs of toxic effects including both macroscopic and microscopic changes in the liver, lungs, and kidneys.[4]

There have been few reported cases of human exposure to ethylene dibromide; however, these reports show that ethylene dibromide is highly toxic to humans by inhalation, ingestion, or skin absorption .[7-11] Symptoms of intoxication are headache, prolonged vomiting, diarrhea, and weak and rapid pulse. Brief exposures may produce conjunctival and respiratory-tract irritation, anorexia, and headache.[8,9] Prolonged or repeated inhalation may cause liver and kidney damage and pulmonary lesions.[8] Fatalities that occur appear to be caused by respiratory or circulatory failure, and may be complicated by pulmonary edema.[8-11] Skin contact may result in burning, pain, erythema, inflammation, and blisters.[7] No epidemiology studies were found that relate to employee exposure to ethylene dibromide.

Ethylene dibromide has been shown to cause antifertility effects in rats, bulls, and chickens.[12-17] Male rats became infertile, because of damage to spermatogenic cells, four weeks after intraperitoneal treatment with 50 mg/kg of ethylene dibromide for 5 consecutive days.[14] The fertility of the rats was restored to normal approximately 3 weeks later, a period of time corresponding to the length of time necessary for spermatozoic maturation in the rat. Ethylene dibromide in feed of 20-30 ppm caused a gradual reduction of egg weight and the eventual irreversible cessation of egg laying in chickens.[12] The fertilization rate, the number of live embryos, and the growth of ovarian follicles were also reduced as a result of ethylene dibromide treatment,[12,13] but the male reproductive capacity was not impaired.[12] Ethylene dibromide also reduced the spermatozoic concentration and mobility of bull semen after administration at 2 mg/kg/day for 10 days to 24 months.[15-17] There was a significant increase in the percentage of abnormal spermatozoa throughout the reproductive tract,[15-17] which reached over 75 percent abnormal spermatozoa in most cases. Removal of the ethylene dibromide treatment reversed the antifertility effect, but resumption of treatment again caused sterility to recur.

Ethylene dibromide induced carcinomas in rats and mice following the intubation of the maximum tolerated dosage (80 mg/kg/day for rats, 120 mg/kg/day for mice) or one-half the maximum tolerated dosage (40 or 60 mg/kg/day for rats or mice, respectively) for over 56 weeks.[18] Squamous cell carcinomas developed in the cardiac portion (forestomach) of the stomach, invaded locally, and metastasized throughout the abdominal cavity. The incidence of tumor formation was greater than 60 percent in male rats at both dosages, and was greater at the lower dosage than at the higher dosage (98 and 62 percent, respectively). Males were more susceptible to tumors than females.

Ethylene dibromide has induced abnormalities in rat and mice fetuses following the inhalation of 31.6 ppm of ethylene dibromide for 23 hours/day during days 6-16 of gestation.[19] Fetuses of rats were found to have ventricular-hydrocephalic and costal anomalies, whereas fetuses of mice were found to display the same costal anomalies in addition to other ossification anomalies.

Ethylene dibromide is an alkylating agent which induces both point mutations and large chromosome alterations. Using *Salmonella* in the host-mediated assay, point mutations have been detected in vivo and in vitro, indicating that the host mice could not detoxify the mutagenic effects of ethylene dibromide.[20] Ethylene dibromide has also induced point mutations in vitro in *Neurospora*.[21,22] In the sex-linked recessive lethal test, ethylene dibromide has been shown to be mutagenic to *Dresophila* by causing genetic cross-linking.[23] Ethylene dibromide has induced somatic mutations in *Tradescantia* and has shown a linear dose-response relationship over a vapor concentration range of 3.6 to 148.2 ppm.[24] Ethylene dibromide has also been shown to induce DNA repair synthesis mechanisms in opossum lymphocyte cultures[25] and has been shown to be mutagenic in mouse lymphoma cell cultures.[26] However, the dominant lethal assay in the mouse did not show mutagenic activity for ethylene dibromide when administered intraperitoneally at doses of 18 or 90 mg/kg, or orally at doses of 50 or 100 mg/kg, for five days.[27]

A more complete and extensive treatise on the biologic effects of ethylene dibromide can be found in the NIOSH Ethylene Dibromide Criteria Document.[28]

DESCRIPTION OF MANUFACTURERS AND USERS

Ethylene dibromide (EDB) is used in the manufacture of antiknock additives for gasoline, as an insecticide for fruit pests, as a spot fumigant on cereal and grain handling equipment, as a soil fumigant, as a source of bromine in organic synthesis processes, in the manufacture of vinyl bromide, as a catalytic agent, and as a specialty solvent for resins, gums, and waxes. Major manufacturers and users of EDB are shown in Table 1.

Of the 350 million pounds of ethylene dibromide produced during 1975, 85 percent was used in the manufacture of antiknock blends for gasoline. These blends vary in composition, with more than 100 different blends being produced. However, a typical blend contains ethylene dibromide, ethylene dichloride, and various tetraalkyl (methyl and ethyl) leads in a ratio of about 1:1:3. Additionally, some blends may contain toluene. The blending process does not involve the chemical reaction of ethylene dibromide with the other components of the mix, but is a physical blending of the constituents. In some blends, a disproportionation reaction among the alkyl lead compounds in the blends is performed.

Since ethylene dibromide is a constituent of leaded gasoline, there is potential occupational exposure to EDB by gasoline station attendants. The average amount of EDB contained in a gallon of leaded gasoline is

Table 1

MANUFACTURERS AND USERS OF ETHYLENE DIBROMIDE

Corporate Location	Production Location
Manufacturers	
Dow Chemical U.S.A. 2030 Dow Center Midland, Michigan 48640	Magnolia, Arkansas (Capacity: 115 million pounds/yr.)
Ethyl Corporation 330 South Fourth Street Richmond, Virginia 23217	Magnolia, Arkansas (Capacity: 150 million pounds/yr.)
Great Lakes Chemical Corp. P. O. Box 2200 West Lafayette, Indiana	El Dorado, Arkansas (Capacity: 60 million pounds/yr.)
PPG Industries, Inc. One Gateway Center Pittsburgh, Pennsylvania 15222	Houston Chemical Company (Division) (Capacity: 35 million pounds/yr.)
Users	
1. Antiknock Mixtures	
E. I. du Pont Nemours and Company 1007 Market Street Wilmington, Delaware 19898	Antioch, California Beaumont, Texas Deepwater, New Jersey
Ethyl Corporation 330 South Fourth Street Richmond, Virginia 23217	Baton Rouge, Louisiana
Nalco Chemical Company 180 North Michigan Avenue Chicago, Illinois 60601	Freeport, Texas
2. Agricultural Products	
Dow Chemical U.S.A. 2030 Dow Center Midland, Michigan 48640	Magnolia, Arkansas
Michigan Chemical Corp. 351 East Ohio Street Chicago, Illinois 60611	El Dorado, Arkansas

0.9-1.0 g. There have been EPA studies to estimate environmental concentrations of EDB generated by leaded gasoline. The concentrations measured in the vicinity (at plant perimeters) of production areas and near gasoline stations along traffic arteries show EDB concentrations to be in the low ppb range.[29] With the increased use of unleaded gasoline and reductions in the lead content of leaded gasoline, environmental concentrations of ethylene dibromide associated with its use as a gasoline additive will be reduced to even lower values. Limited data on exposure of gasoline station attendants to ethylene dibromide show these exposures to be in the low ppb range, with an average of about 7 ppb at the gasoline pumps and less than 0.7 ppb in the office or garage. The number of workers potentially exposed in this occupation is quite large, possibly more than 100,000 persons. However, since this group is not readily suitable for epidemiologic evaluation and since personnel exposures to EDB were extremely low, further evaluation of exposures to EDB in this group was not warranted.

In 1975, about 5 million pounds of EDB was used as a produce fumigant, primarily to control fruit flies. The produce fumigation process involves large fumigation chambers into which EDB is vaporized. It is used in Florida on grapefruit and mangos that are being shipped interstate or out of the country. Hawaii fumigates mainly papayas with EDB. On a smaller scale, Washington fumigates cherries that are being sent to Japan with EDB. California does very little fumigating of produce shipped out of the state with EDB because they do not have a significant fruit fly problem. However, they fumigate some produce shipped in from Mexico or

Hawaii. The predominant produce fumigation activities with EDB in the continental USA are those in Florida. These fumigation chambers are owned and operated by the State of Florida. Therefore, exposure of these workers to EDB was not included in this study.

