U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
CENTER FOR DISEASE CONTROL
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH
CINCINNATI, OHIO 45226

HEALTH HAZARD EVALUATION DETERMINATION REPORT HE 77-73-610

VELSICOL CHEMICAL CORPORATION
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ST. LOUIS, MICHIGAN 48880

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I. TOXICITY DETERMINATION

The following determinations have been made based on environmental air samples collected on June 6-8, 1977, medical examination of employees on October 17-22, 1977, evaluation of ventilation systems and work practices, and available toxicity information.

The accompanying medical report (following this Toxicity Determination Report) produced for NIOSH under contract by Cook County Hospital gives good evidence that workers at the St. Louis, Michigan Velsicol Plant showed a high incidence of acneiform skin lesions quite possibly caused by occupational exposure to halogenated chemicals. Additional evidence is presented that some employees may have had adverse health effects upon either their nervous, cardiovascular, hepatic, immune or respiratory systems. Medical recommendations are included in the following medical report and in Section VI of this report.

Employee exposures to ethylene dichloride (EDC) in the Fine Chemicals and HBCD Department exceeded the NIOSH recommend standard. In the Industrial Bromides Department, employee exposures to carbon tetrachloride exceeded the NIOSH recommended standard. In the Tetrabromophthalic Anhydride Department; employees may be overexposed to sulfur dioxide during the opening of the reactor hatch for raw material addition. Employees were also exposed to a variety of other chemicals for which neither evaluation criteria nor air sampling/analytical methods existed, or whose air samples were below the analytical limits of detection. These included hexabromocyclododecane, trimethylene chlorobromide, bromotrichloromethane, and tetrabromophthalic anhydride. Recommendations to improve or initiate engineering controls are included in Section VI of this report.

DISTRIBUTION AND AVAILABILITY

Copies of this Determination Report are currently available upon request from NIOSH, Division of Technical Services, Information Resources and Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days the report will be available through the National Technical Information Service (NTIS), Springfield, Virginia. Information regarding its availability through NTIS can be obtained from NIOSH, Publications Office at the Cincinnati address.

Copies of this report have been sent to:

a) Velsicol Chemical Corporation, St. Louis, Michigan, and Chicago, Illinois
b) Authorized Representative of Employees - Oil, Chemical and Atomic Workers-International Union - Washington, D.C.
c) Authorized Representative of Employees - OCAW Local 7-224, St. Louis, Michigan
d) U.S. Department of Labor - Region V
e) Michigan Department of Public Health, Lansing, Michigan
f) NIOSH - Region V

For the purpose of informing the approximately 10 "affected employees" remaining at the facility, the employer shall promptly "post" for a period of 30 calendar days Sections I and II of the Determination Report in a prominent place(s) near where exposed employees work. Copies of the entire report should be made available to employees upon request.

III. INTRODUCTION

Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6), authorizes the Secretary of Health, Education, and Welfare, following a written request by an employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

The National Institute for Occupational Safety and Health (NIOSH) received such a request from an authorized representative of employees of the Oil, Chemical, and Atomic Workers Union regarding past employee exposures to polybrominated biphenyls (PBBs) and current employee exposures to a variety of chemicals. The request was received at NIOSH in early April, 1977; following a walkthrough survey by NIOSH industrial hygiene and medical contractor representatives on May 17, 1977, a conference was held with Velsicol Chemical and local OCAW officials. At this conference, the need for a follow-up environmental and medical evaluation was discussed.

The follow-up environmental survey was conducted during June 6-8, 1977, and an interim report containing air sampling results and recommendations was distributed to both parties on August 17, 1977 and October 20, 1977. After obtaining company medical records through an administrative supoena in July, 1977, the medical contractors reviewed them and finally conducted the medical evaluation of employees during October 17-22, 1977. Workers tested were sent letters notifying them of their individual test results in December, 1977.

Operations were discontinued at this facility in September, 1978. By then, certain operations had been already transferred to other Velsicol locations. The Toxicity Determination Report is first, followed by the summary report of the medical contractor with appendices. It is hoped that information contained in this report can be applied to other company sites.

IV. HEALTH HAZARD EVALUATION

A. Conditions of Use

Depending on the market need, between 30-40 chemicals can be produced at this facility. General production areas include Magnesia (Magnesium oxide, hydroxide, carbonate) Calcium Chloride, and Salt (Sodium Chloride). The production of brominated compounds and organic intermediates were given prime importance during the study and will be discussed in detail. PBBs were manufactured here from approximately 1971-1974.

Dimethylaminoethyl Chloride Hydrochloride (DMC) - "Fine Chemicals"

This specific chemical is one of five dialkylaminoalkyl chlorides produced as an intermediate in the production of analgesics, tranquilizers, etc., for the pharmaceutical industry. All five are processed separately in one of two production lines. The Dimethylaminoethyl Chloride Hydrochloride (DMC) manufactured during the survey was produced for about one continuous month. The other four "fine chemicals" are the following:

Diethylaminoethyl Chloride Hydrochloride - DEC (In 50% soluction, also)
Diisopropylaminoethyl Chloride Hydrochloride - DIC
Dimethylaminoisopropyl Chloride Hydrochloride - DMIC
Dimethylaminopropyl Chloride Hydrochloride - DMPC

Production periods for these chemicals vary due to the market needs.

The first step in "charging" the reactor is to set the desired temperature in the reactor. Through a closed system, thionyl chloride is gravity fed. Dimethylamino ethanol is fed into the vessel in a similar manner, over several hours. Ethylene dichloride is used as the solvent and is fed into the reactor through closed plumbing. The reaction takes place for about 4-6 hours. After a cooling period, the product is transferred to two crock filters. The product is rinsed twice with solvent from a loading line, and is shoveled by two operators into the dryer blender. The product is heated and blended in the rotating cone for several hours, and cooled by aeration. Since drumming is also a two man operation, one employee will prod the product out of the blender from on top while the other fills up plastic lined drums at the other end of the blender. This process requires about 30 minutes. Two employees per shift are in charge of the reaction process, filtering, and drumming of the product. Employees have potential exposures to solvent vapors, and dust from drumming.

Industrial Bromides

Many brominated compounds have a potential for being produced here, depending on the market need. Those which were produced or handled frequently will be discussed:

(1) 48% Hydrobromic Acid (HBr)
(2) 62% Hydrobromic Acid (HBr)
(3) Anhydrous Hydrogen Bromide (HBr)

Together these products are needed for the synthesis of inorganic and organic bromides, for manufacture of dyes, drugs, fragrances, and where anhydrous conditions are needed. These products (except for 62% HBr) are made in a small reactor which combines elemental hydrogen (or cracked ammonia) with bromine. A "utility operator" oversees the production of HBr in a closed reactor system. Anhydrous HBr is transferred into cylinders in a closed system by the "#1 operator". The 48% and 62% HBr (the latter produced in a utility reactor) are fed into drums by the "day utility operator". If leaks or line ruptures would occur, employees may have potential exposures to these gases.

(4) Bromotrichloromethane (BTCM)

This chemical is often used as a chain length control agent for polymerization reactions. BTCM is produced in a utility reactor. The #1 operator charges the reactor with one raw material - approximately 600 gallons of carbon tetrachloride - which enters the reactor in a closed system. The operator must then open the hatch of the reactor for about one minute while adding the aluminum chloride catalyst. The hatch is then closed and anhydrous hydrogen bromide is metered into the reactor.

After the reaction cycle is over, the crude product is transferred into a distillation column for refining. Eventually, the BTCM is piped into drums by the day utility operator. This may occur for about 40-50 minutes per batch every 2-3 days. Employees may have potential exposures to the above chemicals when the reactor is open or when leaks occur.

(5) Trimethylene Chlorobromide (TMCB)

This chemical is often used an intermediate in the production of cyclopropane and compounds containing a methylene bridge. It is produced in a reactor similar to BTCM but using a few different catalysts or additives (benzoyl peroxide and allyl chloride). TMCB is drummed out at the same station where the HBr acids are. A quantity of TMCB was being refluxed (refined) during the hazard evaluation survey.

The two-three employees per shift working here have potential exposures to carbon tetrachloride, BTCM, TMCB, HBr, and aluminum chloride. Exposures could occur during periods when reactor hatches are open, during drumming of products, or leaks in lines, spills, etc.

