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Extent of industrial exposure to epichlorohydrin, vinyl fluoride, vinyl bromide and ethylene dibromide

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Industrial hygiene studies of epichlorohydrin, vinyl fluoride, vinyl bromide and ethylene dibromide were conducted as part of an industry-wide evaluation of suspect cancer-causing chemical agents. At present there is no evidence that workers are experiencing adverse health effects at the reported exposure levels. Continued efforts to minimize worker exposure are recommended.

Extent of industrial exposure to epichlorohydrin, vinyl fluoride, vinyl bromide and ethylene dibromide

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introduction

There are many industrial chemicals for which there are insufficient data and experience to determine the extent of worker exposure and the resultant long term health effects. The effectiveness of existing control measures and work practices needs to be evaluated on a total industrial basis.

NIOSH has conducted industrial hygiene surveys for epichlorohydrin and vinyl halides (vinyl fluoride and vinyl bromide) under contract with Tracor Jitco, Inc. and for ethylene dibromide under contract with SRI, International. Composite technical reports containing the findings for these surveys have been prepared and published as NIOSH technical reports.[1-3] The purpose of this report is to present and summarize the pertinent findings of these studies.

method

Walk-through surveys were conducted for each facility to obtain preliminary information about the process, production activity, potential exposures and worker exposure. Based on the walk-through survey, in-depth survey requirements are defined for each plant. Essentially, the in-depth survey procedures are directed toward determining 8-hour TWA personal exposures and characterizing work practices and controls. Sampling is conducted on all shifts (usually three) for potentially exposed workers. Job descriptions are characterized for potentially exposed workers. Appropriate survey sampling and analytical methods formed the basis for methodologies employed in the study.[4,5] Recommended vinyl fluoride sampling methods were not available at the time of the study. Therefore, personal sampling for vinyl fluoride was conducted with 7.7 liter Teflon bags attached to sampling pumps operating at flow rates of 14 to 100 cc/min. The samples were analyzed by gas chromatography within two days after sampling. Laboratory decay tests indicated 10% loss in four days and 50% loss in two weeks for the Teflon bag used. All other samples were collected on standard 150-mg charcoal tubes and analyzed by gas chromatographic techniques.

health concern

The current Federal Standard for epichlorohydrin is 5 ppm (19 mg/m^3) as an 8-hour time-weighted average permissible exposure level. This is based on the known acute (short term) health effects to humans from overexposure, *i.e.*, respiratory tract irritation and systemic poisoning. Skin contact can result in dermatosis and contribute to systemic effects. Exposures occur principally by inhalation and direct skin contact and to a lesser extent by ingestion. After a comprehensive literature review, NIOSH concluded that exposure risks may include carcinogenesis, mutagenesis, and sterility in humans and recommended a time-weighted average occupational exposure limit of 2 mg/m^3 of air (0.5 ppm) and a ceiling limit of 19 mg/m^3 (5 ppm).[6] More recent information on human exposure data has prompted NIOSH to issue a Current Intelligence Bulletin recommending exposures be reduced to the lowest extent feasible.[7]

The vinyl halides including vinyl fluoride and vinyl bromide have been identified as potential carcinogens as a result of the recently reported cancer in vinyl chloride workers. In the absence of definitive Federal Standards for vinyl fluoride and vinyl bromide, NIOSH recommends that exposures be minimized and recommends that exposures be controlled to comply with the Federal Standard for vinyl chloride. The Federal Standard for vinyl chloride is one ppm as an 8-hour TWA exposure limit. The 1978 ACGIH Threshold Limit Value for vinyl bromide is 5 ppm as an 8-hour TWA exposure limit. More recent information on vinyl bromide (aminal studies indicating health effects similar to those of vinyl chloride) has prompted NIOSH to issue a Current Intelligence Bulletin recommending exposures to vinyl bromide be minimized.[8]

The current Federal Standard for ethylene dibromide is 20 ppm determined as an 8-hour time-weighted average occupational exposure level. This is based on the acute health effects to the respiratory tract and systemic poisoning. Direct skin contact may result in skin irritation

TABLE I
Epichlorohydrin Sampling Data Summary
Epichlorohydrin Manufacturers
8-hour TWA Personal Samplers

