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TITLE

ETHYLENE DIBROMIDE EXPOSURES TO OPERATORS IN MANUFACTURING
FACILITIES AND TO GASOLINE STATION OPERATORS IN PUBLIC GAS STATIONS

INFORMATIVE SUMMARY WITH CONCLUSIONS

The ethylene dibromide exposures to the operators in 247 Building, the reaction facility, in 440 Building, the distillation and packaging facility, and in Bay Gasolene Stations are well within acceptable criteria on a time-weighted average basis. However, a two-minute/eight-hour peak exposure to the operator in 440 Building exceeds permissible criteria.

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PROBLEM

Supervision in the Halogen Research Laboratory, responding to Research Personnel Product Stewardship obligations, requested the Industrial Hygiene Section of Chemical Biology Research evaluate the degree of exposure of manufacturing personnel and gasoline station operators to ethylene dibromide.

CONCLUSIONS

1. The Bay Gasolene Station operators are exposed well within permissible levels to ethylene dibromide, tetraethyl lead and total hydrocarbons.
2. The ethylene dibromide operator in 247 Building is exposed within permissible levels to ethylene dibromide.
3. The ethylene dibromide operator in 440 Building is exposed within permissible levels on a time-weighted average basis to ethylene dibromide. However, there is a two-minute per eight-hour shift period that the operator is exposed in excess of the allowable peak concentration for EDB.

DISCUSSION

The acceptable level of ethylene dibromide exposure as defined by the American National Standards Institute, Committee Z-37.31-1970, and adopted by the Occupational Safety and Health Act (OSHA) of the Labor Department, is 20 ppm time-weighted average concentration, with acceptable ceiling concentrations of 30 ppm and an acceptable maximum peak of 50 ppm of no longer than five-minute duration.

The permissible occupational exposure to tetraethyl lead as defined by The American Conference of Governmental Industrial Hygienists and adopted under OSHA is 0.0076 ppm on a time-weighted average basis.

There is no permissible exposure value for gasoline vapors, as it depends on the specific quantity of each hydrocarbon component. However, a value often times used for gasoline mixtures is 500 ppm.

Ethylene dibromide is manufactured at 247 Building by the reaction of ethylene and bromine to yield crude EDB. This is essentially a closed operation with the following exceptions. When leaks around pipe joint seals, or pump packings occur, the EDB is allowed to remain on the floor within a diked area, and eventually washed with water into the sewer system. In addition, samples of the crude EDB are taken, visually checked and spilled into an open bucket.

The crude EDB from 247 Building is then pumped to 440 Building for distillation and packaging. The packaged material is then stored in a tank farm shed prior to shipment.

The EDB is sold as an additive to gasoline, where it is added as a scavenger for the tetraethyl lead anti-knock compound.

The tetraethyl lead (TEL) is added to gasoline at an approximate concentration of 2.5-3 ml TEL per gallon of gasoline. The EDB is added at approximately 1.5 equivalents based on TEL.

The Halogens Lab supervision were concerned about the industrial exposure to EDB at Dow and about occupational exposure to EDB of gasoline station operators. In addition, supervision requested that the exposure of the gasoline station operators to TEL and total hydrocarbons also be evaluated for comparison to EDB exposures.

The EDB exposures at 247 Building and the gasoline stations were sampled by use of breath tubes half filled with silica gel, and the sampled air drawn through the tube by means of a vacuum pump. The EDB in the air was adsorbed on the silica gel as the air was drawn through the tube. The EDB was eluted from the silica gel by hexane and analyzed by electron capture chromatography. The system was calibrated as to air flow, percent EDB adsorbed on silica gel, percent desorbed, and amount of EDB detected by EC. The air flow was 1.0 l/m with 100% adsorption onto and desorption from the silica gel, with a detection limit by EC of 390 nanograms. The effect of other contaminants

on the system were investigated and found not to be significant.

The EDB exposures at 440 Building were previously determined by filling 10-liter saran bags with air and analyzing the air by infrared spectroscopy. The limit of detection by that means was 2 ppm.

The total hydrocarbons were analyzed by means of a J&W Explosimeter, sensitive to all combustible hydrocarbons. The calibration of the J&W meter was based on gasoline vapor concentrations equivalent to that of n-hexane.

The TEL methods tried were unsuccessful, so the values reported are literature values reported in 1962 and related to the time distribution work pattern of the Bay Gasolene Station operators. These values should be considered as maximum order of magnitude exposures.