Tetrabromophthalic Anhydride (PHT4)

This chemical is produced in a separate building. Used as partial replacement for phthalic anhydride, this resin intermediate is used to meet reduced flammability needs. The first step of the process is the charging of the reactor: a manway or hatch is opened by an operator, who manually adds a quantity of bags containing phthalic anhydride in about 10-12 minutes. Approximately one addition per shift occurs. Exposures to the irritant gas sulfur dioxide and phthalic anhydride can occur when this process happens. After closing the hatch, the operator controls the addition of filtrate from a previous batch (98-99% sulfuric acid), liquid sulfur trioxide (SO_3), and bromine (Br_2) through a closed system. After reacting for several hours, gases and vapors are vented off into scrubbers. The product (PHT4) in a slurry form is automatically transferred to a dilution tank, heated, cooled and separated from the strong acid filtrate. The slurry eventually is sent into filter crocks, which collect the solid product in the open atmosphere under a vacuum for about one-two hours. The operators must then shovel the product into the washing tank below the three crocks. One operator requires about 30 minutes to accomplish this, or three operators about 10 minutes. After being washed with water and conveyed to a holding tank, the product is transferred automatically to a centrifuge. The operator must frequently bend over the chute leading to the drier to free product collected in the mouth of the centrifuge. This usually occurs twice per batch. The product moves by gravity through the horizontal dryer. Particulates entrained in hot air blown over the product are collected in dust bags outside. The product is conveyed by an elevator to a blender, and is then bagged. The operator places a 50 pound capacity bag on the unit and folds the sack closed once it is automatically filled. This procedure requires about 45-60 minutes, and occurs approximately once every 12 hours. Approximately two operators per shift are employed here. The operator(s) may be exposed to phthalic anhydride, sulfur dioxide, sulfuric acid, and tetrabromophthalic anhydride, as these are substances which may be released into the ambient atmosphere. Exposures to bromine could occur if accidently released into the air from the piping system.

Hexabromocyclododecane (HBCD)

HBCD is a solid fire resistant material produced in two grades - low and high quality. The raw materials are fed into a closed reactor: ethanol, or ethanol/ethylene dichloride (if purity is needed), 1,5,9-cyclododecatriene (CDT), and bromine. The reaction is monitored continuously by one operator stationed near the reactor. After four hours, excess bromine is neutralized with propylene oxide vacuumed into the reactor. The product is soon ready for filtration. This occurs in three large crock filters equipped with semicircular slot exhausts. The product/solvent slurry is fed into the crock through a loading line. The solvents are drawn off under vacuum and returned to the reactor vessel. Three solvent rinses are done at 45 minute intervals, controlled by two operators. The operators manually shovel the HBCD from the filters into the blender/dryer. After drying, the operators open the bottom hatch, allowing the HBCD to fall into a mobile hopper. The material is pulled by vacuum into a hammer mill grinder and falls into polyethylene-lined drums. The operators move drums in and out of the bagging station and close the filled bags. The two operators per shift perform essentially identical tasks.

One duty of employees not observed during the survey was the cleaning of the interior dryer vessel walls to remove caked-on matter. The operators use hand scrapers while wearing gas masks with universal canisters.

A second duty involves the opening of the dryer to obtain a bulk sample for quality control analysis when the interior reaches a certain temperature. Wearing half face piece organic vapor respirators, the two operators will open up the hatch and use a ladle to get the samples. The procedure requires about five minutes.

A third duty involves the filling of drums with waste solvents near the drumming (HBCD) station. The operator positions the drum below the delivery pipe and lets the wastes fall through the bung of the drum. A round exhaust duct is placed near the bung to capture vapors. The operators may have a potential exposure to solvent vapors from equipment leaks, during crock filtration, and when taking product samples. Exposure to HBCD may happen during drumming procedures.

Methyl Bromide

Methyl Bromide is produced in a vessel which reacts hydrogen bromide and methanol. This occurs in an area adjacent to the Fine Chemicals Department and is monitored by one employee. This worker may spend approximately half the work shift in this area. In a nearby area, methyl bromide is processed into cans with 2% chloropicrin for use as a fumigant. Five employees are involved in the canning. Production did not occur during the environmental study.

B. Evaluation Design

A walkthrough survey was conducted at Velsicol Chemical on May 17, 1977. Background information about processes, materials, work practices, and employee medical records basic to establish a follow-up environmental/ medical study protocol was obtained. A follow-up environmental study was conducted during June 6-9, 1977, in various areas of the plant. An administrative supoena was required in order for NIOSH contract physicians to review company medical records. The review began in July, 1977, and the medical evaluation was conducted during October 17-22, 1977.

C. Environmental Evaluation Methodology (Air Sampling/Analytical Methods)

Atmospheric samples for various organic vapors (carbon tetrachloride, bromotrichloromethane, methylenetrichlorobromide, ethylene dichloride, benzene, 1,5,9 cyclododecatriene) were collected on activated charcoal tubes. Air was drawn through the tubes using battery powered vacuum pumps operating at flow rates of either 50 or 200 milliliters per minute. The pumps and samples were worn by employees to determine personal exposures and also placed in the general work area.

Atmospheric samples for sulfuric acid were collected on cellulose and mixed cellulose ester filters, and total particulates were collected on polyvinyl chloride filters. The filters were encased in plastic three piece field monitor cassettes with face cap on and small plugs removed. Personal samples were taken in the employee's breathing zone using battery-powered gravimetric pumps operating at a flow rate of 1.5 liters per minute. Since the analytical laboratory could not specifically analyze for hexabromocyclododecane nor dimethylaminoethyl chloride hydrochloride (DMC), they were treated as total particulate matter.

Direct atmospheric measurements were taken for carbon tetrachloride, ammonia, methyl bromide, and sulfur dioxide. Samples were drawn through length of stain indicator tubes. Samples were taken near the breathing zone of employees and in the general work area.

Direct atmospheric measurements were taken for total particulates using a battery powered respirable dust monitor. The instrument was positioned near the breathing zone of employees and in the general work area.

The following will list the type and sensitivity of the analytical methods:

Substance	Type	Analytical Limit of Detection per sample
sulfuric acid	titration	0.050 mg
ethylene dichloride	gas chromatography	0.02 mg
benzene	gas chromatography	0.005 mg
trichloroethylene	gas chromatography	0.01 mg
total nuisance particulates	electrobalance	0.01 mg
bromotrichloromethane	gas chromatography	0.1-0.2 mg
trimethylene chlorobromide	gas chromatography	0.02 mg
carbon tetrachloride	gas chromatography	0.02 mg

Detector Tube Range of Measurement

carbon tetrachloride	5-50 ppm
sulfur dioxide	1-25 ppm
ammonia	5-70 ppm
methyl bromide	5-50 ppm

D. Evaluation Criteria (Environmental Standards)

Airborne exposure limits for the protection of the health of workers have been recommended or promulgated by several sources. These limits are established at levels designed to protect workers occupationally exposed to a substance on an 8-hour per day, 40-hour per week basis over a normal working lifetime. For this investigation, the criteria used to assess the degree of health hazards to workers were selected from three sources:

1. NIOSH: Criteria for a Recommended Standard . . Occupational Exposure to various substances.

2. Threshold Limit Values (TLV): Guidelines for Airborne Exposures Recommended by the American Conference of Governmental Industrial Hygienists (ACGIH) for 1978.

3. OSHA Standard: The air contaminant standards enforced by the U.S. Department of Labor-Occupational Safety and Health Administration as found in the Federal Register 29 CFR 1910.1000 (Tables Z-1, Z-2).

Whenever possible, the NIOSH recommended standard will be the environmental criteria applied since it represents the most recent knowledge concerning a substance. If one does not exist, the next most stringent recommended or legal standard will be used.