Plant/Job	Sample Size	Range (PPM)	Median (PPM)
Plant A:			
Chemical Operators	8	N.D.-0.4	0.3
Shift Foremen	3	0.1-0.2	0.1
Drumming Operator	2	0.06-0.08	0.07
Tank Car Loader	1	0.3	.0.3
Pipefitter (Maintenance)	3	N.D.	N.D.
Plant B:			
Chemical Operator	12	N.D.-2.1	0.1
Shift Foremen	3	N.D.-0.3	N.D.
Tank Car Loader	1	0.3	0.3
Maintenance Foreman	1	0.08	0.08

N.D. – Not detected based on the sampling and analytical method.

and may contribute to the systemic effects. A comprehensive review of the literature by NIOSH of animal studies indicate reproductive effects, carcinogenicity, mutagenicity and teratogenicity. Based on these adverse effects possibly associated with human exposure, NIOSH recommended an employee exposure ceiling of 0.13 ppm (1.0 mg/m^3).[9] Based on the preliminary results of animal studies of a toxic interaction between disulfiram and ethylene dibromide. NIOSH recommended that workers should not be exposed to ethylene dibromide during the course of disulfiram therapy.[10]

plant description

epichlorohydrin

Plants A and B are manufacturers of epichlorohydrin of conventional open structure chemical process design. Both facilities manufacture epichlorohydrin for shipment and for use in manufacture of glycerine and epoxy resins. Epichlorohydrin is made by the chlorination of allyl chloride yielding a mixture of dichlorohydrin. These products are washed with a cold dilute alkali solution to remove hydrochloric acid and yield impure epichlorohydrin. The epichlorohydrin is further refined by distillation processes.

Plants A, B, C, D and E manufacture a variety of epoxy resins. The basic process involves reacting epichlorohydrin with bisphenol A under alkaline conditions. Depending on the particular resin being produced, reactants and/or solvents may be introduced to modify the resin properties and the viscosity of the liquified resin products. The reactants, depending on resin specifications may include bisphenol A, tetrabromo bisphenol A, o-cresol, paraformaldehyde, caustic soda, oxalic acid, and p-tertiary butyl phenol. The solvents may include methyl ethyl ketone, methyl isobutyl ketone, acetone, toluene and xylene.

vinyl halides

Plant A is a manufacturer of vinyl fluoride. The basic process involves a pressurized reaction of hydrofluoric acid and acetylene. Difluoroethane is formed as an intermediate product that is cracked to yield ethylene fluoride and hydrogen fluoride. The reaction products are refined by distillation and the off-products are recycled to the process stream. Liquid vinyl fluoride is piped to insulated storage tanks and from there to insulated tank cars for shipment.

Plant B is a manufacturer of polyvinyl fluoride. Vinyl fluoride is received, transferred to storage tanks and piped to the vinyl fluoride polymerization building. The monomer is continuously pumped to a supply tank at the process building and from there injected into water and pumped to the reactor to which an aqueous solution of the reaction initiator is simultaneously added. The reactor is barricaded from the remainder of the processing area since the reaction is conducted under high pressure carefully controlled. The reacted vinyl fluoride, a finely divided precipitate, is separated from the reactor aqueous liquor. Unreacted vinyl fluoride is recycled to the supply tank. The polymer is stored as a 5% aqueous slurry and fed to a rotary filter. The process is a closed system until the slurry (completely polymerized) is fed to the rotary filter. The resulting filter cake (white odorless product) is further dried, collected in bag filters, classified and stored for further processing.

Plant C is a manufacturer of vinyl bromide. Ethylene dibromide is continuously fed to a reactor where caustic dehydrobrominates the dibromide and yields vinyl bromide. The unreacted ethylene dibromide is removed by distillation and recycled. The vinyl bromide is pumped to storage tanks and transferred to railroad cars for shipment. The process is enclosed and the plant structure is open and outside. The process control instrumentation is located in a separate building, where operators monitor the process.

TABLE II
Epichlorohydrin Sampling Data Summary
Resin Manufacturers
8-hour TWA Personal Samplers

Plant/Job	Sample Size	Range (PPM)	Median (PPM)
Plant A:			
Chemical Operators	6	N.D.-0.4	N.D.
Plant B:			
Chemical Operators	16	N.D.-0.8	0.04
Operating Foremen	5	N.D.-0.6	N.D.
Maintenance Foremen	1	N.D.	N.D.
Plant C:			
Chemical Operators	1	0.09	0.09
G.A. in Pump Room	1	1.5	1.5
Plant D:			
Chemical Operators	2	0.05-0.15	0.1
Plant E:			
Chemical Operators	14	N.D.	N.D.
Operating Foreman	1	N.D.	N.D.
Resin Finishing Flaker	2	N.D.	N.D.