The formulation of ethylene dibromide containing fumigants involves very few workers. The largest formulator of these fumigants uses only 3 workers to prepare these formulations.

Milling companies use these formulations as spot fumigants on cereal and grain handling equipment. Monthly application is typically performed when a plant is unoccupied except for the fumigation team. This consists of trained operators who use respiratory protection and wear protective clothing. Reentry is not allowed for 24 hours following the fumigation. Since EDB vapor is generated in the plant for fumigation and since the only occupants during this time use protective measures to minimize exposure, further evaluation of exposure of these workers was not warranted.

The primary structured activities in which daily exposure of workers to ethylene dibromide in low concentrations was identified was in the manufacture of EDB and in its use in the production of antiknock blends. Two major manufacturers and two major users of EDB were selected for detailed industrial hygiene evaluation to characterize worker exposure to ethylene dibromide.

DESCRIPTION AND HISTORY OF PLANTS SURVEYED

Plant A (Manufacturer)

Ethylene dibromide (EDB) is manufactured in an open three-story steel structure using a continuous-flow, closed-system operation. In addition to the ethylene dibromide production unit, other production activities at this plant site include a Styrofoam® plant and units for the production of bromine, sodium hydrogen sulfide (NaHS), and various nematocides. The EDB manufacturing process and several other processes are operated from a common control room. Storage facilities for EDB and for the ethylene and bromine used in its production are outside of the process area and at a distance greater than 100 feet from it. This plant, including the EDB production unit, has been in operation about 10 years.

Plant B (Manufacturer)

Ethylene dibromide manufacturing is a continuous-flow, closed-system operation performed in an enclosed three-story structure with a common wall between the EDB production unit and the adjacent bromine production facility. In addition to ethylene dibromide and bromine production units, other production activities at this plant site include units for the production of vinyl bromide and long-chain alkyl amines. Storage facilities for ethylene and bromine and for ethylene dibromide are located outside of the EDB process structure and at a distance greater than 100 feet from it. The EDB and bromine processes are operated from a common control room located on the second floor between the two processes. The EDB and bromine process controls are in separate areas within the control room, but there are no partitions separating one area from the other. This plant has been in operation since 1969.

Plant C (User)

This is basically a one-product plant producing different antiknock blends containing tetramethyl lead, ethylene dibromide, ethylene dichloride, and toluene. Tetramethyl lead is produced in another area of this plant from methyl chloride and lead. All other raw materials used in the production of antiknock blends are shipped in by tank cars. The blending of tetramethyl lead antiknock products containing ethylene dibromide has been performed at this plant since 1962. Blending is conducted in the open environment using five blending tanks. The control room for monitoring the process is housed in an enclosed one-story building.

Plant D (User)

At this plant, in addition to antiknock compounds, fluorocarbons and organic dyes such as aniline-based and azo-based dyes are produced. The facilities for the production of antiknock blends using ethylene dibromide and either tetramethyl or tetraethyl lead have been in operation since 1923. These facilities occupy only a small portion of the 1 square mile of plant area and consist of three adjacent enclosed brick structures (drumming, blending, reactor). Storage facilities for the antiknock blends consist of 18 tanks located approximately 1/4 mile from the process area. Facilities for unloading tank cars containing EDB and other raw materials used within the plant, and facilities for loading tank cars and tank trucks with antiknock blends are located between the drumming and blending buildings.

Tetramethyl and tetraethyl lead are manufactured at this plant, but the processing area is about 1/3 of a mile from the antiknock blend processing area. In addition to alkyl leads and EDB, the other compounds used in antiknock blend production include ethylene dichloride and toluene. These are unloaded at the same site as ethylene dibromide.

DESCRIPTION OF PROCESSES AND EXISTING CONTROLS

Ethylene Dibromide Manufacture

Ethylene dibromide is produced by the exothermic reaction between bromine and ethylene in countercurrent-flow reactors in which bromine enters at the top and gaseous ethylene is introduced near the bottom. The reaction occurs in the upper portion of a column packed with ceramic chips. The crude liquid product (EDB, ethylene, bromine, traces of HBr and water) flows to the bottom of the reactor. In Plant A the crude EDB is passed through secondary reactor columns to complete the reaction. The EDB is then treated with caustic to neutralize any HBr that may have formed. In Plant A the product at this point is purified by distillation and then dried by passing it through drying columns from which it is transferred to storage tanks for shipment by tank cars. In Plant B the neutralized product is passed through dryers only if it contains excessive moisture; otherwise, it is pumped directly to storage tanks from which it is loaded into tank cars for shipment.

In Plants A and B, the ethylene dibromide manufacturing processes are remotely operated from control room panels. The control rooms also serve, particularly in Plant A, as general meeting areas for production personnel and contain locker room and lunch room areas. The production personnel generally enter the process area only for the performance of certain tasks such as quality control sampling and leak checking. They usually do not remain in the process area after the completion of the tasks for which they entered the area. The tasks with the greatest potential for personnel exposure to EDB are those performed in the production areas or those associated with certain aspects of tank car loading. Except where it is necessary to open a system for activities such as quality control sampling or EDB loading, closed-system operation provides the predominant mechanism for minimizing personnel exposure to EDB. Personnel exposure during the performance of particular tasks with significant potential for exposure, such as quality control sampling, is controlled by the use of gloves and full facepiece respirators with chin-mounted organic vapor canisters. Also, in Plant A, the plant was changed from closed construction to an open steel structure during 1974, allowing increased natural ventilation to more rapidly dissipate EDB vapor that may be generated. Engineering controls include the use of more suitable materials of construction to minimize process leaks, and venting various process equipment to scrubbers for EDB recovery.

Ethylene Dibromide Use in Antiknock Blend Production

Antiknock blends consist of homogeneous mixtures of ethylene dibromide with ethylene dichloride and tetraalkyl (methyl or ethyl) lead. Some blends also contain toluene and a dye.

In Plants C and D, blends are made using batch-type operations in which measured amounts of EDB and the other blend constituents are mixed in blend tanks to obtain homogeneous mixtures. These blends are physical mixtures of the constituents rather than chemical reactions of them, except for the alkyl leads which undergo a disproportionation reaction in some blends produced in Plant D. The finished blends are transferred by pumps to storage tanks for shipment by tank car. From Plant D, blends are also shipped in drums.

Blending is a closed-system operation in which ingredients and products are automatically transported from one point to another by piping and pump systems. Pumps are activated and the process is controlled from a control room. The only manual operations that are conducted include loading and unloading tank cars, taking quality control samples, and for Plant D, the processing and loading of drums. For Plant C, personnel involved in sampling, loading and unloading activities are required to use rubber gloves and full facepiece respirators with chin-mounted organic vapor canisters. For Plant D, required use of this type of personal protective equipment is limited to drum processing and loading and tank car loading and unloading. Quality control sampling is conducted under local exhaust ventilation so only rubber gloves are required for the handling of the sample bottles.

Leak checks and the immediate repair of leaks to maintain the integrity of the closed-system is highly effective in minimizing worker exposure to EDB. In order to make leak checks more effective, Plant D adds a dye to its blends during the blending operation because of the colorless nature of the final blend product. Engineering controls directed toward the venting of EDB vapor away from the workers during tank car loading with a closed-system are used at both plants. Plant D has an extensive local exhaust ventilation system at points in the blending process where normal activities result in the potential for EDB emanation. These include quality control sampling of the blend and key drum processing operations such as drum loading where there is a potential for EDB exposure.

Description of Worker Activity, Job Classifications, and History of Exposure

Operations at each of the four plants surveyed ran 24 hours per day, 7 days per week using four crews to provide the required 3-shift-per-day coverage of the EDB process activities. With the exception of Plant A, crew members work only on EDB related activities and generally remain in the EDB process area. For Plant A, crew members are responsible for more than one process and therefore spend time in other process areas as well. Personnel who work on only the day shift (nonshift workers) are also present in all but one plant (Plant A).