Substance	NIOSH Criteria Document (or update)	OSHA Standard	ACGIH(TLV)
Carbon tetrachloride	(2 ppm C)	10 ppm(25 ppm C)	10 ppm(25 ppm C)
Ethylene dichloride	1 ppm**(2 ppm C)	50 ppm(100 ppm C)	50 ppm(75 ppm C)
Benzene	1 ppm**	10 ppm(25 ppm C)	10 ppm
Trichloroethylene	25 ppm	100 ppm(200 ppm C)	100 ppm(150 ppm C)
Sulfuric acid	1 mg/M^3	1 mg/M^3*	1 mg/M^3
Total particulates	-	15 mg/M^3	10 mg/M^3
Sulfur dioxide	0.5 ppm	5 ppm	5 ppm
Methyl bromide	-	(20 ppm C)	15 ppm
Ammonia	(50 ppm C)	50 ppm	25 ppm(35 ppm C)

*Concentrations, in parts of substance per million parts of air (ppm) or milligrams of substance per cubic meter of air (mg/M^3), are often based on an 8-hour time weighted average exposure (TWA). Values in parentheses represent concentrations which should not be exceeded even instantaneously as commonly measured in a 15-minute period.

**NIOSH recommends benzene or ethylene dichloride exposures be kept as low as possible. One ppm represents the lowest level at which a reliable estimate of exposure can be determined.

E. Medical Evaluation Methodology and Toxic Effects

The methodology will be discussed in the medical report. The toxic effects section for chemicals used or found follows now as well as in the medical report. Information on substances 01-28 was supplied by the medical contractors and 29-32 by the NIOSH author.

BENZENE: The major routes of entry of benzene into the body are by inhalation and skin absorption. Symptoms of acute benzene exposure include: dizziness, weakness, euphoria, headache, nausea, vomiting and tightness of the chest. With high levels of exposure the symptoms can rapidly progress to blurred vision, tremor, shallow and rapid respiration, ventricular irregularity, paralysis, unconsciousness and finally death. The symptoms of chronic low level benzene poisoning may be rather vague and constitute headache, fatigue, and loss of appetite. The main effect of benzene is on the hematopoietic system where it may cause a decrease in the total white blood cell count accompanied by a relative lymphocytosis and a macrocytic normochromic or slightly hyperchromic anemia as well as thrombocytopenia. With more severe exposure or in a sensitive individual, the bone marrow may become aplastic or hyperplastic. Leukemia has also been associated with benzene exposure. Significant chromosomal changes have been reported after chronic benzene exposure. The toxic effects of chronic poisoning may not become apparent for months or even years after the initial contact with the chemical and may in fact appear after all exposure has ceased. Since it is a defattying agent it may also cause dermatitis.

02 BROMINE: Chronic bromine intoxication is known as "bromism" and was seen frequently in the past when bromide containing compounds were sold in over-the-counter preparations as sedatives and anti-acids. Bromine enters the body mainly by ingestion. Bromine vapors are extremely irritating to the eyes and mucous membranes and prolonged contact may cause ulcers and deep burns which are difficult to heal. For this reason inhalation is usually not the major route of entry. Skin absorption is also possible.

Bromine can effect the skin and mucous membranes, the respiratory system, and the central nervous system. Its effect on the pulmonary system is mainly as an irritant, causing copious mucous secretion, epistaxis, respiratory difficulties, and coughing. Dermatologic lesions can include deep burns, ulcerations, and generalized vasicular mobilliform rashes. Central nervous system effects include: vertigo, headache, chest pain, increasing irritability, loss of appetite, joint pain and dyspepsia. With increased bromine intoxication, one may see impaired thought process, impaired memory, dizziness, delirium, and coma. Bromism may mimic psychosis or space occupying lesions in the brain. Thyroid hyperplasia has also been known to occur with bromine exposure. Leukocytosis has also been reported.

Bromine can be measured in the serum. Levels of 9 milli-equivalents per liter or greater, or 50 to 150 mg per deciliter should be regarded as in the toxic range. The laboratory used in this evaluation considered any value greater than 2 milli-equivalents per liter abnormal.

BROMOTRICHLOROMETHANE: Bromotrichloromethane is a colorless liquid which can be absorbed through the gastro-intestinal tract, the pulmonary system, or the skin. It is extremely toxic to the liver and is considered to be 200 times more toxic than carbon tetrachloride. In extremely high doses, it probably also acts as a narcotic.

04 CARBON TETRACHLORIDE: The main route of entry of carbon tetrachloride is through inhalation, although gastro-intestinal and skin absorption can also occur. Carbon tetrachloride concentrates in body fat, liver, and bone marrow and is slowly excreted in expired air, urine, and feces.

Organ systems affected include the liver, the kidney, the skin, and the neurological system. It is a defatting agent for the skin and can cause a chronic septic dermatitis. Systemic symptoms include: dizziness, vertigo, depression, headache, mental confusion, lack of coordination, and at higher concentrations, loss of consciousness and death. At very low vapor concentrations, gastro-intestinal disturbances such as nausea, vomiting, abdominal pain and diarrhea are seen in some individuals. It causes a decrease in blood flow through the kidneys resulting in glomerular and tubular damage. Upon initial exposure there may be anuria which is followed by diuresis. During the diuretic phase, the urine may contain protein, albumin, pigmented casts, and red blood cells. Liver damage includes swollen, fatty appearance of the liver with focal areas of necrosis. With prolonged low level exposure development of fatty metamorphosis and cirrhosis of the liver occurs. This effect is markedly accentuated by simultaneous intake of alcohol.

[Carbon Tetrachloride[32] - NIOSH now considers this chemical to be a suspect carcinogen, which may cause liver cancer.]

05 DDT: DDT was discovered in 1940 and used as an insecticide throughout the world to control malaria and typhus. After World War II, it was used regularly in agriculture and also in the household. This widespread use was based on the belief that it was a harmless substance. In the early 1960's, however, it was discovered that DDT presents a serious ecological hazard. Its use has been restricted in many industrial countries. DDT is a member of an organo-chlorine group of pesticides (OCP's). OCP's as a class, are hepato-toxic and neurotoxic. Additionally, some OCP insecticides are nephro-toxic. Most available information is based on animal studies. Characteristic histopathology is induced in the liver of rodents and other mammals by relatively low doses of OCP's. These include centrilobular macrocytosis, formation of complex intracellular inclusion bodies, hyperplasia, pre-malignant "neoplastic nodules" and centrilobular necrosis at higher concentrations. OCP's are selectively stored in adipose and central nervous system tissues.

Hyper excitability and aggression are induced by relatively low concentrations of OCP and convulsions by higher concentrations. Residual weakness and neuropathy have been reported following DDT poisoning in rats. Chronic gait changes have also been described in rats on a hundred parts per million dietary DDT. In human exposure, there are reports of systolic and diastolic blood pressure changes. The serum cholestrol levels were significantly elevated on 30 subjects with intensive occupational exposure to pesticides. The concentrations of OCP residues in autopsy tissues particularly DDT and Dieldrin in a variety of studies have been claimed to be higher in subjects with malignant rather than non-malignant diseases. The overall implications are suggestive of a possible association. It has also been shown that humans store DDT in the fat. There are teratogenic effects of DDT because it crosses the placenta and is also excreted in human milk. DDT also can produce rare and diffuse histologic damage to the liver.

06 DEC (Di-Ethyl-Amino-Ethyl-Chloride Hydrochloride): For this substance no relevant toxicity data could be found in the literature.

[Diethylaminoethyl chloride hydrochloride (DEC):[29] These white tan powders may cause skin irritation accompanied by a rash and possible swelling.]

07 DIC (Di-isopropyl Amino-Ethyl Chloride Hydrochloride): For this substance no relevant toxicity data could be found in the literature.

08 DMC (Beta Dimethyl Amino Ethyl Chloride Hydrochloride): For this substance no relevant toxicity data could be found in the literature.

[Dimethylaminoethyl chloride hydrochloride (DMC):[29] These white tan powders may cause skin irritation accompanied by a rash and possible swelling.]

09 DMIC (Beta Dimethyl Amino Isopropyl Chloride Hydrochloride): For this substance no relevant toxicity data could be found in the literature.

[Dimethylaminoisopryopyl chloride hydrochloride (DMIC):[29] This crystalline, light tan solid may cause skin and eye irritation. Irritation of the upper respiratory tract is possible also which could lead to pulmonary edema.]

10 DMPC (Gamma-Dimethyl Amino Propyl-Chloride Hydrochloride): For this substance no relevant toxicity data could be found in the literature.

[Dimethylaminopropyl chloride hydrochloride (DMPC):[29] These white tan powders may cause skin irritation accompanied by a rash and possible swelling.]