N.D. – Not detected based on the sampling and analytical method.

ethylene dibromide

Plants A and B are manufacturers of ethylene dibromide in continuous flow, closed system operations. Ethylene dibromide is produced by the exothermic reaction of bromine and ethylene in a countercurrent flow reactor. With bromine entering the top and gaseous ethylene entering the

TABLE III
Vinyl Halide Sampling Data Summary

Plant/Job/Location	Sample Size	Result (PPM) Range	Median
		(Vinyl Fluoride)	
Plant A:			
Plant Operator	4	N.D.	N.D.
Plant Operator (start-up process)	1	21	21
G.A. in Control Room	3	N.D.	N.D.
Plant B:			
Polymer Operator	7	1-4	2
G.A. in Supervisor's Office	3	1-2	2
G.A. in Pump Room	1	5	5
Plant C:			
		(Vinyl Bromide)	
Plant Operator	4	0.1-0.4	0.3
Lab. Technician	2	0.3-0.5	0.4
Loading Crewman	1	1.2	1.2
Loading Crewman (1 hr. sample)	1	6.3	6.3

Results are 8-hr. TWA samples unless indicated.

G.A. – general area samples.

N.D. – not detected based on sampling and analytical method.

TABLE IV
Ethylene Dibromide Sampling Data Summary
8-hour TWA Personal Sample Results

Plant/Job	Sample Size	Range (ppb)	Median (ppb)
Plant A:			
Control Room Operator	4	20-140	80
Surveillance Technician	8	N.D.-1600	370
Lab Technician	4	N.D.-570	140
Brine Field Technician	4	N.D.-30	10
Plant B:			
Control Room Operator	7	3-160	40
Crew Leader	2	40-950	495
Product Loader	4	50-620	360
Laboratory Technician	2	10-80	45
Plant C:			
Blend Operator	5	4-58	22
Lab Technician	6	0.2-12	4
Shift Superintendant	3	0.1-0.4	0.2
Plant D:			
Blend Operator	6	1-9	6
Relief Operator	2	0.5-7	4
Reactor Operator	2	1-3	2
Drum Loader	4	8-18	14
Drum Processing	3	12-36	16
Raw Material Handler	2	27-82	54
Lab Technician	4	0.1-0.5	0.4
Compound Bulk Operator	2	1-8	4

N.D. – Not detected based on sampling and analytical method.

bottom, the reaction occurs in the upper portion of a column packed with ceramic chips. The crude liquid product is further refined, stored and loaded into tank cars for shipment. These processes are operated and monitored from remote control rooms. Potential exposures to operating personnel occur for quality control sampling and analysis, loading and maintenance operations.

Plants C and D produce antiknock blends using ethylene dibromide. Antiknock blends consist of homogeneous mixtures of ethylene dibromide, ethylene dichloride, tetraalkyl lead and may contain toluene and a dye. Raw materials are generally received by tank car, stored and pumped to the process area. Blending is performed in outdoor blending tanks. The batch-type process is activated and monitored from a control room. Manual operations involving potential worker exposure include loading and unloading tank cars, quality control sampling and analysis and drum loading.

results

epichlorohydrin manufacturing

the results of 8-hour TWA personal sampling at two manufacturing plants are presented in Table I. The greatest exposure, although well below the Federal Standard of 5 ppm, occurs with the tank car loaders. For 20 TWA personal samples taken in both facilities, exposures to chemical operators ranged from below detectable levels to 2.1 ppm with a median exposure of 0.2 ppm. For two TWA personal samples taken, one at each plant, the tank car loader exposure level was 0.3 ppm. The lowest detectable limit was determined to be about 0.05 ppm epichlorohydrin.

The production of epichlorohydrin operations are located out of doors with automated operations monitored from a control room. For normal operation, operators are seldom in the process areas. They are in the production areas for routine inspection of equipment, product sampling and occasional on-stream maintenance. Maintenance work is supervised by the shift foreman with work practices in effect.

TABLE V
EDB Ceiling Level Personal Sampling
(Sample time varies 1 to 20 min)

Plant/Task	Sample Size	Range (PPM)	Median (PPM)
Plant A:			
Quality - Control Sampling	3	5.3-23	12.0
Plant B:			
Quality Control Sampling	2	0.3-0.5	0.4
Plant C:			
Quality Control Sampling	1	1.5	1.5
Plant D:			
Quality Control Sampling	2	0.04-0.7	0.4
Loading Tank Car	1	0.1	0.1
Unloading Tank Car	1	1.6	1.6

Pumps and pipe flange seals are maintained to prevent leakage.