Several job classifications have been identified which have a potential for EDB exposure at each of the four plants. These job classifications have been divided into five general categories on the basis of the types of duties that are performed:

- Supervisory, in which the personnel have basic responsibility for the smooth operation of the process and all process activities.
- The Control Room Operators monitor the process (EDB manufacture or antiknock blending) using the panel board in the control room.
- Surveillance, whereby periodic inspection tours are made of the process area to check for leaks and malfunction of associated process equipment.
- Product Loading involves the loading of shipping containers, primarily tank cars, with EDB or antiknock blends containing EDB. For the user facilities, this category also includes the unloading of EDB.
- Peripheral Operations include activities associated with the processing of EDB but occurring outside of the process area. This category also includes the maintenance workers who enter the EDB area only on an as-needed basis.

Table 2 lists these job classifications by category as well as the number of workers involved per shift.

The activities assigned to each job classification within each category vary from plant to plant with overlaps between the five general categories. For example, Plant A does not have a designated loader but uses one of the two Surveillance Technicians in this capacity. This overlapping of assignments among the job classifications does not allow a precise comparison of EDB exposure by job categories within the four plants surveyed.

A description of the duties of these job classifications is presented below by job categories.

Supervisory

- Crew Leader (Plant B)

  The Crew Leader functions as a foreman for manufacturing. He oversees the production of ethylene dibromide, vinyl bromide, bromine and sulfur. Depending on the problems, he may spend more time in one area than another. Therefore it is difficult to determine what the percentage of his time in EDB area may be on a particular day. However, a long-term average would be about 25 percent of his time.

- Shift Superintendent (Plant C)

  The Shift Superintendent is responsible for the overall operation of the plant. His work involves supervising the Blend Operator and the Laboratory Technicians. He tours the plant frequently.

Control Room Operator

- Panel Board Technician (Plant A)

  The Panel Board Technician (Process Leader) has major responsibility for the safe and efficient operation of the EDB, bromine, NaHS, and nematocide production units on his shift. He provides

Table 2

NUMBER OF WORKERS INVOLVED IN EDB PRODUCTION OR USAGE, BY JOB CLASSIFICATION AND SHIFT AT FOUR PLANTS SURVEYED

Category	Job Classification	Plant[a]	Nonshift (Day Only)	Shift: Day	Shift: Afternoon	Shift: Midnight	Total[b]
Supervisory	Crew Leader	B		1	1	1	3
	Shift Superintendent	C		1	1	1	3
Control Room Operator	Panel Board Technician	A		1	1	1	3
	Control Room Operator	B		1	1	1	3
	Blend Operator	C		1	1	1	3
	Blend Operator[c]	D		3	3	3	9
	Reactor Operator	D		1	1	1	3
Surveillance	Surveillance Technician	A		2	2	2	6
Product Loading	Loader	B	3				3
	Material Handler	C	1				1
	Drum Loader[d]	D	16				16
	Raw Material Handler	D	1				1
Peripheral Operators	Laboratory Technician	A		1	1	1	3
		B	1				1
		C		2	2	2	6
		D	1				1
	Brine Field Technician	A		1	1	1	3
	Compound Bulk Operator	D	1				1
	Total		24	15	15	15	69

[a] A and B are manufacturers of EDB, while C and D are users of EDB in the formulation of antiknock blends.

[b] Total on three shifts at any one time. However, to maintain continuous operation 24 hours per day, 7 days per week, four crews are used to provide the required 3-shift-per-day coverage.

[c] Includes two blend operators and one relief operator who relieves and acts as the assistant for the blend operators.

[d] Includes all personnel involved in drum processing and loading. Of the 16 personnel, only two load drums during the day. However, they alternate tasks such that over the long term all load drums.

any necessary coordination of the activities of the other four technicians on his shift. The Panel Board Technician works about 95 percent of his time in the pressurized control room where his predominant responsibility is to monitor process variables of the various production units. He makes routine adjustments of the variables by use of the process control instrumentation in the control room. This technician spends about 2 percent of his time outside obtaining effluent salt water samples for halogen analyses which are performed under a ventilated hood in the control room. He occasionally makes a tour through the production areas.

- Control Room Operator (Plant B)

The Control Room Operator spends most of his time in the control room checking the control panel for EDB production. The bromine control panel is in the same room and when the bromine operator goes out on checks, the EDB Central Room Operator may man the bromine panel. In addition, about every 2 hours, the operator makes rounds of the EDB production area, EDB storage tanks and bromine storage tanks. He walks around checking dial gauges for the levels of the chemicals in each tank and checking for leaks. Leaks are detected visually or by sense of smell. Each round that the Control Room Operator makes lasts about 10 minutes. If a leak is detected, the maintenance crew would be notified and would perform the required repairs. If a tank is found to be filled to a certain specified mark the Control Room Operator will direct the flow to another tank. This operation entails simple valve switching; no changes in line connections are required.

An additional task is performed by the Control Room Operator during the midnight shift. Samples of ethylene dibromide are withdrawn for quality control checks during the midnight shift. This task involves opening the sample port on the surge tank, filling a small glass bottle, closing the port and capping the bottle. Only one sample is withdrawn and the whole task takes less than one minute. The Control Room Operator takes the sample bottle to the quality control laboratory where routine checks are made on the sample by the Laboratory Technician.

- Blend Operator (Plant C)

The Blend Operator is responsible for unloading all liquid raw materials including ethylene dibromide, ethylene dichloride, toluene, methyl chloride, and tetrahydrofuran from tank cars to storage tanks, blending of the raw materials and loading the final product into tank cars. Ethylene dibromide tank cars are unloaded once every three days during the night shift and the product is loaded mainly during the day shift. Unloading tank cars involves withdrawing a sample for quality control, grounding the tank car to prevent buildup of static electricity, connecting the hose to the valve underneath the tank car, and pumping to the storage tank. Exposure may result if there is a spill during connecting the hose or while withdrawing a sample. The blending operation involves metering various calculated amounts of raw materials to the blend tanks. This is performed from the control panel which is located in the blend control room. When an appropriate blend is ready in the blend tank, the Blend Operator collects a sample from a Strahman sample valve at the blend tank and takes it to the control laboratory for analysis. If the sample is deemed to be of unacceptable quality, the Blend Operator will adjust the blend to make it acceptable. Again, this requires him to be in the blend control room. If the sample is acceptable, the Blend Operator meters the blended product to one of the storage tanks. From here the blended product is shipped. The Blend Operator may load a tank car through a weigh tank or by having the tank car on a weigh scale. Each tank car is grounded prior to loading to prevent a buildup of static electricity. The Blend Operator loads the tank car by connecting the appropriate hose at the top of the car. He also makes another connection which is to vent the vapor that is being displaced from the tank car. This vapor is scrubbed with toluene in a packed column. Any liquids are removed in a tank and then the vapor is burned in a flare stack. When the tank car is loaded, the Blend Operator disconnects the car and seals it for shipment.

- Blend Operator (Plant D)

The primary duties of the Blend Operators consist of mixing blends, loading the finished blend products into tank cars and occasionally tank trucks and making rounds of the blend building to check for leaks. Blend mixing occurs on all three shifts, and tank car loading is performed as needed and may involve any of the shifts. The blend operation is performed by use of a control panel located next to the blend tank and does not involve any handling of the blend ingredients by workers. Ingredients are transferred to the blend tank through a control valve until the desired amount has been added as determined by a weight sensing device located in the blend tank. The blend is allowed to mix by recirculating the mixture and this process is overseen by the operator. With the completion of blending, a sample is taken using an enclosed, locally exhausted hood and taken to the laboratory for analysis. If the blend is deemed of unacceptable quality, the Blend Operator will adjust the blend to make it acceptable. The adjustment takes place using the control panel and does not involve any increase in exposure to EDB. If acceptable, the blend is transferred to tank cars, the main storage tank, or to storage tanks on the third floor for drum loading. All transfer operations are performed by the adjustment of the necessary control valves to divert the blend to its proper destination and do not involve, under normal conditions, any additional exposure to EDB.

Tank car loading as described earlier involves the coupling of a 2-inch feeder line and 1-inch vent line to the appropriate valves on the top of the empty tank car. The tank car is grounded to prevent the buildup of static electricity. The operator must enter the blend building to start the pumping operation. Plant D currently averages six tank cars per 24-hour period, so the maximum that any one operator would handle would be six cars.