11 ETHYLENE DICHLORIDE: Ethylene dichloride is used as a solvent in industry, and as a fumigant in pesticide control. It has multiple toxic effects on the human organ systems. It can be readily absorbed through the lungs, the gastro-intestinal tract, and also the skin if prolonged contact occurs.

Exposure to ethylene dichloride vapors in dogs produces clouding of the cornea which can progress to endothelial necrosis, infiltration of the cornea by lymphocytes, and later infiltration of the connective tissue cells. The effect on the nose and throat is that of an irritant.

When ethylene dichloride comes in contact with the skin, it can cause rough, red, dry skin due to the extraction of fatty materials. It also can lead to severe irritation. Moderate edema and necrosis may be observed.

In the kidney, liver and adrenal glands, exposure to ethylene dichloride can lead to pathological changes, liver dysfunction, congestion, and fatty degeneration. Effects on the gastrointestinal system are as follows: nausea, vomiting, epigastric distress, loss of appetite, diarrhea. It affects the hematological system by causing leukocytosis and anemia. Ethylene dichloride can also cause severe central nervous system depression, mental confusion, tremors, nystagmus, and the narcotic effect is very strong.

[Ethylene dichloride[30] - NIOSH considers the evidence of carcinogenicity of ethylene dichloride reported by the National Cancer Institute to be conclusive in two mammaliam species - the rat and mouse. Since it causes progressive, malignant disease of various organs in these species, it is recommended that ethylene dichloride be considered carcinogenic in man, and that no safe exposure level exists.]

2 & 13 FIREMASTER BP4A (tetra-bromo bisphenol, Firemaster 680, 100, 695: Toxic substance medical data is presented under 28 - polybrominated biphenyls.

14 HBCD (Hexabromocyclododecane): For this substance no relevant toxicity data could be found in the literature.

[Hexabromocyclodedecane(HBCD):[29] This white to gray amorphous powder is water insoluble. The toxicology of this substance is not well known. Upon heating to high temperatures, the material will decompose and form hydrogen bromide.]

15 HYDROCHLORIC ACID: The main effect of hydrochloric acid is as a corrosive to the mucous membranes, skin, and respiratory tract. It is capable of producing burns. The severity of these burns are dependent upon the concentration of the material. Vapors, in high enough concentrations, are capable of causing laryngitis, bronchitis, and pulmonary edema.

16 HYDROBROMIC ACID - HYDROGEN BROMIDE: Hydrogen bromide may be absorbed through the respiratory tract or the gastrointestinal tract. Its action is as a local irritant and is similar to hydrochloric acid.

17 IODINE: Iodine is absorbed by the respiratory tract. It causes a "halogen like" toxicity when in contact with the skin, respiratory tract or mucous membrane. Severe mucous membrane irritation and deep skin burns may result from contact with iodine vapor. When absorbed systemically, iodine is concentrated in the thyroid gland and various metabolic disturbances may result. Chronic absorption of iodine may cause " iodism" a disease characterized by tachycardia, tremor, weight loss, insomnia, diarrhea, conjunctivitis, rhinitis, and bronchitis.

18 LEAD: In adults, lead affects three major systems. It affects both the central and peripheral nervous system, causing slowing of impulse conduction in the peripheral nerves, leading to weakness in the muscle groups innervated by these nerves. The most commonly affected nerves are those innervating the wrist and ankle extensors. The exact pathophysiologic effects on the central nervous system are not well known, but such symptoms as convulsions, irritability, personality change, forgetfulness, decrease in intellectual functioning, ataxia, headache, optic atrophy, and other signs of encephalopathy are all evidence of its central nervous system toxicity.

The hematopietic system is also affected by exposure to lead. Lead inhibits the activity of several enzymes in the metabolism of heme and thus leads to anemia, shortened red blood cell life span and the presence of immature types of red blood cells in the peripheral blood.

Adults with chronic lead poisoning develop toxic, i.e., interstitial nephropathy with nonspecific morphologic changes in the kidney. Nuclear inclusions bodies are seen on kidney biopsy, and with continued exposure, interstitial fibrosis may develop, then tubular atrophy, reduced glomerular filtration, and finally renal failure.

There are many types of tests that can be done to estimate body burden of lead, blood lead being one of the most common. The sample necessary for analysis is approximately 5ml of venous whole blood drawn after careful cleaning of the skin to prevent contamination.

19 METHYL ALCOHOL, METHANOL, CARBONAL, WOOD ALCOHOL: Acute exposure by ingestion is the most common form of methyl alcohol poisoning. The substances oxidize in the body to form formic acid and formaldehyde. Incorrectly used as a substitute for ethyl alcohol, methyl alcohol ingestion results in blindness due to optic nerve degeneration, depressed breathing and cardiovascular dysfunction, delirium, acidosis, pancreatic injury and death. Inhalation of the vapors and skin penetration are main forms of toxic exposure to methyl alcohol among workers. This results in irritation of the mucous membranes, headaches, ringing in the ears, vertigo, insomnia, nystagmus, dilated pupils, clouded vision, nausea, vomiting, colic, and constipation. There may also be skin injuries because of the solvent action of methyl alcohol. Methyl alcohol has caused death in experimental animals by skin penetration.

20 METHYL BROMIDE: Methyl Bromide attacks almost every major organ system and can damage the brain, heart, lungs, spleen, liver, adrenals, kidneys, and also causes central nervous system depression. Locally, methyl bromide is an extreme skin irritant and may produce severe burns. In cases where there is not severe narcosis, symptoms can be delayed by hours or even days. The symptoms related to methyl bromide exposure are loss of appetite, nausea, vomiting, headache, giddiness, visual disturbances, seizures, lethargy, and faintness. In the body methyl bromide is hydrolized to form inorganic bromide and the systemic effect of methyl bromide is an unusual form of bromism with intracellular penetration of bromide. The brain becomes acutely edematous and cortical degeneration occurs. In acute cases of methyl bromide intoxication, pulmonary edema may occur, the kidneys are affected and there is tubular degeneration leading to uremia. Damage to the vascular system is also indicated by hemorrhage in the lungs and the brain. The liver can become enlarged. Symptoms may be delayed up to 48 hours after exposure.

21 TETRABROMOPHTHALIC ANHYDRIDE (PHT4): Route of absorption and systemic effects are largely unknown. The compound is capable of acting as a strong skin and upper respiratory tract irritant upon contact. It has been reported to have caused conjunctivitis, bloody nasal discharge, atrophy of the nasal mucosa, hoarseness, cough and bronchitis, as well as attacks of bronchial asthma.

22 SULPHURIC ACID & LIQUID SO3: Sulphuric acid and fuming sulphuric acid by virtue of their great reactivity, are generally not absorbed into the body. Effects of exposure to sulphuric acid range from irritation to burning and charring of the tissue depending upon the concentration of the substance. Target organs include the skin, mucous membranes, and respiratory tract. Dental enamel is also affected due to the corrosive affect. Symptoms include irritation of all mucous membranes, tickling of the nose and throat, sneezing, coughing, and a reflex increase in the respiratory rate accompanied by diminution of the depth. Reflex broncho constriction may also occur and with higher and more prolonged exposure, bronchitic symptoms may develop. A single massive exposure to sulphuric acid may lead to laryngeal, tracheobronchial, and pulmonary edema which may result in chronic pulmonary fibrosis, residual bronchietasis, and pulmonary emphysema.

23 TRIS (2,3-Dichloropropyl) Phosphate: This material may be absorbed through the skin or the gastrointestinal tract. Absorption through the respiratory system has not been studied. Studies have shown this compound to be mutagenic in bacterial systems, and carcinogenic in some studies on rats. Data also suggests that this compound may be hepatotoxic.

24 YTTRIUM and Rare Earths: These compounds have been found to cause chronic productive inflammation with moderate fibrosis of the lungs, and nodular granules of the lungs in rats exposed via the respiratory tract. It has also been shown to cause an effect on the peripheral blood system, including a decrease in the hemoglobin and erythrocyte count and changes in the leukocyte formation. The main route of entry is through the pulmonary system.