The survey was conducted during the weeks of September 18 and 25. The data are reported in Tables I to III.

Table I lists the data for the Bay Gasolene Station operators. The time-weighted average (TWA) exposures of the drive (pump) attendant are 0.005 ppm EDB, 0.0014 ppm TEL, and 49 ppm total hydrocarbons. The TWA exposures of the garage mechanic are 0.003 ppm EDB, 0.0011 ppm TEL, and 30 ppm total hydrocarbons.

The exposures listed are maximum TWA concentrations. The work at different gas stations varies considerably depending on volume of business (number of cars serviced).

Table II lists the exposure values for the EDB operator at 247 Building. The TWA concentration to the operator is 2.9 ppm with a range from 0.4 ppm to 38.4 ppm.

Although the author and one other person present during the survey experienced moderate eye irritation and moderately objectionable odor response to concentrations around 17 ppm and strong odor irritation to 38 ppm, the operator did not complain of the same symptoms. However, the presence of bromine vapors was not determined. For the time duration of work involved in each area (four minutes at 38.4 ppm, the remainder of the time under 20 ppm), the exposure profile is within permissible criteria from a systemic toxicity standpoint.

Table III lists the exposure values for the EDB operator at 440 Building. The TWA concentration of EDB exposure to the operator is 4 ppm with a range of (0) to 110 ppm. Although the TWA concentration is within permissible criteria, the ceiling value of 50 ppm is exceeded for the two minute 110 ppm exposure in the EDB Tank Farm Shed. The sampling in 440 Building was accomplished between 10/7/70 and 6/8/71 and has been reported in Report No. NBH2.41-2-2(3) dated 10/6/71.

Table I. Exposure of Gasoline Station Operators to Ethylene Dibromide, Tetraethyl Lead and Total Hydrocarbons

<u>Job Location</u>	<u>Time (min)</u>	<u>Concentration EDB (ppm)</u>		<u>Concentration TEL* (ppm)</u>		<u>Conc. Total HC (ppm)</u>	
		<u>Range</u>	<u>Average</u>	<u>Range</u>	<u>Average</u>	<u>Range</u>	<u>Average</u>
<u>Drive Attendant</u>							
1) By gas pumps	360	<0.0007- 0.010	0.007	0.0009- 0.0085	0.0015	10-1000	60
2) Office, garage	120		<0.0007		0.0009	10-60	15
Tim -Weighted Average Exposure							
= $\sum \frac{(\text{Time})(\text{Conc})}{480}$ =	480		0.005		0.0014		49
<u>Garage Mechanic</u>							
1) Garage, office	330		<0.0007		0.0009		15
2) By gas pumps	160		0.007		0.0015		60
Time-Weighted Average							
Exposure = $\sum \frac{(\text{Time})(\text{Conc.})}{480}$ = 480			0.003		0.0011		30

*Based on data reported in December, 1962 (Archives of Environmental Health, Vol. 5, pp. 527-531, 1962)

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Table II. Exposure of the Ethylene Dibromide Operator to EDB Vapors, 247 Building

<u>Work Location</u>	<u>(A)</u> <u>Time</u>	<u>(B)</u> <u>Concentration EDB</u> <u>ppm</u>		<u>(A)x(B)</u> <u>480</u>
		<u>Range</u>	<u>Average</u>	
1) EDB reactor area	60	7.3-13.9	10.7	1.34
2) Sample taking, EDB reactor area	8	13.9-38.4	26.2	0.44
3) Laboratory	52		7.3	0.79
4) Control room and iodine area	360		0.4	0.30
Time-Weighted Average Exposure	= 480			2.9

Table III. Exposure of the Ethylene Dibromide Operator to EDB Vapors, 440 Building

<u>Work Location</u>	<u>(A) Time</u>	<u>(B) Conc. EDB ppm</u>	<u>(A) x (B) 480</u>
1) EDB still and panel board	95	6	1.19
2) Drier room	100	5.2	1.08
3) Drier room (high concentration)	20	23	0.96
4) Tank car unloading	60	(0)	(0)
5) EDB tank farm	73	(0)	(0)
6) EDB tank farm shed	2	110	0.46
7) Venturi room	40	2	0.17
8) EDB wet tanks	15	2	0.06
9) Waste water area	15	2	0.06
10) Lunchroom	60	(0)	(0)
Time-Weighted Average Exposure =	480		3.98 ~4 ppm

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