- Relief Operator (Plant D)

The Relief Operator has a number of odd jobs such as the testing of all emergency showers within the blend area. Duties which result in potential exposure to EDB include assisting the Blend Operator in the loading of tank cars, overseeing the mixing of the blends, and relieving the Blend Operators and Reactor Operator during their lunch and break periods (two 15-minute breaks per shift).

- Reactor Operator (Plant D)

The Reactor Operator spends all of his time in the vicinity of the reactor building overseeing the reactor control panel. The reaction is a continuous flow process controlled from the control area on the first floor and does not involve any direct exposure to EDB except during the taking of quality-control samples once every 2 hours. Sampling is conducted in an enclosed, locally exhausted hood by the operator with rubber gloves. This task generally takes less than 2 minutes to complete. The operator makes a 5-minute round of the building once each hour to check for leaks. Duties outside the building involve checking the supply of caustic and catalyst in their respective storage tanks every hour.

Surveillance

- Surveillance Technician (Plant A)

The two Surveillance Technicians on duty each shift have the responsibility for monitoring by personally observing the equipment operation in four different process areas, including the EDB production unit. The other three areas are the bromine, NaHS, and nematocide production units. Specific duties include recording data from field mounted instruments, switching process flows between tanks, unloading raw materials, and loading products including EDB into tank cars. Routinely, at the beginning of each shift, one of the Surveillance Technicians collects quality-control samples of process streams for laboratory analysis. The analyses are performed by the Laboratory Technicians.

The Surveillance Technicians spend approximately 90 percent of their time outside in the plant and the remaining 10 percent in the control room to communicate with the Panel Board Technician, as well as to eat and take break periods. About 1-1/2 hours cumulatively are spent by each of the two Surveillance Technicians on each shift in different locations within the EDB production unit. The routine sample-collecting process at the beginning of each shift by one of the Surveillance Technicians takes about 30 minutes (10 minutes in the EDB unit), and involves collecting samples at about 15 sampling sites (5 sites in the EDB unit). The tank car loading operation requires from 1 to 1-1/3 hours and is performed by a Surveillance Technician. These loading operations are sporadic due to the necessity of corresponding with shipping schedules.

Product Loading

- Loader (Plant B)

The Loaders are responsible for loading and unloading in all parts of the plant. There are three Loaders on the day shift; none is specific for EDB loading. Depending on the train schedules and tank car availability, as many as 5 cars may be loaded during a typical day. Three or four cars can be loaded simultaneously. The Loaders connect the pipe from the storage tank with a hose into the tank car. Filling is started by turning on a pump about 50 feet away. The Loaders are responsible for withdrawing samples of EDB from the tank car for visual checking of clarity. This is done by lowering a glass bottle on a long handle into the tank car, dipping and filling the bottle and lifting it up. The Loader checks for clarity and if acceptable, pours it into a sampling bottle and takes it to the laboratory for further analysis. If the clarity is not acceptable, the EDB from another storage tank may be blended with it until the desired quality is obtained, or the EDB may be pumped through alumina dryers prior to the tank car loading.

The three Loaders change around in performing the various EDB loading tasks. That is, on one day one Loader may perform the activities on the platform at the tank car dome, including sampling, while another Loader does the ground preparation activities. The potential for worker exposure to EDB on the platform would generally be greater than that for the worker on the ground. The third Loader would generally be performing other loading or unloading activities not involved with EDB. On another day, another of the three Loaders may perform the platform activities associated with EDB loading. Over an extended period, all three Loaders would perform all of the loading tasks.

On a normal day, a Loader may load or unload ethylene dibromide, vinyl bromide, bromine, chlorine, allyl chloride, chlorobutyro nitrile, caustic (NaOH), dimethyl amine, ammonia, long-chain alkyl dimethyl amines, and long-chain aliphatic olefins. Once the filling operation has begun, a Loader does not stay in the area but may go to another area to initiate another loading procedure. He or another Loader will return to stop the flow at the appropriate time, remove the hose and close the tank car.

- Material Handler (Plant C)

The Material Handler is responsible for assisting the Blend Operator in all his duties during the day shift. He may assist in loading the product and unloading the raw materials. He normally would not withdraw samples for quality control checks, but occasionally may be asked to fill in.

- Processing of Drums, Including Drum Loaders (Plant D)

This process involves the performance of 10 different tasks. Of these tasks, however, only two are considered to present a potential problem with regard to EDB exposure. These are drum washing and drum loading. On a normal operation, an average of 100 drums are loaded per day by the two Drum Loaders.

Drum loading is conducted in the drum building using two enclosed locally exhasted hoods. Each 55-gallon drum is equipped with a double bung to minimize leakage. Drums are placed in either of two hoods and coupled to the feeder line. The valve control is located outside the hood and is operated only after the hood is closed. A scale located in the hood is used to determine when the drums are filled. Filled drums are sealed with the bungs and stored for 24 hours on their sides with the bung side facing the floor to test for leakage. In a normal operation, an average of 100 drums is loaded per day by the two Drum Loaders.

Leaking drums and drums containing water or other impurities are set aside for later reclamation at the end of the shift. An enclosed, locally exhausted hood is used in the reworking of the blends in these drums. A drum is placed within the hood; the bung is removed and a suction hose is placed in the drum. With the hood closed, the blend is pumped through a vacuum line to the heels tank for reclamation.

Drums used in drum loading are reusable and must undergo a cleaning operation prior to reuse. Users of this product flush the drums with gasoline prior to shipping the drums back to Plant D. As they are received at Plant D, the bungs are removed from each drum by an employee wearing a half-mask respiratory with organic vapor cartridge. The drum is then placed in an enclosed, locally exhausted hood and a water hose is placed in the drum. The drum is flushed in the closed hood and aspirated manually to remove excess water. Chains are then added to the drum and the drums are mechanically rotated to loosen any scale formation. Drums are steam cleaned to remove the scale and are then dried. The outer surface of the drums is grit blasted in an enclosure to remove old paint and rust and is repainted. The cleaned and painted drums are then inspected for damage prior to drum loading.

- Raw Material Handler (Plant D)

The Raw Material Handler is on day work and has been assigned a number of duties such as the shipping of small packages and supply inventory which do not involve handling of EDB or other chemicals. Of special relevance to this survey were his duties involving the unloading of raw materials and keeping an inventory of these raw materials. The Raw Material Handler is responsible for unloading raw materials coming into the plant in tank cars; these include EDB, ethylene dichloride, and toluene. The unloading operation consists of coupling a hose to a valve located on the bottom of the tank car and opening a valve on the top of the car to prevent the creation of a vacuum while unloading. The raw material is then pumped to the proper storage tank. The handler does use rubber gloves, chemical goggles, and a half-mask respirator with organic vapor cartridge during this task.

Prior to unloading EDB, a quality-control sample is taken using a glass sample bottle attached to a long metal rod. A sample is dipped out of the tank at the top and sent to the laboratory for analysis. The same personal protective equipment is used in this task as in the unloading operation.

A raw material inventory is made of all storage tanks by checking their levels on a periodic basis. Most tanks are equipped with a metering device which allows checking of tank levels without physically opening the tanks. In the case of ethylene dichloride, the level has to be measured with a dipstick twice a week. This task consists of lowering into the tank a ruler to measure the distance between the surface of the liquid and the top of the tank. Half-mask respirators with organic vapor cartridges, chemical goggles, and rubber gloves are used.

Peripheral Operations

- Laboratory Technician (Plant A)

The Laboratory Technician (Analytical Technician) generally spends nearly all of his time in the air-conditioned laboratory building performing quality-control analyses related to the production of EDB, bromine, NaHS and numatocides. Normally the samples are gathered by a Surveillance Technician and brought to the laboratory. Sample analyses are performed in ventilated hoods in the laboratory. Occasionally, the Laboratory Technician will go into the plant to take special nonroutine samples. A series of such samples was collected during the period of this survey. Twice per shift, at the beginning and middle, the Laboratory Technician went into the production area and collected a single sample of crude EDB. This sampling operation was of short duration, lasting about 2 minutes.