25 MAGNESIUM OXIDE: The fumes of magnesium oxide have been known to cause metal fume fever when they make contact with the respiratory tract. There have been reports of a higher than usual incidence of digestive disorders in a magnesium plant and a relationship has been suggested between magnesium-absorption and gastroduodenal ulcers.

26 CALCIUM CHLORIDE: Calcium chloride may be absorbed into the body by the GI tract. However, the major toxicity of this material is due to its action upon contact with the skin and mucous membranes. It has powerful irritant action which may cause erythema, peeling of facial skin, lacrimation, eye discharge, burning sensation and pain in the nasal cavities with occasional nose bleeds and tickling in the throat. Cases of perforation of the nasal septum have been reported after exposure to calcium chloride.

PHENOL: Phenol may be rapidly absorbed through the respiratory tract, the skin, and the gastrointestinal tract. The main effect of acute phenol poisoning is on the central nervous system. These symptoms develop rapidly, and include headache, dizziness, muscular weakness, dimness of vision, tinnitis, irregular and rapid breathing, weak pulse, and dypsnea. These may progress to loss of consciousness, followed by collapse and death. When phenol is ingested symptoms include nausea, vomiting, severe abdominal pain and intense burning, followed by local anesthesia of the lips, mouth, throat, and esophagus. There is damage to the kidneys, liver, pancreas, spleen and sometimes to the lungs.

Symptoms of chronic phenol poisoning include: digestive disturbances including vomiting, difficulty in swallowing, excessive salivation, diarrhea, and loss of appetite, nervous system disorders evidenced by headache, fainting, dizziness, and metal disturbances. Chronic poisoning cases have been known to terminate fatally. There is evidence of damage to the kidneys, liver, and dermatitis with chronic contact.

28 POLYBROMINATED BIPHENYLS

The polybrominated biphenyls (PBB's) are fat soluble and extremely water insoluble. The main route of entry is through the gastrointestinal tract, although animal studies have shown that respiratory tract absorption is possible. In animals, PBB affects the immune system by causing an increase in immunologic activity with a decrease in immulogic competence. Lesions in the liver have included an increase in liver size with extensive swelling and vaculation of hepatocytes. Induction of hepatic enzyme systems have also been observed.

There is very little reliable human data on PBB's. Michigan farmers exposed to PBB's reported increased fatigue, decreased mental functioning, and bone and joint symptoms. PBB's are not known to be carcinogenic at this time.

The toxicity of the PBB's is probably similar to the toxicity of the polychlorinated biphenyls (PCB's). The toxicologic picture in PCB intoxication includes: retarded growth, neurol endocrine disturbances, enzyme induction, disturbances in the respiratory system, and abnormal lipid metabolism. Dermatologic lesions include: acneiform eruptions and pigmentation. Occular symptoms and even blindness can result from PCB intoxication. PCB's have been shown to be teratogenic and carcinogenic in experimental animals.

The following information was gathered by the NIOSH project officer.

Trimethylene chlorobromide[29] (TMCB) - exposures to this liquid compound may result in effects on the liver and kidneys. Inhalation of the vapors may cause a deep stupor. Thermal decomposition will evolve hydrogen bromide, also.

Ammonia[31] - a colorless, strongly alkaline and very soluble gas with a characteristic pungent odor. Contact with it or its aqueous solutions is very irritating to mucous membranes, skin, and eyes. Headache, burning of the throat, nausea, and vomiting may follow mild to moderate exposure. Usually an individual will be forced to leave an area before suffering a severe exposure which would lead to bronchitis or pneumonia.

Phthalic Anhydride[31] - This white solid with needle like crystals is moderately flammable. It is a potent irritant of the eyes, skin, and respiratory tract, especially on moist surfaces. Inhalation of the dust or vapors may cause coughing, sneezing, and a bloody nasal discharge. Repeated exposure may result in bronchitis, emphysema, allergic asthma, and chronic eye irritation.

V. EVALUATION RESULTS AND DISCUSSION

A. Environmental

1. HBCD Department

Table 1 illustrates the results of atmospheric sampling for various organic vapors. The samples for benzene were below the evaluation criteria. However, two out of nine samples taken for carbon tetrachloride in the breathing zone of the #1 operator (8 and 2.8 ppm) exceeded the recommended ceiling standard of 2 ppm. Since this solvent is not a raw material or by-product of HBCD production, the nature of the exposures is questionable. 1,5,9-cyclododecatriene was found in one personal sample, but this result is questionable since the sampling media was very wet when analyzed. Only one sample contained propylene oxide, resulting in a concentration below evaluation criteria.

Two #1 operators - afternoon shift - were exposed to ethylene dichloride in excess of the NIOSH recommended 8-hour time-weighted average (TWA) standard of 1 ppm. The first operator's breathing zone levels of 11.6 and 2.9 ppm correspond to an 8-hour TWA exposure of 7.0 ppm. The other operator's breathing zone levels of 10.3 and 7.8 ppm correspond to an 8-hour TWA exposure of 6.7 ppm. These samples were taken during processes involving the shoveling of crock filters, removing a sample from the blender/dryer, drumming, and taping waste products into drums.

Direct reading measurements were taken for total particulates during drumming of HBCD by two operators. Area concentrations ranged from 0.7-1.9 mg/M^3, below all evaluation criteria for total particulates (Table 2). Personal monitoring was also conducted on two operators during half of one workday and during a 25-minute drumming period. Concentrations (0.9-7.7 mg/M^3) were below evaluation criteria (Table 3). Since there are no evaluation criteria for HBCD or any of the Fine Chemicals (such as DMC discussed in the next section), the total particulates evaluation criteria were used. Good industrial hygiene practices would be to keep the dust levels as low as practicable until more is known about the toxicity of these substances.

Ventilation measurements were taken at the semicircular slots of the three crock filters used to control vapor emissions arising during filtration. Slot velocities ranged from 200-600 feet of air per minute (fpm), while velocities across from the slots where the operators would stand ranged from 70-100 fpm. At all points where solvent vapors might arise, a capture velocity of 100-200 fpm is needed.

2. Fine Chemicals (DMC) Department

Table 1 illustrates the results of atmospheric sampling for ethylene dichloride and benzene. All personal samples for benzene were below evaluation criteria. One #1 operator and one "in-training" operator were exposed to ethylene dichloride in excess of the NIOSH recommended 8-hour TWA standard of 1 ppm. The #1 operator's breathing zone concentrations of 13.8 and 1.7 ppm corresponded to an 8-hour TWA of 7.3 ppm. The "in training" operator's breathing zone concentrations of 11.5 and 1.8 ppm corresponded to an 8-hour TWA of 6.3 ppm.

Thionyl chloride, a very reactive substance, was not analyzed for, since it is doubtful that is was trapped by the charcoal collection media.

Direct reading measurements for total particulates were taken during drumming of DMC. Samples recorded near the #1 operator (non-detectable and 0.5 mg/M^3) were below the evaluation criteria of 10 mg/M^3 (Table 2). Personal monitoring for total particulates was also conducted during this drumming. The evaluation criteria were not exceeded (Table 3).

Ventilation measurements were also taken at the slot exhausts for the crock filters and blender/dryer. Slot velocities ranged from 600-900 fpm, while the velocities across from the slots where the workers would stand ranged from 25-75 fpm. A capture velocity of 100-200 fpm would better control solvent emissions.

3. Industrial Bromides Department

Table 4 illustrates the results of atmospheric sampling for organic vapors. Breathing zone samples of the #1 operator and day utility operator ranged from non-detectable to 4.9 ppm for carbon tetrachloride, 0.4 to 5.1 ppm for trichloroethylene, and non-detectable to 8.7 mg/M^3 for trimethylene chlorobromide (TMCB). The production of TMCB, or 1-chloro-3-bromopropane, could theoretically result in other reaction products such as TMCB isomers or dibromochloropropane (DBCP). NIOSH has said that the possible health effects on the health of employees chronically exposed to DBCP may include sterility, diminished renal function, and liver problems. However DBCP was not detected in these analyses. The concentrations for trichloroethylene are below evaluation criteria while there is no evaluation criteria for TMCB. However, four out of eight samples taken in the breathing zones of the #1 and Day Utility Operators exceeded the NIOSH recommended ceiling standard of 2 ppm for carbon tetrachloride.