Tank cars and trucks are cleaned and inspected by a contractor before loading. Loading involves connecting supply lines and vent lines (to storage tank), loading tank car in which the operator is located at a control site some distance away and disconnecting once the tanks are filled. The most significant exposure to the loader is during the disconnect procedure. Drumming operations employ local exhaust ventilation systems.

epoxy resin manufacture

The results of 8-hour TWA personal sampling at five plants are presented in Table II. Exposure to epichlorohydrin was found to be less for the resin production operations. Resin process chemical operator exposures were found to be less than 0.8 ppm for 39 TWA personal samples. The highest level reported (1.5 ppm) is that for a general area sample taken in the isolated pump room of Plant C. This demonstrates the potential for exposure from equipment leakage.

Epoxy resin processes are located both indoors and outside, with a variety of natural, general and local types of ventilation control. Reaction kettles are equipped with vent lines. Epichlorohydrin was fully reacted in processes studies so that packaging and shipping of finished products did not present epichlorohydrin exposure to workers.

vinyl halide manufacturers

A summary of the vinyl halide sampling data for the three plants surveyed are presented in Table III.

The vinyl fluoride sampling results at Plant A were generally not determined due to interference from difluoroethane. Difluoroethane was measured at 5 ppm and less. The vinyl fluoride was estimated to be less than 2 ppm for 7 personal and general area samples. One TWA personal operator sample was 21 ppm for the start-up process on the first shift. This demonstrates that during a work shift with abnormal or unusual work operations, a greater potential for exposure exists. With continued caution on the part of the operators and the use of respiratory protection, protective clothing and face shields during these operations the actual worker exposure is minimized.

Sampling results for the vinyl fluoride polymer plant, Plant B, (Table III) indicate TWA exposure levels below 5 ppm vinyl fluoride. Samples ranged from 1 to 4 ppm with a median of 2 ppm for 7 TWA personal samples of polymer operators. One general area sample in the pump room was 5 ppm vinyl fluoride.

Operator exposures to vinyl bromide in Plant C (Table III) range from 0.1 to 0.4 ppm with a median of 0.3 for 4 samples. Higher levels were associated with the laboratory analysis and loading operations. A level of 6.3 ppm for a one hour sample during loading vinyl bromide tank cars was reported.

The primary control in these processes involves enclosed processes and process equipment located out of doors. The integrity of process systems are maintained to present minimal exposure hazards to plant workers. Certain potential exposure situations such as sample collection, coupling or decoupling tank lines and maintenance of process equipment require specialized controls and work practices.

ethylene dibromide manufacturers

The results of 8-hour TWA personal sampling at two manufacturing and two user industries (antiknock blending operations) are presented in Table IV. The results for ceiling level personal sampling for the four facilities are presented in Table V. Ethylene dibromide median exposures by similar job types on the manufacturing processes ranged from 10 to 500 ppb for 35 TWA personal samples. For

normal plant operations the greatest potential for exposure to ethylene dibromide is related to open system operations and more specifically the taking of quality control samples. This is apparent from the short exposure levels reported in Table V and are reflected in the 8-hour TWA results in Table IV for the control room operator, surveillance technician, and product loader.

The sample collection process varies from 5 to 30 minutes depending on the number and location of sampling. Process stream sampling is conducted generally at the beginning of each shift. Tank car loading requires about one to two hours and may be sporadic depending on shipment schedule.

EDB blending

The results of sampling for various operations for antiknock blending operations indicate lower overall exposures than occur in manufacturing. The results of 8-hour TWA personal sampling for two plants ranged from 0.2 to 54 ppb for 39 samples. Again, the higher exposures result from open system operations such as loading and unloading, drum cleaning, and sample collection. Drum loading is conducted using enclosed local exhaust hoods. The drums are reusable and undergo cleaning prior to reuse. Drum cleaning is conducted in an enclosed exhaust hood and the operators wear respiratory protection.

discussion

The reported exposure levels are considered typical of the industries represented. The primary control for each operation is the closed processing of chemicals. This is also typical of the chemical processing industry in general. Particular attention needs to be given to those operations and processes which can not be conducted as closed processes and to routine maintenance to detect and correct leaks and accidental chemical releases. The potential for health effects associated with the materials studied is significant enough to warrant application of ventilation systems, personal protection and safe work practices.

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