- Laboratory Technician (Plant B)

The Laboratory Technician is responsible for quality control checks of the brine bromine and ethylene dibromide. He checks the brine for its bromine and H_2S content. He also checks the bromine for water, chlorine or organics present. He analyzes the ethylene dibromide for density, water and acid content. The Laboratory Technician works only during the day shift (8:00 a.m.-4:30 p.m.) and spends about 2 hours per day on ethylene dibromide analysis. Normally his duties do not require him to go to the ethylene dibromide production area. However, he does go out in the plant to obtain brine samples for H_2S analysis. He obtains the brine samples at the opposite end of the plant from the EDB production area. The technician is also responsible for returning the spent brine from the laboratory back to the brine feed pond. This takes about 1/2 hour and he wears a respirator and protective clothing while performing this activity. This is done once per day.

Once the analysis is done and the quality found acceptable, the ethylene dibromide is transferred from the "day tank" to the storage tank from which it is loaded into tank cars.

- Laboratory Technician (Plant C)

The Laboratory Technician is responsible for conducting quality control tests on both the ethylene dibromide raw material and the finished blended product. The samples are brought to him by the Blend Operator. The Laboratory Technician performs a refractive index and specific gravity test on EDB samples. In addition, chromatographic and specific gravity tests are run on blended product samples. Approximate time spent per each sample is less than five (5) minutes. After the tests are finished, the Laboratory Technician returns the samples to the Blend Operator (who comes to the laboratory to get them). Therefore, the Laboratory Technician does not spend any time in the plant during a routine day. Other responsibilities include similar quality control analysis of other raw materials such as diethyl ether, tetraethylene glycol, toluene, tetrahydrofuran, hydrochloric and sulfuric acids, tetramethyl and tetraethyl lead and methyl and ethyl chloride.

- Laboratory Technician (Plant D)

  The Laboratory Technician's responsibilities are the same as for Plant C. He spends all of his time in the laboratory and does not venture into the production area. Samples are brought to him by the Blend Operators and the analyses of blend and EDB samples take about 1/4 - 1/3 of his time using tests similar to those of Plant C. All analyses are performed in hoods having face velocities of 100 fpm.

- Brine Field Technician (Plant A)

  The Brine Field Technician spends nearly all of his time surveying brine field facilities which are outside of the plant. He covers the large area by truck. He comes in contact mainly with systems containing salt water (brine) and sour gas. He is in the control room for a few minutes at the beginning and at the end of his shift for transition purposes. This constitutes a total of about 30 minutes. Occasionally, he may come into the plant if additional assistance is required for some special situation.

- Compound Bulk Operator (Plant D)

  The Compound Bulk Operator is stationed in the bulk storage area which is remote from the EDB processing area. His primary duty is to patrol the bulk storage area once every hour for leaks and to oversee from his control room the loading of storage tanks or the transfer of material from the storage tanks to the blend or reactor room. He is also responsible for checking the level of blends in the bulk storage tanks by physically measuring with a tape rule the distance between the surface of the blend and tank top.

- Maintenance

  At all four plants, the maintenance crews work on an as-needed basis in the EDB area and are therefore only sporadically exposed to EDB.

As far as could be ascertained, the duties for each of the job classifications identified have remained fairly constant over the past years. However, engineering modifications have been made to the processes to increase production efficiency and to control exposure to EDB and other constituents of the processes. These modifications included:

- The use of more suitable materials of construction to reduce the incidence of process leaks.

- The installation of venting or recycling systems at points in the process where the integrity of the closed-system must be temporarily broken to perform a task such as quality-control sampling or loading of the final product.

Besides these modifications, three of the plants surveyed have also provided additional controls to reduce worker exposure to EDB. Plant A converted their EDB processing area from a closed to an open-structure to reduce the background level of EDB and other constituents and to facilitate maintenance. Plant C built their storage tanks and blending units over water which serves as a blanket for the heavier antiknock blends in cases of severe leakage. Plant D utilized local exhaust ventilation at selected points in the process where antiknock blends containing EDB are handled and placed the entire blending process under a nitrogen plug to reduce leakage. Through these modifications worker exposure to EDB is expected to be below what it was in the past.

DESCRIPTION OF SURVEY METHODS

Procedures

The survey procedures involved a discussion with appropriate corporate and plant personnel to obtain general information regarding each activity associated with the manufacture or use of EDB, together with an identification and description of each pertinent job classification. A walk-through observation of the EDB manufacturing or blending process was then made. Detailed information about the process, each production activity, and each job classification was obtained from appropriate plant personnel. A personal monitoring schedule was established to obtain data for an evaluation of worker exposure to EDB in each job classification on each shift. Based on observations made during the walk-through, on measurements previously made by the companies, and, except in Plant A, on measurements made throughout the production and storage areas with a Century Systems Model 128 Organic Vapor Analyzer, appropriate area monitoring sites were identified to supplement the personal monitoring and to define potential exposure areas. In addition, short-term personal monitoring samples were taken during performance of specific tasks such as quality control sampling and tank car loading and unloading activities which were considered to present a significant potential for personnel exposure to EDB. Essentially, the survey procedures were directed toward determining 8-hour TWA concentrations of EDB to which each worker was exposed. These procedures were not directed toward determining 15-minute ceiling concentrations as recommended by NIOSH in a standard[28] established after this sampling was performed. Therefore, values obtained in this study may not be directly comparable with the current NIOSH criteria for a recommended standard for occupational exposure to ethylene dibromide.[28]

Limitations

In each of the four plants, this industrial hygiene study represents an evaluation of conditions present during the three days of sampling in each plant. Sampling was done on all three shifts. Plants A, B, and C were said to be operating at normal capacity. Conditions monitored during this study are considered to be representative of typical plant conditions, except as noted. In Plant A, the only activity noted that deviated from the normal routine was the collection of additional process samples for another purpose by Laboratory Technicians. During the sampling period, Plant D was not operating at its normal capacity. The reactor room operation was shut down on 7-8 July 1977 because of an excess of "Tetramix" product and drumming operations were below normal on the same two days (32 and 85 percent less than normal, respectively). Results of these samples would therefore reflect a lower than normal exposure to EDB.

Evaluation Criteria

The American Conference of Governmental Industrial Hygienists (ACGIH) adopted in 1953 a threshold limit value (TLV) of 25 ppm as an 8-hour time-weighted average (TWA) exposure concentration for 1,2-dibromoethane.[30] In 1954, the ACGIH[31] changed the name to ethylene dibromide in the official

TLV list, and in 1973[32] the name was again listed as 1,2-dibromoethane. In 1965, the ACGIH [33] recommended that special emphasis be given to the skin absorption potential of ethylene dibromide by adding the designation "skin" after the name in the TLV list. This notation refers to the potential contribution to overall exposure by the dermal route, particularly by direct contact with ethylene dibromide. This designation was intended to suggest that appropriate measures for the prevention of dermal absorption are necessary in addition to measures to control potential airborne exposure.

In 1966, the ACGIH[34] recommended that the TLV of 25 ppm as a TWA concentration for EDB be changed to a ceiling limit of 25 ppm. In 1971, the ACGIH[35] recommended changing the ceiling limit of 25 ppm to a TLV of 20 ppm as an 8-hour TWA concentration, as it is currently listed.

The present federal standard (29 CFR 1910.1000) for occupational exposure to EDB is 20 ppm as an 8-hour TWA concentration limit, with an acceptable ceiling concentration of 30 ppm and an acceptable maximum peak above the acceptable ceiling concentration for an 8-hour work shift of 50 ppm for 5 minutes.[36] This standard was adopted from the American National Standards Institute's (ANSI) recommendation Z37.31-1970.[2]

Based on highly suggestive evidence that EDB can be mutagenic, teratogenic, or carcinogenic, on the potential of EDB to cause irreversible damage in experimental animals, and on the total lack of quantitative data which clearly delineate no-effect concentrations from those at which adverse effects occur, NIOSH recommends that the employer control workplace concentrations of ethylene dibromide so that no employee is exposed in his workplace to ethylene dibromide at a concentration greater than 1 mg/m^3 (0.13 ppm) as a ceiling limit determined by a sampling period of 15 minutes.[28]

Sampling and Analytical

NIOSH Method No. P&CAM 260 (Draft)[37] formed the basis for all sampling and analyses. Sampling was done by drawing a known volume of air at an accurately determined nominal rate of 200 ml per minute through a charcoal tube to trap the EDB (1,2-dibromoethane) vapor present. Generally, Bendix Super Sampler Permissible Air Pumps adapted for low flow sampling at 200 ml per minute were used for personal monitoring for TWA concentration determinations and SKC Model 222-3P Air Check Personal Pumps operating at a nominal flow rate of 200 ml per minute were used for obtaining the short-term and area samples.