Direct reading indicator tubes were used to measure carbon tetrachloride. Various measurements taken near the reactor vessel failed to detect the vapor during different processes (Table 2). The indicator tube results are questionable, since the more reliable charcoal tube sampling method did indicate the presence of carbon tetrachloride vapor.

Bromotrichloromethane (BTCM) was very insensitive to gas chromatographic analysis, based on a bulk sample provided. BTCM could not be confirmed by mass spectrometry in any of the samples collected. Only trace amounts of allyl chloride could be determined in a few of the samples.

Direct reading tubes were also used to measure ammonia when the #1 operator prepared two pails of ammonium hydroxide by passing ammonia from a gas line directed into water. During preparation and pouring of the solution into a column, greater than 30 ppm of ammonia was recorded at the operator's breathing zone (Table 2). Since the detector tube readily overloaded, it is probable that all evaluation criteria were exceeded. This procedure can be avoided by prior precautions in preparation of the batch mixture.

4. Tetrabromophthalic Anhydride (PHT4)

Table 5 illustrates the results of personal and area sampling for sulfuric acid and total particulates. For the purpose of comparing two sampling and two analytical methods for sulfuric acid, several employees and area locations were fitted with two different collection devices. While the analytical methods yielded varying concentrations for the same employee or fixed location in several instances, none of these samples exceeded the evaluation criteria.

Personal and area concentrations of total particulates did not exceed evaluation criteria. The result of a sample for phthalic anhydride will not be reported due to analytical problems.

Direct reading measurements for sulfur dioxide (SO_2) were taken at the reactor hatch area and at the crock filters (Table 2). At least 25 ppm was recorded during opening of the reactor hatch prior to its charging. This value (25 ppm SO_2) exceeds the permissible excursion value of 10 ppm as recommended by the ACGIH. The excursion to 10 ppm is based on the permissible time-weighted average concentration of 5 ppm.

5. Methyl Bromide Department

Direct reading measurements were taken for methyl bromide near the halogen-detecting bunsen burner. Two measurements of approximately 20-30 ppm of methyl bromide were recorded on June 8, 1977. While these concentrations are at or above the OSHA ceiling standard of 20 ppm, the operator's actual exposure is difficult to define as he only spends about one half the work shift in this area. More frequent monitoring would be necessary to determine actual exposures and to detect where any leaks might occur.

Many of the processes studied require as many as 30 hours for completion. In most cases environmental samples were collected over time periods representative of complete cycles.

B. Medical

The accompanying medical report produced for NIOSH under contract by Cook County Hospital gives good evidence that workers at the St. Louis, Michigan Velsicol Plant showed a high incidence of acneiform skin lesions quite possibly caused by occupational exposure to halogenated chemicals. The report also states that workers demonstrated impaired performance on a psychomotor dexterity test and exhibited a seemingly high incidence of psychological complaints. These neurological abnormalities could have been caused by the work exposure to the many solvents and PPBs that were present in the factory in the past several years. Additional data suggested that there may have been a higher than expected number of Velsicol employees who had high blood pressure or elevated blood levels of low density lipoprotein (LDL).

In addition medical investigators state that many employees may have occupational liver disease since a high proportion of employees had abnormally elevated liver enzymes (indicative of liver damage) and 84% had enlarged livers (>11cm span in MCL) upon physical examination.

These abnormalities could be caused by solvent and PBB exposure, although no significant relation between an employee's exposure to known liver toxic compounds (organ risk index) and liver size could be found. Unfortunately, the medical report does not detail the usual alcoholic comsumption of the workforce or their possible exposure to other liver toxins outside the workplace so non-occupational causes of the documented liver abnormalities cannot be completely ruled out.

60% of the employees tested had band neurophill white cells in their peripheral blood. The laboratory performing the analysis considers the presence of any band cells to be abnormal but since most hematologists consider the presence from 3-5% band cells per 100 white cells to be normal, the significance of this finding in the Velsicol employees is uncertain. A large number of employees were found to have abnormalities in their red blood cell indices. 14% had an abnormal Mean Corpuscular Volume (MCV) which measures the average size of the red blood cell, and 29% had an abnormal Mean Corpuscular Hemoglobin (MCH) which measures the average amount of hemoglobin in a red cell. It is possible that solvent or other chemical exposures may have affected the red blood cells but the long term health effects of such an alteration are unknown.

39 employees with a history of PBB emposure underwent a lymphocyte blastogenesis test. 60% of these workers had an abnormal result which may indicate an abnormality in the function of their immune system, but unfortunately no mention is made of possible recent ingestion by the tested employees of drugs such as aspirin which may affect the blastogenesis test. Immuno Electrophoresis tests (which measure antibody produced by the immune system) were done on 23 of the PBB exposed employees and were judged to be normal by the medical investigators. No relation between an abnormal lymphocyte blastogenesis test and an increased incidence of illness was found. Therefore, the significance of the lymphocyte blastogenesis test results as it relates to the long term health of the exposed employees is not clear.

27% of the employees tested were found to have an FEV_1/FVC ratio of less than 70%. (A ratio below 70% generally indicates the presence of obstructive lung disease.) After standardization for age and smoking history, the employees in the high lung risk index group tended to have a lower FEV_1/FVC ratio thus suggesting that the high prevalence of obstructive lung disease is related to work exposure but the relation was not significant at P.05 level.

The medical findings are more descriptive than analytical but the evidence taken as a whole shows that at least a portion of the Velsicol employees suffered adverse health effects because of chemical exposures encountered at the St. Louis, Michigan Plant.

RECOMMENDATIONS

A. Environmental

It must be remembered that operations ceased at the Velsicol facility in September, 1978. It is assumed that production processes not ended permanently were transferred to company sites in other states. These recommendations are provided in the event other similiar processes or structures begin elsewhere or are reactivated at the St. Louis, Michigan site.

1. Fine Chemicals Department/HBCD Department

The local exhaust system for all the crock filters should be improved. Since NIOSH has recommended that ethylene dichloride be handled as a human carcinogen, the first choice would be to enclose them as much as possible. A hinged lid could be put on top of each filter, and with the applied vacuum any leakage will result in the flow of external air into the filter crock. The next most effective means of control would be an improvement of the exhaust slots currently used. They should be positioned around the top of the filter sufficiently to capture solvent emissions. The vapors can be effectively controlled with a capture velocity ranging from 100-200 fpm, with a slot velocity of 1000 fpm.

A local exhaust system for the drumming station in the Fine Chemicals Department should be inplemented. The operation should be enclosed as much as possible to control particulate emissions. An adaptation of the design in Figure 1 (for barrel filling) might be possible. The exhaust system for the HBCD drumming station could be improved by a more complete enclosure. The exhaust slots should be placed at the top of the barrel, not below it where more air must be used to capture particulate emissions. Reduce leakage from all points in this area, such as from the broken latch on the duct door at the grinder hopper and at the grinder housing.

The ventilation system for the "1/2-hour loss" sample should be improved. A flexible, duct type exhaust hood could be positioned along the top of the dryer/blender. A capture velocity of 100-200 fpm should control vapor emissions. The local exhaust system must draw contaminated air away from the breathing zone of the employees. The canopy hood over the blender/dryer and floor fan adjacent to it are not good for controlling emissions and should not be used. Employees in the HBCD Department must often enter the dryer/blender and remove the scale from the interior walls with a scraper. This operation may take approximately 1/2 - 1 hour. The worker normally wears a canister gas mask, and is observed by another worker standing outside the tank. It is recommended that a supplied air device be used instead for this operation, since there might be an oxygen deficiency in the tank or contaminated air concentrations beyond the protection capability of the gas mask. For example, a pressure demand air-line respirator could be used in which the supplied air could come from a compressed air source (compressor or cylinder). The observer should be equipped with a self-contained breathing apparatus (SCBA) in the event of an emergency within the tank.

2. PHT4 Department (Tetrabromophthalic anhydride)

The local exhaust ventilation at the reactor hatch should be improved. A flexible, elephant type hood shaped to fit the reactor opening could be designed. As one employee is removing the cover, another could get the hood ready for rapid placement over the opening. A flanged hood larger than the opening would better control SO_2 emissions, which are intense at the time of opening. Capture velocities of 200-500 fpm are recommended for the system. However, if this could not be used due to the access needed to the opening, a lateral exhaust flanged hood could be possibly positioned so as to draw emissions away from the employee's breathing zone during the addition to phthalic anhydride.