The charcoal tubes consist of glass tubes with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600^{o}C prior to packing. The adsorbing section contains 100 mg of charcoal and the backup section contains 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than 25 torr at a flow rate of 200 ml per minute.

Personal samples were collected in the breathing zone of individual employees. These were obtained by attaching the sampling tube to the shirt collar or lapel of the employee to collect the sample in the employee's breathing zone, without interfering with the employee's freedom of movement. Plastic tubing was used to connect the sampling tube to the personal sampling pump on the employee's belt. The flow rate through this sampling train was determined both before and after sampling by use of a buret (soapbubble meter).

Immediately after sampling, the charcoal tubes were placed in dry ice. At the end of the survey, all samples were shipped by air to SRI's laboratories in Menlo Park, California. The samples, still packed in dry ice, were received the same day that they were shipped.

All analyses were performed by SRI's laboratory which is accredited under the Laboratory Accreditation Program of the American Industrial Hygiene Association. In accordance with NIOSH Method No. P&CAM 260 (Draft), the analyte was desorbed from the charcoal with 10.0 ml of 99:1 benzene-methanol (v/v). An aliquot of each desorbed sample was later subjected to gas chromatographic analysis using an electron-capture detector.

Two tubes containing charcoal from the same batch as the sample tubes were treated in the same way as the samples, except that no air was drawn through them. Both ends of each of these tubes were broken off, the tubes were resealed with the caps supplied by the manufacturer, and then they were packed in the dry ice with the samples. These tubes served as blanks. Analysis showed no blank correction to be necessary.

The front and backup sections of each tube were desorbed separately, and all front sections were analyzed. The backup sections from the tubes with the greatest amount of EDB in the front sections were then analyzed. For Plants A, B, C, and D, 3, 5, 5, and 9 backup sections, respectively, were analyzed. Since EDB was not detected (less than 40 nanograms) in these sections, the remaining backup sections from the tubes which had collected less EDB were not analyzed.

DISCUSSION OF RESULTS

Job classifications have been identified in a survey of two manufacturer and two user facilities in which there exists a potential for EDB exposure. The 8-hour TWA concentration was determined for each job classification. The median results are given in Table 3, with sample size and range data. For comparison purposes, the job classifications are grouped according to duties in Table 3 using the five general categories previously described. These categories are Supervisory, Control Room Operations, Surveillance, Product Loading, and Peripheral Operations.

The Material Handler at Plant C, a user facility, is not listed in Table 3 although he is potentially exposed to EDB, because the tubing on the sampling train became detached for an unknown period of time during sampling, not allowing the air volume sampled to be accurately determined. From observations of the duties of the Material Handler, his exposure is considered to be less than that of the Blend Operator whom he assists because tasks such as the taking of quality control samples and the actual hooking up of tank cars for blend loading are done by the Blend Operator, while the Material Handler's duties involve activities with a lesser potential for exposure.

At Plant D, the reactor building in which the Reactor Operator works was not in operation on one of the two days during which the Reactor

Table 3

MEDIAN 8-HOUR TWA CONCENTRATION BY JOB CLASSIFICATION

Category	Job Classification	Plant[a]	Sample Size	Range (ppm)	Median (ppm)
Supervisory	Crew Leader	B	2	0.04-0.95	0.50
	Shift Superintendent	C	3	0.0001-0.0004	0.0002
Control Room Operators	Panel Board Technician	A	4	<0.02-0.14	0.08
	Control Room Operator	B	7	0.003-0.16	0.04
	Blend Operator	C	5	0.004-0.058	0.022
		D	6	0.001-0.009	0.006
	Relief Operator	D	2	0.007-0.0005	0.004
	Reactor Operator	D	2	0.001-0.003	0.002
Surveillance	Surveillance Technician	A	8	<0.00002-1.60	0.37
Product Loading	Loader	B	4	0.05-0.62	0.36
	Drum Loader	D	4	0.008-0.018	0.014
	Drum Processing	D	3	0.012-0.036	0.016
	Raw Material Handler	D	2	0.027-0.082	0.054
Peripheral Operations	Laboratory Technician	A	4	<0.00002-0.57	0.14
		B	2	0.01-0.08	0.05
		C	6	0.0002-0.012	0.004
		D	4	0.0001-0.0005	0.0004
	Brine Field Technician	A	4	<0.00002-0.03	0.01
	Compound Bulk Operator	D	2	0.001-0.008	0.004

[a] A and B are manufactuers of EDB; C and D are blenders of antiknock formulations.

Operator was sampled. A comparison of this data with that of a normal operating day showed no difference in exposure, suggesting that exposure is not dependent on the reactor operation and is representative of background levels.

Results for the Drum Loaders at Plant D must be considered to be below the normal exposure because drum loading activities were 32 percent-85 percent below the normal average of 100 drums per day during the 2-day sampling period. The drum processing tasks, which by their nature would be expected to have a lower exposure potential, are similar to drum loading with regard to exposure levels.

There is not complete uniformity in the duties assigned to each job classification, by plants, within each category. Therefore, task assignments for a given job classification can overlap into more than one category, making a meaningful comparison of exposure levels between plants difficult.

Differences of this type are prevalent enough among the job classifications used by the four plants that they do not lend themselves to direct comparisons for characterizing and evaluating worker exposure within the ethylene dibromide industry. However, some general observations are possible based on the results in Table 3. A comparison of job classifications within each category shows that workers in manufacturing facilities are generally exposed to EDB at higher concentrations than are their counterparts in the user facilities. Plant D had the most elaborate engineering controls of the four plants and this was reflected in their having the best record of the four plants in controlling worker exposure to EDB.

In the survey of the four plants, tasks of a similar nature were identified where there was a potential for exposure to EDB. Short-term samples were taken over the duration of these tasks and results are given in Table 4. The unloading of EDB utilizes two separate steps, the connecting of the feeder line and the subsequent uncoupling of the line, with measured concentrations of 2.39 ppm and 0.085 ppm, respectively. A time-weighted average of 1.56 ppm was calculated for this task.

Area monitoring was conducted at each of the four plants at selected sites which were routinely entered or occupied and where there existed a potential for EDB exposure. Samples were taken at breathing zone height and the results are given in Table 5. EDB levels were within the same magnitude for each of the two manufacturers although, numerically, Plant A was consistently higher. For the user facilities, Plant D had consistently lower values but was apparently of the same magnitude as Plant C with regard to exposure provided local exhaust ventilation was not present.

With the exception of Plant A, workers from all job classifications that were identified worked only in EDB process-related activities and tended to remain within the area. For these workers, primary exposures were limited to constituents of the process. For Plant B, a manufacturing facility, those chemical agents include ethylene, bromine, and EDB. For the user facilities, Plants C and D, the chemical agents were EDB, toluene, ethylene dichloride, and tetramethyl and tetraethyl lead. Alkylleads

Table 4

EDB CONCENTRATIONS FOR SPECIFIC TASKS IN THE EDB INDUSTRY

Task	Site	Plant[a]	Sampling Time	Concentration (ppm)
Taking quality-control sample of EDB or product containing EDB	Process Area	A	18 min	23.4
	Process Area	A	15 min 36 sec	12.0
	Process Area	A	1 min 18 sec	5.3
	EDB Holding Tank	B	4 min	0.29
	EDB Tank Car	C	5 min 39 sec	1.52
	Blend Tank[b]	D	3 min 33 sec	0.037
	EDB Tank Car	D	13 min 10 sec	0.699
Analyzing samples	Laboratory	A	8 hours	0.14
	Laboratory	B	8 hours	0.05
	Laboratory	C	8 hours	0.004
	Laboratory	D	8 hours	0.0004
Loading EDB or products containing EDB	Tank Car Station	B	14 min 16 sec	0.54
	Tank Car Station	D	7 min	0.14
Unloading EDB from tank car	Tank Car Station	D	13 min	2.39) 1.56
	Tank Car Station	D	7 min 23 sec	0.085)

[a] Plants A and B are manufacturing facilities; C and D are user facilities.

[b] Conducted under local exhaust ventilation.