An alternative would be to open the reactor only after it has been emptied of as much of the gaseous volume as possible.

3. Industrial Bromides

Engineering controls should be instituted or improved on all reactors to control exposures to vapors and gases. For example, the exhaust duct positioned approximately two feet to the side of the unity reactor hatch is ineffective at capturing vapors leaving the reactor. While 600 fpm of air was being exhausted at the face of the duct, only 10-30 fpm was available above the hatch. This latter air velocity is insufficient to capture rising vapors. The duct should be extended to cover as much of the hatch opening as possible, and a capture velocity of 50-100 fpm should be required at points where vapors leave the reactor hatch. All locations where carbon tetrachloride vapor might escape from vessels should be inspected and kept closed or sealed.

During the time period necessary to install or modify engineering controls, supplied air respirators or self-contained breathing apparatuses should be worn by employees. Employees should also be instructed to use proper work practices.

A recommendation is made for modifying the ventilation at the BTCM and TMCB drumming stations. Instead of attaching the flexible exhaust tubing to the 1" loading line to control vapors arising through the bung in the drum, the tubing could be placed around the loading line and could rest directly on top of the drum top. In this way there would be a better enclosure of the operation.

4. General Recommendations

1. All piping should be marked with the name of the chemicals carried within them.

2. Emissions from a red waste treatment building adjacent to the Fine Chemicals building should be contained; gases and vapors entering the building pose a potential health hazard to employees.

3. If not already accomplished, the company should institute a written respiratory protection program. The minimum requirements as outlined in 29 CFR 1910.134 are a good starting point. The program should give the necessary information on the training of employees in their proper use and limitations. The program should state exactly which individuals are responsible for the various program features such as training and maintenance. However, respirators should not be used as a substitute for good engineering controls.

B. Medical

Workers in the plant should be informed of the extent and severity of damage which has taken place within the population.

Workers who show evidence of damage to the hepatic, nervous, immune, or hematologic system should be removed from further exposure to solvents and other toxic materials at least until such time as their test results return to normal limits. Biological monitoring at reasonable intervals should be continued to insure that pathological processes have been reversed.

A concerted effort must be made to improve working conditions in every area of the plant. Attention should be paid to improving the workplace environment not only during normal operating procedures, but also during intermittent processes such as quality control sampling, repair of equipment, and addition of raw materials. Materials which are spilled should be cleaned up immediately. The environment should be tested for PBB and any accumulation of this material should be cleaned up.

A number of these workers have been exposed to known carcinogens such as benzene and TRIS. They should be permanently removed from these exposures and followed for an indefinite period. In addition, workers exposed to PBB's and/or found to have high serum levels of PBB should be carefully monitored for long term effects from their exposure.

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30 NIOSH: Criteria for a revised recommended standard . .occupational exposure to ethylene dichloride, HEW Publication No. (NIOSH) 78-211, Cincinnati, Ohio, U.S. Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, 1978.

31 NIOSH: Occupational Diseases - a guide to their recognition, U.S. Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, U.S. Government Printing Office, June, 1977.

32 NIOSH: Revised Recommended Carbon Tetrachloride Standard, June 9, 1976.

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Table 1

Results of Air Samples for Various Chemicals
Breathing Zone Samples

Velsicol Chemical
St. Louis, Michigan

June 6-8, 1977

Location	Employee/date	Sample Number	Sampling Period (hrs/min)	Concentration-ppm[1] Carbon Tetrachloride	1,2 dichloroethane (ethylene dichloride)	1,5,9-cyclododecatriene	Benzene
HBCD (day shift)	#1 Operator 6/7	H 1	4/25	1.3	ND[2]		ND
	#1 Operator 6/7	H 3	3/25	ND	ND		ND
	#1 Operator 6/7	H 2	4/10	8.0	ND		ND
	#1 Operator 6/7	H 4*	3/25	1.0	1.7	144 mg/M^3	ND
	#1 Operator 6/8	H 5	3/09	1.6	5.1		ND
	#1 Operator 6/8	H 6	3/35	1.1	2.7		ND
	#1 Operator 6/8	H 7	3/35	0.9	1.4		ND
(afternoon shift)	#1 Operator 6/8	H 8	4/40	2.8	11.6		0.1
	#1 Operator 6/8	H 10	0/40	ND	2.9		ND
——	#2 Operator 6/8	H 9	4/40	1.5	10.3		0.2
	#2 Operator 6/8	H 11	0/40	ND	7.8		ND
DMC (day shift)	#1 Operator 6/7	D 1	3/50		1.6		0.1
	#1 Operator 6/7	D 2	3/15		2.0		ND
	#1 Operator 6/8	D 3	3/40		13.8		0.2
	#1 Operator 6/8	D 5	4/20		1.7		0.1
— (day shift)	In-training Operator 6/8	D 4	3/40		11.5		0.2
	Operator 6/8	D 6	4/20		1.8		ND
afternoon shift)	#1 Operator 6/8	D 8	2/35		13.2		0.4
	#1 Operator 6/8	D 10	0/45		3.0		ND
	#1 Operator 6/8	D 7	-	Bad pump	-	-	-
	#1 Operator 6/8	D 9	0/45		0.6	-	0.2

(1) Parts of contaminant per million parts of air, except where noted
(2) ND = none detectable
* Charcoal in tube very wet, results questionable

Evaluation Criteria: (in ppm)

	Carbon Tetrachloride	1,2 dichloroethane	Benzene
NIOSH	2	1	1
OSHA	10	50	10
TLV	10	50	10

Table 2

Results of Direct Reading Measurements for Various Substances

Velsicol Chemical
St. Louis, Michigan

June 6-8, 1977

Location	Date	Substance	Concentration	Comment
Industrial Bromides Department	6/7	Carbon Tetrachloride (CCl_4)	0 ppm(1)	near reactor (2:40pm)
	6/7		0 ppm	near meter (2:41pm)
	6/8	CCl_4	0 ppm	at bottom of reactor during flushing of product to rinse tank (8:45am)
	6/8	CCl_4	0 ppm	At meter during addition of CCl_4 to reactor (9:40am)
	6/8	CCl_4	0 ppm	near operator during addition of aluminum chloride (10:00am)
	6/8	Ammonia (NH_3)	>30 ppm	during production of ammonia solution (11:30am)
Methyl Bromide Room	6/7	Methyl Bromide(CH_3Br)	<5 ppm	near bunsen burner (second floor) (9:00am)
	6/8	Ch_3Br	25-30 ppm	near bunsen burner (6:30pm)
	6/8	CH_3Br	20-30 ppm	near bunsen burner (6:45pm)
	6/9	CH_3Br	20 ppm	near bunsen burner (10:00am)
HBCD Area	6/7	Total particulates (FM-100)	0.7 mg/M3(2) 0.4 mg/M^3 1.2 mg/M^3	near employee at bagging unit during drum-out (10:30am)
	6/7	Total particulates (FM-100)	0.5 mg/M^3	near employee at hopper below blender/drier (10:30am)
	6/8	(HBCD)	1.0 mg/M^3 1.9 mg/M^3 1.0 mg/M^3	near employee at bagging unit during drum-out (afternoon)
Fine Chemical Dept.	6/8	Total Particulates (DMC)	0 mg/M^3	near employee at bagging unit during drum-out (9:30pm)
	6/8	Total Particulates (DMC)	0.5 mg/M^3	around drier in dust cloud produced by floor fan (9:30pm)
PHT 4 Dept.	6/7	Sulfur Dioxide	0 ppm	near employee at filter crocks
	6/7	Sulfur Dioxide	0 ppm	near employee at filter crocks
PHT 4 Dept.	6/9	Sulfur Dioxide	>25 ppm	near employee after opening reactor hatch before charging reactor
	6/9	Sulfur Dioxide	1-2 ppm	near employee while adding phthalic anhydride, also during hatch closing

(1) ppm = parts of substance per million parts of air
(2) mg/M3 = milligrams of substance per cubic meter of air