Table 5

AREA SAMPLING FOR ETHYLENE DIBROMIDE AT BREATHING ZONE HEIGHT

Site	Description	Plant[a]	Concentration (ppm)[b]
Control Room	At EDB panel board	A	0.91
	EDB control room	B	0.08
	Blend Control Room at Control board	C	0.003
	Adjacent to blend tank controls	D	0.002
Laboratory	Adjacent to hood	A	0.73
	General Area, Center	B	0.51
	Laboratory bench where EDB analyses conducted	C	0.018
Quality Control Sampling Port	For crude EDB	A	1.32
	EDB (Sampling port)	B	1.04
	At blend tank sampling port	C	0.167
	Near blend pump sampling port	C	0.044
Process Site	Pump Area	A	<0.00007
	Heat Exchanger-east side	A	1.50
	Heat Exchanger-west side	A	5.80
	Bottom of dryers-2nd level	A	0.23
	Primary reactor-3rd level	A	0.18
	3rd floor-center	B	1.08
	By ethylene block valve	B	0.90
	Loading rack	C	0.051
	Drum loading site[c]	D	0.008
	EDB storage tank-3rd floor	D	0.008

[a] Plants A and B are manufacturers; C and D are users.

[b] Samples were taken over essentially entire shifts.

[c] Local exhaust ventilation was present.

were considered to be the principal health concern to employers. Other production facilities were present at Plants B and D, but are sufficiently removed from the EDB process area that their contribution to the EDB process worker's overall exposure is considered to be negligible.

With regard to Plant A, personnel in each job classification are responsible for the EDB production unit and three other production areas producing bromine, sodium hydrogen sulfide (NaHS), and a family of nematocides. Potential exposures for these workers are to a broader range of chemicals than are present for their counterparts in Plant B and include besides ethylene, bromine, and EDB the chemicals NaHS, the nematocides, chlorine which is used in bromine production, and hydrogen sulfide, a byproduct of bromine production.

Conclusions

Existing engineering controls at the four plants surveyed were found to be adequate in maintaining ethylene dibromide vapor concentrations within the 20 ppm 8-hour TWA concentration limit established by the present federal standard and the ACGIH TLV. Additional protective measures in the form of respiratory protection are, however, provided at all four plants by management for use during the performance of selected tasks, such as quality control sampling and the loading or unloading of tank cars containing EDB, where there is a potential for exposure to EDB.

A current reassessment by NIOSH of ethylene dibromide toxicity has resulted in the recommendation of a ceiling limit of 1 mg/cu m (0.13 ppm) for ethylene dibromide as determined by a 15-minute sampling period. Applying this ceiling limit to the EDB industry, conditions exist in all four plants which could lead to a worker's exposure exceeding this ceiling limit. This is especially true in the manufacturing facilities, where monitored 8-hour TWA concentrations in job classifications approached or exceeded an EDB concentration of 0.13 ppm, indicating that the potential exists for a worker's exposure to exceed the ceiling limit while performing his normal routine duties. The presence of EDB concentrations approaching or exceeding 0.13 ppm in area monitoring results in the manufacturing facilities is also indicative of the potential for a worker's exposure to exceed the ceiling limit during the performance of the normal routine duties. These findings show a need for improving existing engineering control measures to reduce background levels in the process areas and to control worker exposure to EDB during normal routine assignments.

With regard to controlling a worker's overall exposure to EDB in these manufacturing facilities, short-term sampling results (Table 4) and general observations of the duties of the monitored job classifications have shown that a few selected tasks made major contributions to the worker's overall exposure. By controlling worker exposure during the performance of these tasks, which include quality control sampling and the loading or unloading of tank cars containing EDB, it should be possible to effectively reduce the 8-hour TWA concentration of the monitored job classifications. However, the ceiling limit of 0.13 ppm may be exceeded during the performance of some tasks. The use of proper respiratory protection while performing these tasks may be adequate to effectively control worker exposure to EDB.

For the user facilities, the potential for worker exposure to exceed the ceiling limit was associated with tasks involving the handling of EDB or products containing EDB, such as taking quality control samples and unloading EDB-containing tank cars or loading tank cars with antiknock blends containing EDB. At Plant D, local exhaust ventilation has been used effectively in controlling exposures during the taking of quality control samples. Respirators are used at these facilities by workers during the performance of these tasks and provide an additional measure of protection with regard to exposure to EDB.

Recommendations

High background levels and 8-hour TWA concentrations found in the manufacturing facilities are indicative of the need for improving existing control measures for industry to meet the NIOSH recommendation of 0.13 ppm as a ceiling limit for a 15-minute sampling period. Improvements should include engineering controls at specific activities with the potential for worker exposure to EDB at high concentrations, work practices to control worker exposure while performing normal duties, and maintenance of the integrity of closed-system processes to reduce background levels. Improvements should include the following:

- Provide local exhaust ventilation at specific tasks when practical. For example, Plant D had great success in controlling worker exposure with local exhaust ventilation at sampling ports.
- Reevaluate the processes at manufacturer and user facilities to identify emission sources such as vent systems, pump packing glands, and valves at which emissions may be controlled or eliminated.

- Evaluate other types of equipment and materials of construction for seals, gaskets, and fittings to determine if materials more resistant to EDB are available to minimize leaks.

- Instead of the current maintenance-as-needed policy practiced by the plants surveyed, a periodic maintenance schedule should be strongly considered especially with regard to equipment parts which are prone to develop leaks due to wear.

- For blenders of antiknock compounds, which are colorless mixtures, add a dye to the blends as practiced in Plant D, to facilitate the checking for leaks in the process.

- Provide workers involved with the handling of EDB with the necessary respiratory protection.

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Appendix 1

TIME-WEIGHTED AVERAGE EXPOSURE TO ETHYLENE DIBROMIDE

By Job Classification and Shift

Table 1

TIME-WEIGHTED AVERAGE EXPOSURES TO ETHYLENE DIBROMIDE BY JOB CLASSIFICATION AND SHIFT AT MANUFACTURING PLANT A

Sample	Job Classification	Date	Shift	EDB, ppm
1	Panel Board Technician	6/7/77	Afternoon	0.06
2		6/8/77	Day	0.14
3		6/8-9/77[a]	Midnight[c]	<0.00006
4		6/8-9/77[b]	Midnight[c]	0.03
5		6/9/77	Day	0.10
1	Surveillance Technician	6/7/77	Afternoon	1.60
2		6/7/77	Afternoon	0.16
3		6/8/77	Day	0.23
4		6/8/77[a]	Day[c]	0.62
5		6/8/77[b]	Day[c]	0.41
6		6/8-9/77	Midnight	0.30
7		6/8-9/77	Midnight	<0.00002
8		6/9/77	Day	0.64
9		6/9/77[a]	Day[c]	0.46
10		6/9/77[b]	Day[c]	0.43
1	Laboratory Technician	6/7/77	Afternoon	0.57
2		6/8/77	Day	0.22
3		6/8-9/77	Midnight	<0.00002
4		6/9/77	Day	0.05
1	Brine Field Technician	6/7/77	Afternoon	<0.00002
2		6/8/77	Day	0.02
3		6/8-9/77	Midnight	<0.00003
4		6/9/77	Day	0.03

[a] First half of shift

[b] Remainder of shift

[c] Shift was divided between two crew members due to a shortage of workers to properly cover the three shifts.

Table 2

TIME-WEIGHTED AVERAGE EXPOSURES TO ETHYLENE DIBROMIDE BY JOB CLASSIFICATION AND SHIFT AT MANUFACTURING PLANT B

Sample	Job Classification	Date	Shift	EDB Conc., ppm
1	Control Room Operator	6/14/77	Day	0.08
2		6/14/77	Afternoon	0.01
3		6/14-15/77	Midnight	0.003
4		6/15/77	Day	0.12
5		6/15/77	Afternoon	0.03
6		6/15-16/77	Midnight	0.04
7		6/16/77	Day	0.16
1	Crew Leader	6/15/77	Day	0.04
2		6/15/77	Afternoon	0.95
1	Loader	6/15/77	Day[a]	0.62
2		6/15/77	Day	0.31
3		6/16/77	Day	0.40
4		6/16/77	Day[b]	0.05
1	Laboratory Technician	6/14/77	Day	0.01
2		6/15/77	Day	0.08

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[a] Performed unusually heavy schedule of tank car loading and quality control sampling activities.

[b] Performed duties on ground level; did not perform activities such as quality control sampling at the tank car opening.

Table 3

TIME-WEIGHTED AVERAGE EXPOSURES
TO ETHYLENE DIBROMIDE BY JOB CLASSIFICATION AND
SHIFT AT USER PLANT C

Sample	Job Classification	Date	Shift	EDB Conc. (ppm)
1	Shift Superintendent	6/28/77	Afternoon	0.0002
2		6/29/77	Midnight	0.0001
3		6/30/77	Day	0.0004
1	Blend Operator	6/28/77	Afternoon	0.004 } 0.022
2		6/28/77	Afternoon	1.52 [a] }
3		6/29/77	Midnight	0.058
4		6/30/77	Day	0.005
5		6/30/77	Afternoon	0.004
6		6/30/77	Midnight	0.032
1	Laboratory Technician	6/28/77	Afternoon	0.007
2		6/28/77	Afternoon	0.007
3		6/28/77	Midnight	0.0003
4		6/28/77	Midnight	0.0002
5		6/30/77	Day	0.0002
6		6/30/77	Day	0.012

[a] Short-term sample while taking Quality Control Sample from EDB tank car; 8-hour TWA concentration from Blend Operator samples 1 and 2 is 0.022 ppm.

Table 4

TIME-WEIGHTED AVERAGE EXPOSURES TO ETHYLENE DIBROMIDE BY JOB CLASSIFICATION AND SHIFT AT USER PLANT D

Sample	Job Classification	Date	Shift	EDB, ppm[a]
1	Blend Operator	7/6/77	Afternoon	0.002
2		7/6/77	Afternoon	0.001
3		7/6/77	Midnight	0.006
4		7/6/77	Midnight	0.007
5		7/7/77	Day	0.009 (0.007)
6		7/7/77	Day	0.009
7	Reactor Operation	7/6/77	Afternoon	0.001
8		7/7/77	Day	0.003
9	Compound Bulk Operator	7/6/77	Afternoon	0.001
10		7/7/77	Day	0.008
11	Laboratory Technician	7/6/77	Afternoon	0.0001
12		7/6/77	Afternoon	0.0003
13		7/8/77	Day	0.0004
14		7/8/77	Day	0.0005
15	Drum Loader	7/7/77	Day (nonshift)	0.018
16		7/7/77	Day (nonshift)	0.014
17		7/8/77	Day (nonshift)	0.008
18		7/8/77	Day (nonshift)	0.015
19	Raw Material Handler	7/7/77	Day	0.082 (0.01)
20				0.027 (0.004)
21	Relief Operator	7/6/77	Afternoon	0.007
22		7/7/77	Day	0.0005
23	Drum Washer	7/7/77	Day (nonshift)	0.016[b]
24	Drum Inspector	7/7/77	Day (nonshift)	0.012
25	Operator[c]	7/8/77	Day (nonshift)	0.036[d]
26	Operator[c]	7/8/77	Day (nonshift)	0.036[d]

[a] Values in parentheses are the results of long-term sampling. The TWAs are calculated on the basis of these values and short-term samples given in Appendix 3, Table 3. In those cases where there are no values given in parentheses, the long-term values are equivalent to the TWA.

[b] Wore respirator entire shift.

[c] These are odd-job people in drum processing area. On day of sampling they moved empty and filled drums to different sites as needed by rolling drums.

[d] Left work early--total sampling time 2 hours 19 minutes.

Appendix 2

RESULTS OF AREA MONITORING

Table 1

AREA SAMPLING FOR ETHYLENE DIBROMIDE AT BREATHING ZONE HEIGHT IN EDB PROCESS WORK AREAS, PLANT A

Sample	Date	Description	EDB Conc., ppm
1	6/8/77	Control Room, at EDB Panel Board[a]	0.91
2	6/8/77	Laboratory, adjacent to Hood	0.73
3	6/8/77	Pump Area (Figure 2)	<0.00007
4	6/8/77	Near Lab. Tech. Sampling Area (Figure 2)	1.32
5	6/9/77	Near Heat Exchanger, East Side (Figure 2)	1.50
6	6/9/77	West Side of Heat Exchanger (Figure 2)	5.80
7	6/9/77	Bottom of Dryers (West Side) by Catwalk, 2nd level (Figure 3)	0.23
8	6/9/77	South of Primary Reactor, on Catwalk, 3rd level (Figure 4)	0.18

[a] Area at which Panel Board Technician makes adjustments to EDB process controllers, requiring several seconds at a time periodically throughout each shift.

Table 2

AREA SAMPLING FOR ETHYLENE DIBROMIDE AT BREATHING ZONE HEIGHT IN EDB WORK AREAS, PLANT B

Sample	Description	Date	EDB Conc., ppm
1	EDB Plant, 3rd Floor, Center	6/15/77	1.08
2	EDB Plant, Near Ethylene Block Valve	6/15/77	0.90
3	EDB Plant, EDB Control Room	6/15/77	0.08
4	EDB Plant, Ground Floor, Above Sampling Port	6/15/77	1.04
5	Laboratory, General Area, Center	6/16/77	0.51

Table 3

AREA SAMPLING FOR ETHYLENE DIBROMIDE AT BREATHING ZONE HEIGHT IN ANTIKNOCK BLEND WORK AREAS, PLANT C

Sample	Date	Description	EDB Conc. (ppm)
1	6/28/77	At EDB Sample Analysis Laboratory Bench	0.018
2	6/30/77	Control Room at Control Board	0.003
3	6/30/77	At Blend Tank where Blend Operator draws sample	0.167
4	6/30/77	Near Blend Pump where sample is withdrawn	0.044
5	6/30/77	Near Loading Rack; EDB Unloading	0.051

Table 4

AREA SAMPLING FOR ETHYLENE DIBROMIDE AT BREATHING ZONE HEIGHT IN ANTIKNOCK BLENDING AREA, PLANT D

Sample	Date	Description	EDB Conc., ppm
1	7/8/77	EDB tank car unloading area; no unloading in process during sampling	0.050
2	7/8/77	At the drum loading site with sampler attached to exhaust hood	0.008
3	7/8/77	Adjacent to blend tank controls in blending building	0.002
4	7/8/77	Adjacent to EDB storage tank on third floor of blending building	0.008

Appendix 3

SHORT-TERM PERSONAL MONITORING DATA

Table 1

PLANT A
EDB CONCENTRATIONS PRESENT DURING PRODUCTION
(QUALITY CONTROL) SAMPLING, SHORT-TERM PERSONAL MONITORING

Personal Sample	Quality Control Sampler	Date	EDB Conc.[a] (ppm)
1	Surveillance Technician	6/8/77	23.4
2	Surveillance Technician	6/9/77	12.0
3	Laboratory Technician	6/7/77	5.3

[a] The Surveillance Technician used protective equipment, including a gas mask, as noted in the text.

Table 2

PLANT B
EDB CONCENTRATIONS PRESENT DURING QUALITY
CONTROL SAMPLING, SHORT-TERM PERSONAL MONITORING

Personal Sample	Quality Control Sampler	Date	EDB Conc., ppm
1	Control Room Operator	6/15/77	0.29
2	Loader	6/16/77	0.54

Table 3

PLANT D
EDB CONCENTRATIONS FOR SHORT-TERM PERSONAL MONITORING OF SPECIFIC TASKS

Sample No.	Worker Title	Task Description	Duration of Task	EDB Conc. (ppm)
1	Raw Material Handler	Attaching hose to Tank Car for unloading EDB[a]	13 min.	2.39
2	Blend Operator	Disconnecting vent and filler lines after filling tank car with blend[a]	7 min.	0.14
3	Blend Operator	Taking quality-control sample of blend in locally exhausted hood	3 min. 33 sec.	0.037
4	Raw Material Handler	Disconnect hose from EDB tank car after unloading[a]	7 min. 23 sec.	0.085
5	Raw Material Handler	Determining level of EDB in storage tank[a]	2 min.	0.299
6	Raw Material Handler	Taking quality-control sample of EDB from tank car prior to unloading[a]	13 min. 10 sec.	0.699

[a] Respirators are worn during the performance of these tasks.