Evaluation Criteria:	Carbon Tetrachloride	Ammonia	Methyl Bromide	Total Particulates	Sulfur Dioxide
NIOSH	2 ppm	50 ppm	-	-	0.5 ppm
OSHA	10 ppm	50 ppm	20 ppm	15 mg/M^3	5 ppm
TLV	10 ppm	25 ppm	15 ppm	10 mg/M^3	5 ppm

Table 3

Results of Air Sampling for Total Particulates
Breathing Zone Samples

Velsicol Chemical
St. Louis, Michigan

June 6-8, 1977

Location	Employee/date	Sample Number	Sampling Period (hrs/min)	Concentration (mg/M3) (1)
HBCD	#1 Operator 6/7	V 1	4/15	0.9
	#1 Operator 6/7	V 2	4/10	2.0
	#1 Operator 6/8	V 3	0/25	7.7
	#1 Operator 6/8	V 4	0/25	5.9
DMC	#1 Operator 6/8	V 5	0/40	0.5
	#1 Operator 6/8	V 6	0/40	0.3

(1) mg/M^3 = milligrams of substance per cubic meter of air

Evaluation Criteria: (in mg/M^3)

NIOSH	-
OSHA	15
TLV	10

Table 4

Results of Air Samples for Organic Vapors
Breathing Zone Samples

Velsicol Chemical
St. Louis, Michigan

June 6-8, 1977

Location	Employee/date	Sample Number	Sampling Period (hrs/min)	Concentration: Carbon Tetrachloride	Concentration: Trichloroethylene	Concentration: TMCB[(2)]	Concentration: TMCB Isomers (A)	Concentration: TMCB Isomers (B)
Industrial Bromides	#1 Operator 6/7	B 1	3/50	3.6 ppm[(1)]	2.5 ppm	3.9 mg/M^3	ND[(3)]	ND
	#1 Operator 6/7	B 3	3/30	1.5 ppm	3.3 ppm	3.8 mg/M^3	ND	ND
	Day Utility 6/7	B 2	3/40	2.3 ppm	1.2 ppm	8.7 mg/M^3	ND	ND
	Operator 6/7	B 4	3/30	1.4 ppm	3.1 ppm	2.2 mg/M^3	ND	ND
	#1 Operator 6/8	B 6	3/15	4.9 ppm	5.1 ppm	7.7 mg/M^3	2.2 mg/M^3	4.4 mg/M^3
	#1 Operator 6/8	B 7	4/10	ND	0.4 ppm	ND	2.7 mg/M^3	ND
	Day Utility 6/8	B 5	3/20	1.6 ppm	2.1 ppm	2.3 mg/M^3	3.5 mg/M^3	2.3 mg/M^3
	Operator 6/8	B 8	4/10	2.6 ppm	3.6 ppm	2.6 mg/M^3	4.3 mg/M^3	ND

(1) ppm = parts of substance per million parts of air
(2) TMCB = trimethylene chlorobromide, in milligrams of substance per cubic meter of air
(3) ND = none detectable

Evaluation Criteria: (in ppm)

	Carbon Tetrachloride	Trichloroethylene	TMCB	TMCB Isomers (A)	TMCB Isomers (B)
NIOSH	2	25	-	-	-
OSHA	10	100	-	-	-
TLV	10	100	-	-	-

Table 5

Results of Air Samples for Sulfuric Acid & Total Particulates

Velsicol Chemical
St. Louis, Michigan

June 6-8, 1977

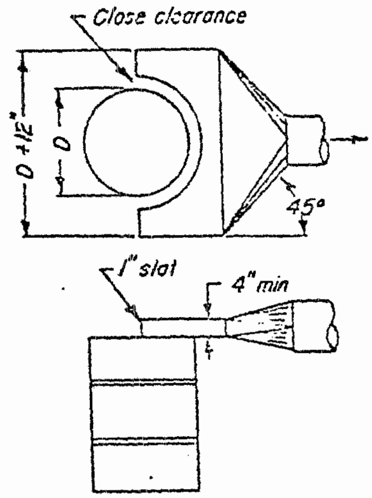
Location	Employee/Date		Sample Number	Type Sample (1)	Sampling Period (hrs/min)	Concentration mg/M^3 (2) Sulfuric Acid	Total Particulates
PHT 4 Building	#1 Operator	6/7	AA 41	P	3/58	0.12	
	#1 Operator	6/7	AA 45	P	3/52	0.29	
	#1 Operator	6/7	V 24	P	7/50		1.1
	#1 Operator	6/7	AA 40	P	4/0	0.10	
	#1 Operator	6/7	AA 43	P	3/54	-*	
	#1 Operator	6/7	V 19	P	7/54		1.3
	Between Reactor Vessels	6/7	AA 42	A	3/41	0.27	
		6/7	W 1	A	3/43	0.53	
		6/7	AA 44	A	3/43	0.07	
		6/7	W 2	A	3/41	0.51	
	#1 Operator	6/8	AA 31	P	4/16	0.08	
	#1 Operator	6/8	W 3	P	4/15	0.10	
	#1 Operator	6/8	AA 39	P	3/26	0.24	
	#1 Operator	6/8	W 8	P	3/27	0.79	
	#1 Operator	6/8	AA 34	P	3/30	0.09	
	#1 Operator	6/8	W 4	P	3/30	0.13	
	#1 Operator	6/8	AA 26	P	3/41	0.13	
	#1 Operator	6/8	W 7	P	3/39	0.21	
	#1 Operator	6/8	AA 38	P	3/41	0.08	
	#1 Operator	6/8	W 5	P	3/41	0.11	
	#1 Operator	6/8	AA 33	P	3/15	0.13	
	#1 Operator	6/8	W 6	P	3/15	0.15	
	#1 Operator	6/8	AA 37	P	3/30	0.07	
	#1 Operator	6/8	AA 36	P	3/38	0.09	
	#1 Operator	6/8	V 12	P	2/10		2.4
	Between Reactor Vessels	6/8	AA 27	A	4/06	0.40	
		6/8	AA 35	A	3/20	0.90	
	At Filter Crocks	6/8	AA 28	A	4/03	0.14	
		6/8	AA 32	A	3/16	0.11	
	At Bagging Unit	6/8	V 11	A	3/12		0.70

(1) P = Personal, A = Area
(2) mg/M^3 = Milligrams of substance per cubic meter of air
* Interference present

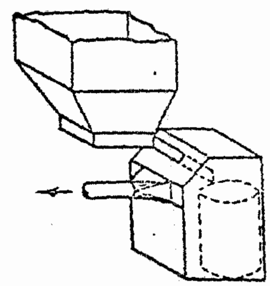
Evaluation Criteria: (in mg/M^3)

	Sulfuric Acid	Total Particulates
NIOSH	1	-
OSHA	1	15
TLV	1	10

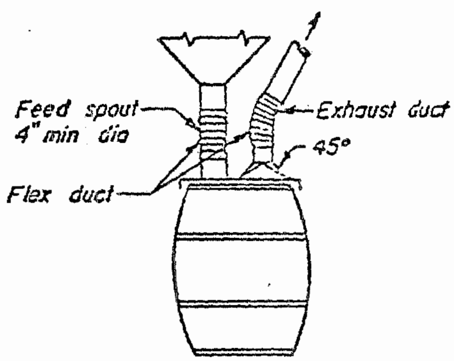
Figure 1



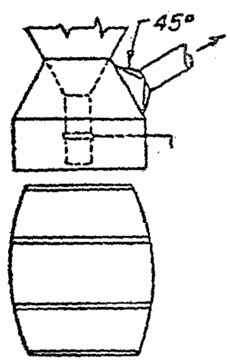
Q = 100 cfm/sq ft barrel top min
Duct velocity = 3500 minimum
Entry loss = 0.25 VP + 1.78 slot VP
Manual loading.



Q=150 cfm/sq ft open face area
Duct velocity = 3500 fpm minimum
Entry loss = 0.25 VP for 45° taper



Q= 50 cfm × drum dia (ft) for weighted lid
150 cfm × drum dia (ft) for loose lid
Duct velocity = 3500 fpm minimum
Entry loss = 0.25 VP



Q = 300-400 cfm
Duct velocity = 3500 fpm min
Entry loss = 0.25 VP

Reference: Industrial Ventilation-A Manual of Recommended Practice, 13th ed., American Conference of Governmental Industrial Hygienists, Lansing, Michigan, 1974.

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